SYNTHESIS OF 1-CHLORO-1,2,4,6-SELENATRIAZINES AND SOME PRODUCTS OF REDUCTION

JIAMIN ZHOU

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ABSTRACT

A general route to 1-chloro-1,2,4,6-selenatriazines with substituents on 3,5 positions has been developed by the reactions of *N*-imidoylamidines with selenium tetrachloride. The mechanism for these reactions is discussed according to the observed intermediates. At least two intermediates exist. One of the intermediates, 1,1-dichloro-3-trichloromethyl-4-H-5-diisopropylphenyl-1,2,4,6-selenatriazine, was identified by ^{1}H NMR, Mass spectroscopy and X-ray crystallography. 1-Chloro-1,2,4,6-selenatriazines were synthesized in high yield and fully characterized. Five 1-chloro-1,2,4,6-selenatriazine crystal structures were obtained

Reduction of 1-chloro-1,2,4,6-selenatriazines with triphenylamtimony immediately produced the corresponding selenatriazinyl radicals in hot acetonitrile. Pure radicals were obtained by *in-situ* crystallization as their dimers from reaction. Two crystal structures were obtained for 3-trifluoromethyl-5-*p*-tolyl-1,2,4,6-selenatriazinyl dimer and 3-trifluoromethyl-5-*p*-methyloxyphenyl-1,2,4,6-selenatriazinyl dimer. EPR spectroscopy measured all radicals coupling to three unique nitrogen atoms with 7 broad lines. There is no resolvable hyperfine coupling to ^{77}Se, $^{37}Cl/^{19}F$ and phenyl protons.

ACKNOWLEDGEMENT

My time at the University of Lethbridge has been great. I have enjoyed myself working in Dr. René Boeré's laboratory. I cannot give enough thanks to my supervisor, Dr. René Boeré. His encouragement has given me so much confidence. When I succeeded, he gave me great congratulation and encouragement. When I failed, he consoled, encouraged me. He is such a capable instructor and mentor that he can always help me to solve problems. His kindness, patience, positive direction lightened the way of my graduate studies here. I especially thank him for spending numerous hours on my project, along with getting this thesis through its final stages.

My thanks also go to my lab mates, Tracey Roemmele, who helped me so much to analyse data and gave me a lot of advice; and Yuankui Zhang, who helped me go though the general chemistry knowledge. Thanks all of Dr. René Boeré's group members for those wonderful cooperation, advice and friendship. Sharing lab space was never a problem.

Thanks also go to Dr. Michael Gerken and his group member Johnathan Mack for obtaining the Raman spectra; Kris Fischer for glassblowing and technical support; Dr. Peter Dibble and his group members for cooperation and sharing the lab.

My wife has solved my family difficulty during my graduate work here. The family support I have received has been crucial to the finishing of this work, and for this I especially thank my wife Nan and my mother-in-law. I also thank my son Kevin for giving up time with me. With all their support and encouragement, I finished my graduate work smoothly.

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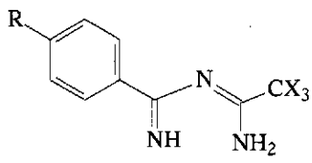
List of Abbreviations

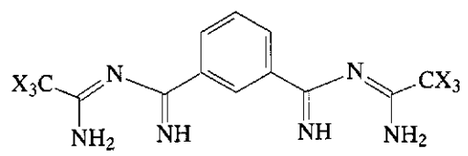
DFT	Density Functional Theory
Dip	2,6-diisopropyl
Dipp	2,6-diisopropylphenyl
EPR	Electron paramagnetic resonance
g	gram
G	Gauss
hfc	Hyperfine coupling
HOMO	Highest occupied molecular orbital
Hz	Hertz
IR	infrared
LCAO	linear combination of atomic orbitals
LUMO	Lowest unoccupied molecular orbital
mL	milliliter
mmol	millimole
mp	Melting point
MS	Mass spectroscopy
NMR	Nuclear magnetic resonance
NRC	Neutral radical conductor
ORTEP	Oakridge thermal ellipsoid plot
Ph	phenyl
ppm	Parts per million
RIC	Radical ion conductor
TCNQ	7,7,8,8-tetracyano-p-quinodimethane
TMS	trimethylsilyl
TTF	tetrathiafulvalene

Compound Numbering Scheme



	X = Cl R
A1	OCH_3
A2	CH_3
A3	H
A4	Cl
A5	Br
A6	CF_3
A7	CN
A8	2,6-diisopropyl

	X = F R
A9	OCH_3
A10	CH_3
A11	H
A12	Cl
A13	Br
A14	CF_3
A15	CN
A16	2,6-diisopropyl



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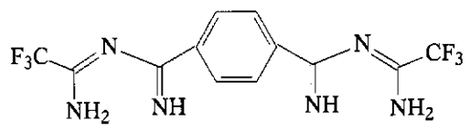
A18 X = F



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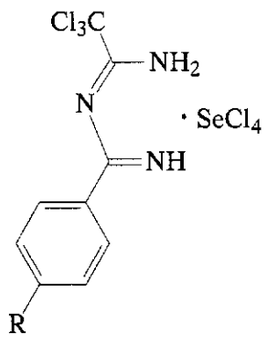
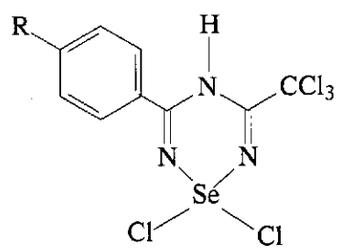


B2 R = CH_3
B4 R = Cl



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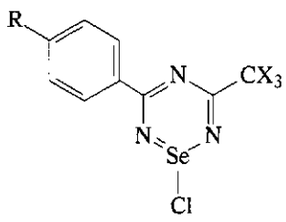
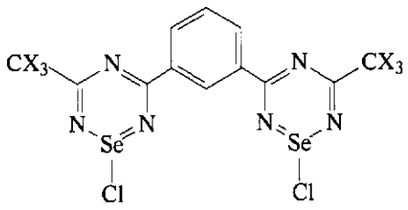
C4 R = Cl
C8 R = 2,6-diisopropyl



	X = Cl R		X = F R
D1	OCH_3	**D9**	OCH_3
D2	CH_3	**D10**	CH_3
D3	H	**D11**	H
D4	Cl	**D12**	Cl
D5	Br	**D13**	Br
D6	CF_3	**D14**	CF_3
D7	CN	**D15**	CN
D8	2,6-diisopropyl	**D16**	2,6-diisopropyl



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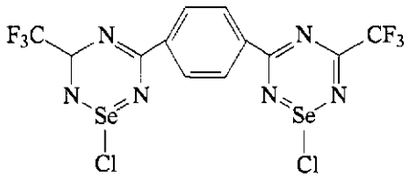

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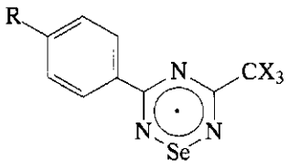
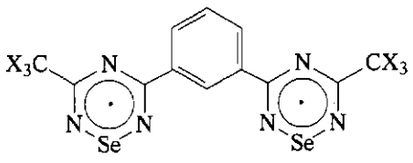


	X = Cl R		X = F R
E1	OCH_3	**E9**	OCH_3
E2	CH_3	**E10**	CH_3
E3	H	**E11**	H
E4	Cl	**E12**	Cl
E5	Br	**E13**	Br
E6	CF_3	**E14**	CF_3
E7	CN	**E15**	CN
E8	2,6-diisopropyl	**E16**	2,6-diisopropyl



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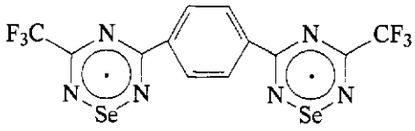
E18 X = F



E19

Chapter 1 Introduction

Over the past few decades a large number of sulfur-nitrogen compounds have been prepared, displaying diversity of structures and physical properties.[1] In contrast, few selenium-nitrogen compounds have been structurally characterized. Undoubtedly, one of the main Achilles' heels in the preparation of new Se-N compounds has been the lack of suitable stable precursors that can be prepared in good yields. For example, preparations of Se-N compounds have often been limited to reactions of amine derivatives with the corresponding chalcogen halogenides or by the use of the explosive Se_4N_4. We therefore wish to report our recent success in preparing and characterizing the new and stable compounds of 1-chloro-1,2,4,6-selenatriazines with substitutents on 3,5 positions, and the corresponding 1,2,4,6-selenatriazinyl radicals.

This thesis is divided into several sections. Chapter 2 is a literature survey of background to this work. The survey reviews the heterocycles and their electronic and magnetic properties. Heterocycles reviewed include four membered rings to eight membered rings, and contains carbon, nitrogen, sulfur and/or selenium. Synthetic work is the main focus.

In Chapter 3, the procedures for preparing 1-chloro-1,2,4,6-selenatriazines with substitutents on 3,5 positions are described. The reaction mechanism and intermediates are discussed. The products are fully characterized. Finally, bis(1-chloro-1,2,4,6-selenatriazine)benzene derivatives are described.

Chapter 4 discusses a successful synthetic route to 1,2,4,6-selenatriazinyl radicals. *In-situ* crystallization of radical dimers was carried out from reactions. Some radicals or

their dimers were characterized by infrared spectroscopy, mass spectroscopy, and X-ray crystallographic analyses. EPR data were obtained for some selenatriazinyl radicals.

Chapter 5 is a discussion of the crystal structures of two selenatriazinyl radicals, five 1-chloro-1,2,4,6-selenatriazines and one of the intermediates. Chapter 6 presents the details of the experimental procedures used to synthesize the 1-chloro-1,2,4,6-selenatriazines, 1,2,4,6-selenatriazinyl radicals and their precursors, along with crystallographic data tables.

Unless otherwise specified, all numerical data in this thesis is accurate to ±1 in the last digit reported.

Reference

1. Sulfur-Nitrogen Compounds In Gmelin Handbook of Inorganic Chemistry; Springer-Verlag: Berlin, 1977, 1985, 1987, 1990; Parts 1-5.

Chapter 2

Literature Survey: Synthesis of Heterocycles as Conducting Materials

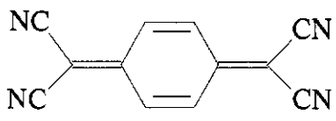
The power and flexibility of synthetic chemistry are well known and generally recognized. Synthesis is applied to many field, including pharmaceuticals, analytical reagents, and the testing of new theories. Synthesis of entirely new materials is a current focus of organic, inorganic and organometallic chemistry. One area of materials in synthetic chemistry is interesting and useful electronic and magnetic properties. Among these are the organic charge-transfer salts since the flat planar molecules involved lead to anisotropic structures with pseudo-one-dimensional electronic properties. In contrast to the conventional molecular crystals (composed of neutral organic molecules held together by van der Waals forces), charge-transfer salts have unpaired electrons on the acceptor (A) or donor (D), or both, as a result of simple electron transfer. This result opens up a new area of electronic phenomena, for if the unpaired electrons delocalize over all molecular sites, the electronic property of a "metallic" state may result.

2.1 Molecular conducting materials

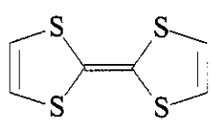
It is well known that few molecular materials possess electrical conductivity. Even fewer still have conductivities approaching those of metals.[1,2] These have been classified as 'organic metals' or 'molecular metals'. Conductivity arises in these systems from the formation of a partially filled energy band that can arise from π-orbital overlap between one-dimensional stacks of molecules. The first molecular conductor 'Kupferglänzenden' was prepared by Knop[3] in 1842. Kupferglänzenden, or copper-shining crystals were

created by partial oxidation of $K_2[Pt(CN)_4]$ with chlorine or bromine, which was discovered to have electrical conductivity later by Bechgaard *et. al.*[1,2] These molecular conductors usually consist of radical ion pairs or charge transfer salts which allow for the migration of electrical charge though the solid-state lattice.

The molecular conducting materials can be classified as two classes: radical ion conductors (RIC) and neutral radical conductors (NRC). The first class has historically been dominant, and primarily includes the majority of charge transfer salts modeled on the donor tetrathiafulvalene (TTF)[4] and acceptor 7,7,8,8-tetracyano-p-quinodimethane (TCNQ).[5] Routes to molecular superconductivity using organic compounds began with the combination of TTF and TCNQ in a 1:1 ratio. RIC's are two component conductors (cations and anions), and usually only one of the components is active in conduction.



TCNQ



TTF

The other conducting system, neutral radical conductors (NRC), was first put forward by Haddon[6,7] using odd-alternant hydrocarbons as a proposed model for a conducting system without the use of permanently charged radicals for the conduction pathway, thus avoiding the significant Coulombic repulsion that accompanies the attempt to form conducting stacks of radicals.[8] NRCs are a new approach that involve the use of neutral rather than charged π-radicals, and hence eliminate the need for counter ions.

To attain the conductivity in a molecular solid requires the following basic conditions:[9,10] (1) the existence of unpaired electrons; (2) a uniform crystal structure such that, in the absence of electron-electron interactions, the unpaired electrons would

delocalize into a single metallic band; (3) relatively weak electron-electron repulsive interactions; and (4) maximisation of the intermolecular transfer integral.

The first requirement is straightforward. Generally, the unpaired electrons would reside in a single nondegenerate state corresponding to the lowest available energy level of the π system of the neutral molecule. In the solid, these states form the basis for a single narrow band whose width is proportional to the intermolecular electron-transfer integral, which takes an electron from one site to another. This can be exemplified by TCNQ. The band structure may be calculated in the linear combination of atomic orbitals (LCAO) tight-binding approximation (Figure 2.1).[11] The intermolecular transfer integral, **t**, arises from overlap of the molecular wave functions on adjacent sites. Such a band structure need not be metallic.

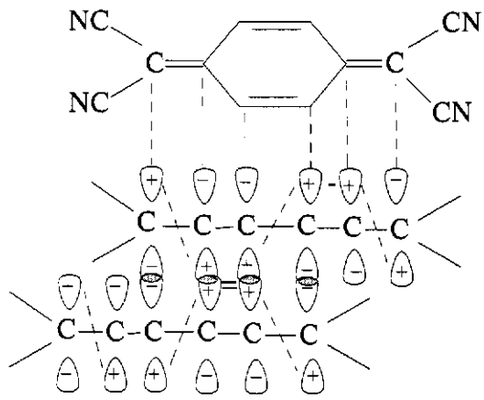


Figure 2.1 Tight-binding band formation among TCNQ sites.

2.2 Redox-active heterocycles

No matter what kind of molecular conducting system, almost all of them have a common character: multiple bonding and conjugation to form π bonds in a ring. The electrons localize or delocalize over the π system. Polycyclic aromatic compounds, for

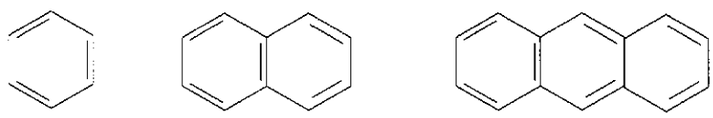
example, can be chemically or electrochemically reduced, often forming stable radical anions. Based on structure, some compounds can be easily reduced while some cannot.

Heteronuclear π linkages involving heavier elements in combination with the lighter elements are more common, e.g. phosphorus, sulfur. In a double bond, the polarity of the π-bond leads to a high reactivity. For example, the conjugation of –B=N– bonds, as in borazines, stabilizes the skeletal π-system and such molecules as $B_3N_3H_6$ have been described as inorganic analogues of benzene. To be more explicit, –B=N– and –C=C– are isoelectronic, but the electronegativity difference between boron (1.90 Pauling scale, Mulliken-Jaffé, sp^3 orbital, as pure p orbital value not avaible) and nitrogen (2.28 Pauling scale, Mulliken-Jaffé, p orbital)[12] highly polarizes the π-electron density, and results in much greater chemical reactivity than is observed for aromatic organic compounds.

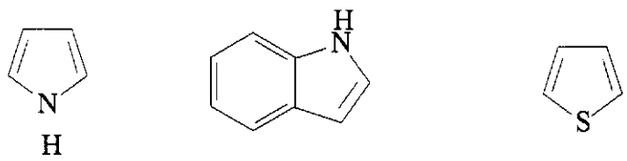
The properties of heterocyclic molecules built from catenated –S=N- units provide stronger evidence for π-electron delocalization. Because the electronegativity differences between sulphur (2.31 Pauling scale, Mulliken-Jaffé, p orbital) and nitrogen (2.28 Pauling scale, Mulliken-Jaffé, p orbital)[12] are small, and because of efficient overlap between sulfur $3p_\pi$ and nitrogen $2p_\pi$ orbitals, π-interactions in conjugated S=N units are strong. The construction of heterocycles containing one or more S=N units can lead to aromatic $4n+2$, anti-aromatic $4n$ and odd-electron radical systems depending upon the number of S=N units involved. As a result of the 'electron rich' structure (more π-electrons than atomic centers) of the S=N unit, the π-frameworks of these heterocycles are weaker and more reactive than those of organic rings.

The difference of ability to reduce a polycyclic aromatic compound or heterocyclic compound can be described by the term 'redox window': the voltage range within which

the central oxidation state is stable. Generally, the smaller the redox window, the lower the disproportionation energy and hence the greater potential the compound has as a molecular metal component. Benzene has a very large redox stability window that stretches from approximately –3 to +3 Volts. It is thus decidedly redox-inactive. However, with increasing ring conjugation the redox stability window decreases. This behavior has been correlated to both the raising of the HOMO and the lowering of the LUMO. Thus the redox stability window of naphthalene is 4.04 Volts in acetonitrile,[13] while that of anthracene is only 2.87 Volts in the similar solvent DMF.[14] Compared to these carbocycles (e.g benzene, naphthalene, anthracene), heterocycles such as pyrrole, indole, and thiophene have decidedly smaller redox windows. These are redox-active ring compounds.



benzene naphthalene anthracene



pyrrole indole thiophene

Thiazyl compounds are remarkable for the relatively large number of species for which the neutral state is a thermally-stable free radical. The 1,2,3,5-dithiadiazolyls have a redox window of approximately 1.5 Volts and extensive research has gone into their potential as candidates for NRCs. The heterocyclic ring systems studied thus far for their

potential as NRC candidates vary in many ways including ring size, heteroatom substituents, and tunability. Many of the recent advances in the chemistry of sulfur (or selenium) nitrogen heterocyclic compounds have focused on the study of radical species,[15,16] and the use of such compounds in the design of synthetic metals.[17-22] Compounds that combine the structural stability of carbocyclic π systems with the interesting redox properties of sulfur-nitrogen linkages are of great interest.

In this latter context, the generation of planar ring systems that can exist in a variety of stable oxidation states (cation, anion, and radical) is a particularly appealing target. The following briefly reviews the preparation, behavior and electronic properties of such heterocycles.

2.3 Binary S,N compounds

The simplest binary sulfur-nitride is the four-membered ring compound S_2N_2, disulfur dinitride. To prepare S_2N_2 or polysulfur nitride, the starting material in all current work is tetrasulfur tetranitride, which is most commonly prepared by the reaction between ammonia and disulfur dichloride.[23,24] S_2N_2 was first prepared in 1910 by cleaving tetrasulfur tetranitride, S_4N_4, by passing the hot vapor in *vacuo* over heated silver gauze.[25] The cleavage of S_4N_4 vapor is thought to occur in two stages.[26] Firstly, S_4N_4 reacts with Ag in a nearly complete decomposition; Secondly, the Ag_2S catalyzes the thermal splitting (Figure 2.2).

$$S_4N_4 + 8Ag \longrightarrow 4Ag_2S + 2N_2$$

$$S_4N_4 \xrightarrow{Ag_2S} 2S_2N_2$$

Figure 2.2 Thermal cleavage of S_4N_4 to S_2N_2

S_2N_2 is a clear colorless crystalline solid at room temperature. The molecule is formed from 6 pi electrons in three-center bonds and four unshared electron pairs superimposed on a square-planar (D_{2h} symmetry) σ-bond structure (Figure 2.3).[27] S_2N_2 is stable only at low temperatures, and polymerizes to (SN)x even in the solid state at ambient temperature. Polysulfur nitride is diamagnetic and forms fibre-like crystals with a metallic sheen, and shows the remarkable property that it is a semiconductor. The resistance of the powder decreases with rising temperature.[28] It is the first example of a polymeric metal.

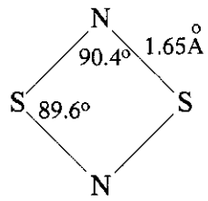


Figure 2.3 The structure of disulfur dinitride

The chemistry and physics of (SN)x developed very rapidly. Several reviews on the preparation and properties of (SN)x have been written. A descripion of the chemical properties of (SN)x and related materials is given by Heal.[29] Labes[30] summarized the preparation of polysulfur nitride and listed previous reviews in detail.

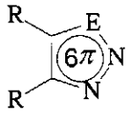
2.4. Five-membered rings

The possibility of emulating the electronic properties of the (SN)x polymer by incorporating carbon atoms into conjugated sulfur-nitrogen chains has provided a stimulus for research in organothiazyl chemistry. As a result the preparation and

characterization of a variety of novel heterocyclic thiazyl/selenazyl compounds have been studied intensively and extensively. We simply group these to five-, six-, seven-, and eight-membered rings.

When conventional five-membered heterocycles such as pyrrole, indole, or thiophene are electrochemically oxidized, they polymerize and often deposit a polymeric film right on the electrode surface. The films are found to be electrically conducting, and belong to the class of small-band gap π-conjugated polymers.[30-32] All of these compounds are irreversibly oxidized because they form polymers. The tendency to polymerize, or even to dimerize, upon oxidation or reduction is a common theme in carbocyclic redox chemistry. The effect tends to be minimized by including more elements of Group 15/16.

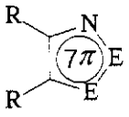
Five–membered heterocycles have been by far the most studied ring size. They can be split up into the following categories (Figure 2.4).



1,2,3-thiadiazoles (E=S)
1,2,3-selenadiazoles (E=Se)

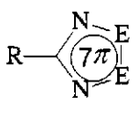
1,2,5-thiadiazoles (E=S)
1,2,5-selenadiazoles (E=Se)

1,2-dithioles

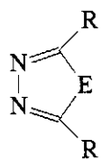


1,2,3-dithiazoles (E=S)
1,2,3-diselenazoles (E=Se)

1,3,2-dithiazoles (E=S)
1,3,2-diselenazoles (E=Se)



1,2,3,5-dithiadiazoles (E=S)
1,2,3,5-diselenadiazoles (E=Se)



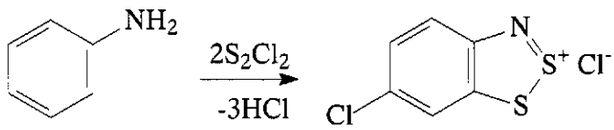
1,3,4-thiadiazoles (E=S)
1,3,4-selenadiazoles (E=Se)

Figure 2.4 Five-membered thiazyl/selenazyl heterocycles

2.4.1 Dithiazolyls & diselenazolyls

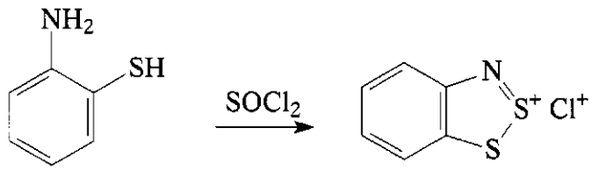
The synthesis of dithiazolyls was carried out by first preparing its precursors, the 6π dithiazolium cations, which were then reduced to the 7π dithiazolyl radicals.

The first 1,2,3-dithiazolium salts were reported by Herz[33] in 1922 from the reaction of aniline hydrochloride, and its derivatives, with an excess (4-5 molar equivalents) of S_2Cl_2. Almost invariably the aromatic ring becomes substituted by chlorine *para* to the amine N atom (Figure 2.5). Whilst the stoichiometry of the reaction appears simple, the reaction mechanism is not well-understood, despite numerous studies.[34-37] The Herz reaction provides a convenient route to many dithiazolium salts; the prevalence for chlorination of the aromatic substituent has led to the development of several other approaches to 1,2,3-dithiazolium salts and 1,2,3-dithiazolyl radicals.



aniline

Figure 2.5 Hertz reaction to dithiazolium salts



ortho-amino-thiophenols

Figure 2.6 Huestis' condensation reaction to dithiazolium salts

For the unsubstituted aromatic derivatives, a particularly convenient route was reported by Huestis and co-workers.[36] This route involves the mild condensation reaction between thionyl chloride and *ortho*-amino-thiophenols (Figure 2.6).

Afterward, Oakley and co-workers[38] reported a variant on this reaction in which condensation of diaminobenzenedithiol with S_2Cl_2 led to ring closure at both sites to form a benzo-bis(1,2,3-dithiazolium)salt. Other variants on this condensation reaction are the condensation of bis(*ortho*-aminoaryl)disulphides with SCl_2 to form the 1,2,3-dithiazolyl radicals in good yield, and the thermolysis of bis(*ortho*-azidoaryl)disulphides.[39] Thermolysis of thiobisamines, bis(aminothio)amines and the hydrolysis product of Herz salts all produce the 1,2,3-dithiazolyl radicals directly[40] (Figure 2.7).

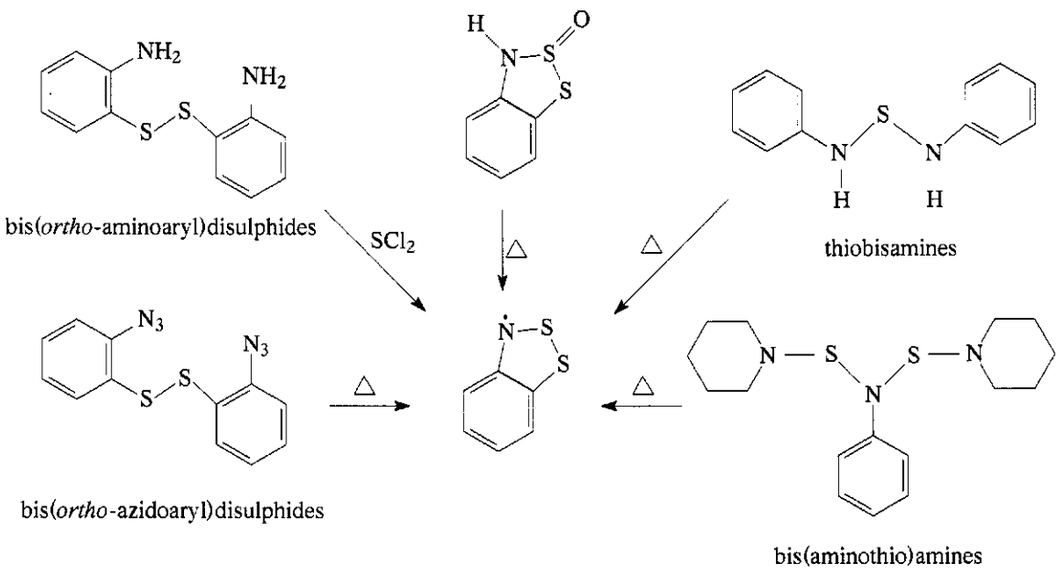


Figure 2.7 Several synthetic routes to 1,2,3-dithiazolyl radicals

The methodology developed by Huestis[36] for the synthesis of non-chlorinated Hertz compounds has been adapted to allow the preparation of the different selenium-for-

sulphur substituted derivatives, as outlined in Figure 2.8. Oakley[38] reported that the 1-thia-2-selenazolium salts could also be formed by condensation of $SeCl_4$ with *ortho*-aminothiophenols (see Figure 2.6), although chlorination of the aromatic ring also occurred in this case.

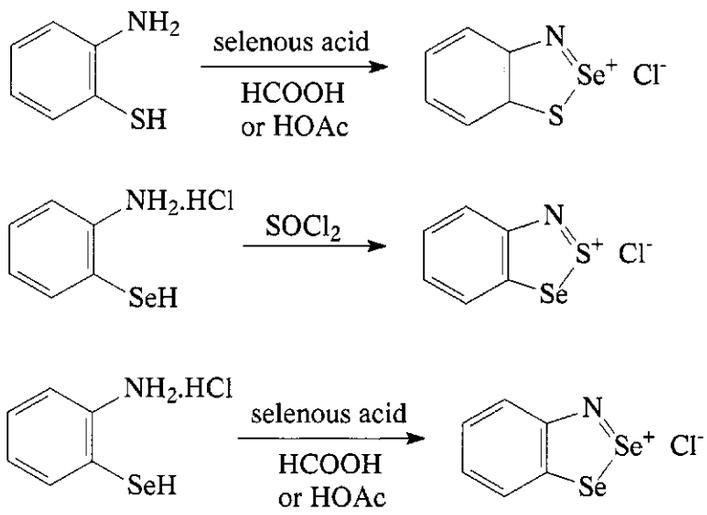
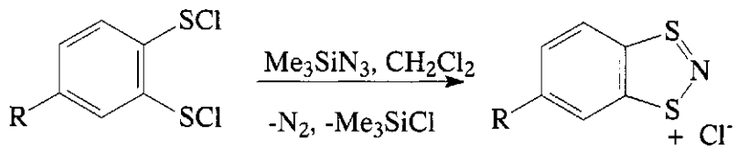
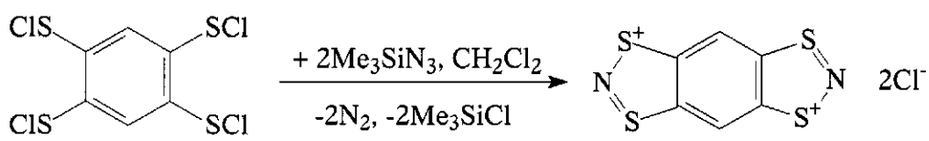


Figure 2.8 Preparation of the selenium-sulphur mixed five-membered rings



ortho-bis(sulphenyl chlorides)

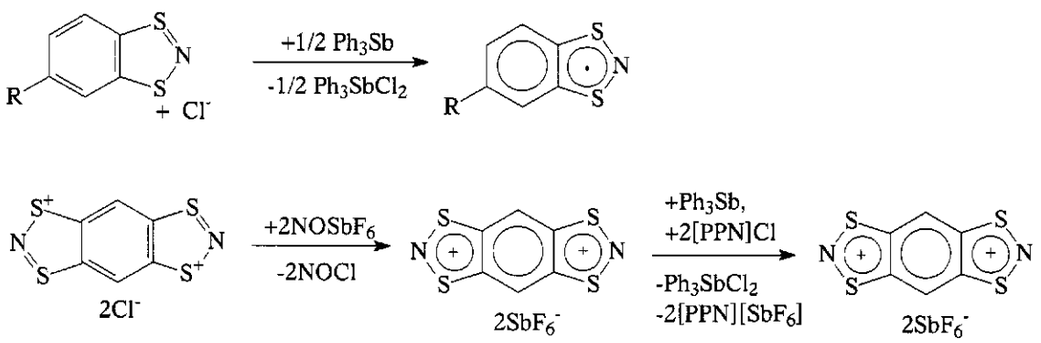


benzene-1,2,4,5-tetrathiol

Figure 2.9 Preparative routes to benzo-fused 1,3,2-dithiazolium salts

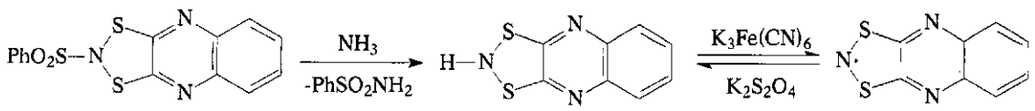
The primary route to benzo-fused 1,3,2-dithiazolium salts derives from the methodology described by Wölmershauser and co-workers.[17,41] This approach involves the reaction of ortho-bis(sulphenyl chlorides) with trimethylsilyl azide, the chloride salt precipitating from the CH_2Cl_2 solution (Figure 2.9). This approach works for simple benzo-fused derivatives. A variety of preparative routes to 1,3,2-dithiazolium salts have been developed, including bis and tris(1,3,2-dithiazolium) salts.[19,20, 42] The sulphenyl chlorides can be readily converted from direct chlorination of 1,2-dithiols with Cl_2 or $SOCl_2$.[42]

In contrast to the isomeric 1,2,3-dithiazolyl radicals which have only been characterized by solution EPR studies, a number of fused-1,3,2-dithiazolyl radicals have been isolated and fully-characterized in the solid state. There are two routes to the 1,3,2-dithiazolyl radicals; either reduction of the corresponding 1,3,2-dithiazolium cations with reducing agents such as silver powder, triphenyl antimony, sodium dithionite.[17,43,44] (Figure 2.10); or via oxidation of the dithiazolyl-imine using mild oxidizing agents such as molecular O_2 or $K_3[Fe(CN)_6]$[45] (Figure 2.11).



PPNCl: bis(triphenylphosphine)iminium chloride

Figure 2.10 Synthetic routes to the 1,3,2-dithiazolyl radicals by reduction



1,3,2-dithiazolo[4,5-*b*]
quinoxaline-2-benzensulfonamide

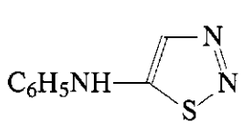
1,3,2-dithiazolo[4,5-*b*]
quinoxalin-2-yl

Figure 2.11 Synthetic routes to the 1,3,2-dithiazolyl radicals by oxidation

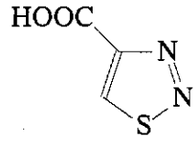
Compared to 1,3,2-dithiazoles, 1,3,2-diselenazoles are much less studied. Only a single selenium-containing species was reported electrochemically.[46] The literature on 1,2,3- and 1,3,2- dithiazoles/diselenazoles is extensive[39] and includes entries in comprehensive heterocyclic chemistry.[47]

2.4.2 Thiadiazoles and Selenadiazoles

Two early methods are known for the synthesis of monocyclic 1,2,3-thiadiazoles. One involves reaction of diazomethane and an isothiocyanate such as phenyl isothiocyanate, which yields 5-anilino-1,2,3-thiadiazole.[48] The other involves reaction of 1,2,3-oxadiazoles with ammonium hydrosulfide. The oxadiazoles are known also as diazoanhydrides or α-keto diazo compounds and are prepared by diazotization of α-amino ketones. Using this method, Wolff[49] was able to synthesize 1,2,3-thiadiazole-4-carboxylic acid. Neither of these methods is well suited for synthetic purposes.



5-anilino-1,2,3-thiadiazole



1,2,3-thiadiazole-4-carboxylic acid

In 1955, Hurd and Mori[50] developed a route to 1,2,3-thiadiazoles in an unexpected way by interaction of thionyl chloride and acylhydrazones of the general structure $RCH_2CR'{=}N{-}NX$, wherein R' = COOH, C_6H_5, etc., and X = $COOC_2H_5$, etc. The synthesis of Figure 2.12 is illustrative with a yield of 53%. This method with suitably chosen conditions provided a simple and direct synthesis of 4,5-disubstituted-1,2,3-thiadiazoles. This is the well-known Hurd-Mori reaction and is widely used in the synthesis of substituted-1,2,3-thiadiazoles and 1,2,3-selenadiazoles.[50-53]

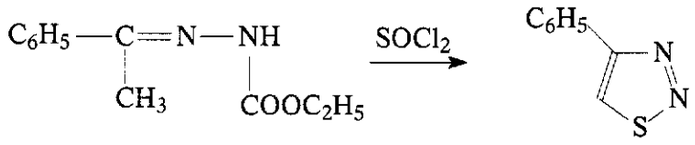


Figure 2.12 Synthetic route to 1,2,3-thiadiazoles

By using a different acylhydrazone, $RCH_2CR'{=}N{-}NCONH_2$ reacting with selenium dioxide in acid medium, Lalezari[54] found a new route to 1,2,3-selenadiazoles (Figure 2.13). No report mentioned whether this reaction is suitable for preparing sulfur analogues.

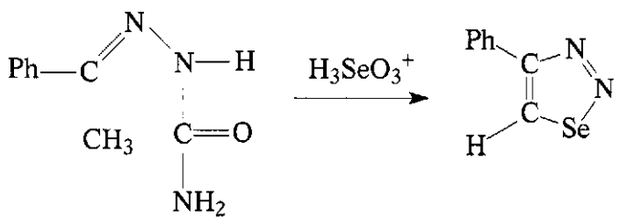


Figure 2.13 Synthetic route to 1,2,3-selenadiazoles

1,2,5-thiadiazoles (also called 2,1,3-thiadiazoles) bear a —N=S=N— linkage. This is the well-known sulfur diimide group. It is a very stable group and its redox chemistry and reactivity have been studied for the acyclic case. The first 1,2,5-thiadiazole was synthesized by Carmack and co-workers.[55] Afterward, numerous derivatives were formed by a number of cyclizations, from the reaction of sulfur dioxide with potassium cyanide, or from the reaction of ethyl-substituted aryl hydrocarbons with tetrasulfur tetranitride (S_4N_4). The methods of formation of this ring system by cyclization reactions encompass several classes of acyclic compounds with NCCN group, in which the N-C functions are varied over the oxidation levels of amine, imine, cyanide, and oxime. Aliphatic compounds which contain these functionalities in any combination react with sulfur monochloride or, in some cases, sulfur dichloride to form an appropriately substituted 1,2,5-thiadiazole. Based on this idea, a large number of readily available acyclic compounds can be constructed which serve as starting materials in these syntheses, e.g., α-diamines,[56] α-aminonitriles, alkyl cyanoformimidates, α-amino acid amides,[57] α-aminoamidines, dialkyl oxalimidates, alkyl oxamimidates, α-dioximes, α-isonitrosoamides, cyanogens,[58] α-isonitrosonitriles, and α-isonitrosocyanoacetamide.[59] Various acyclic compounds are employed in these reactions and the derived 1,2,5-thiadiazoles are summarized in Figure 2.14.[60]

The benzo-fused 2,1,3-benzothiadiazole was first synthesized[61] from *o*-phenylenediamine. In this case the N-chlorodithio intermediate is cleaved at the S-S bond by nucleophilic attack of the *ortho* amino group (Figure 2.15).

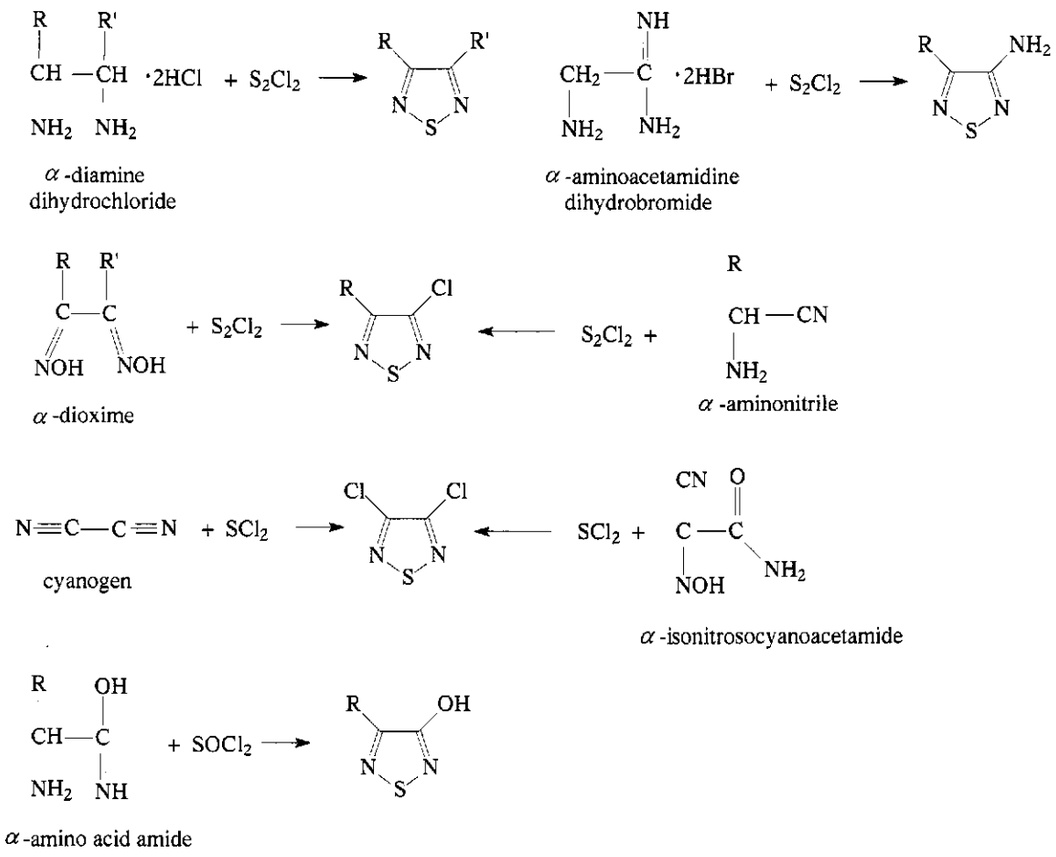


Figure 2.14 Synthetic routes to 1,2,5-thiadiazoles

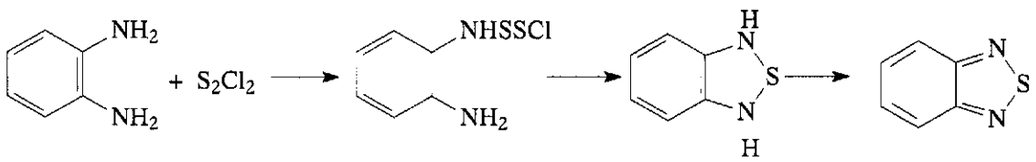
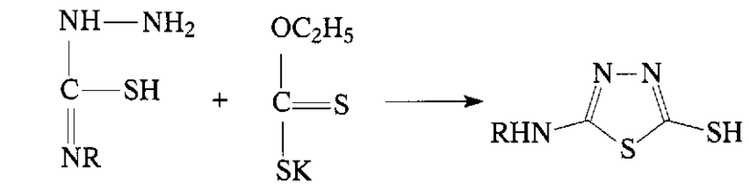


Figure 2.15 Synthetic route to benzo-fused 2,1,3 thiadiazole

The synthesis of 1,2,5-selenadiazole is analogous to the one-step preparation of 1,2,5-thiadiazole. Ethylenediamine dihydrochloride was allowed to react with selenium monochloride (molar ratio 1:8) in dimethylformamide, first for 1 hour at –20 °C and then

for 6 hours at 0 °C. Subsequent steam distillation of the reaction mixture afforded 1,2,5-selenadiazole.[62]

1,3,4-thiadiazoles and derivatives have been widely studied for analytical and industrial applications such as bioactive compounds, metal chelating agents, lubricant additives like corrosion inhibitors and antiwear agents, cross-linkers for polymers, components of cathode material battery systems, and as heterocyclic compounds for electrochemical studies.[63] The first 1,3,4-thiadiazoles were reported by Guha (Figure 2.16).[64] A series of 1,3,4-thiadiazoles were synthesized from substituted and unsubstituted thiasemicarbazides reacting with carbon disulfide in the presence of alcoholic potassium hydroxide. These are mercapto-substituted compounds. Relatively less has been reported about non-functionalised substituted 1,3,4-thiadiazoles. Mazzone et.al[65] successfully synthesized 2,5-bis(2-pyridyl)-1,3,4-thiadiazole. Mercapto-1,3,4-thiadiazoles have been recently studied in electrochemical redox processes.[66] As an application of conductivity, the mercapto-1,3,4-thiadiazoles are widely used as cathode-active material for lithium secondary batteries.[67]

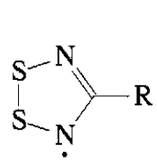


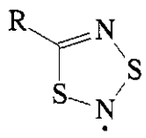
thiasemicarbazide carbon disulfide

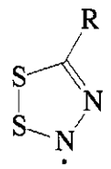
Figure 2.16 Synthetic routes to 1,3,4-thiadiazoles

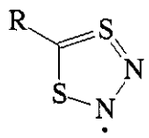
2.4.3 Dithiadiazoles and diselenadiazoles

The RCN_2S_2 heterocycles, known as dithiadiazoles (or dithiadiazolyls), can exist in four possible isomeric forms, of which only the 1,2,3,5-isomer and the 1,3,2,4-isomer have been prepared to date.


1,2,3,5-


1,3,2,4-

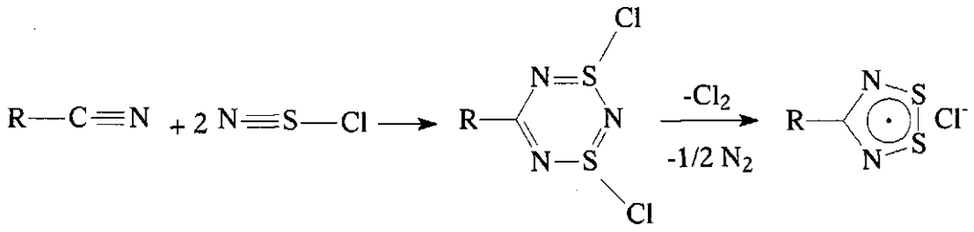

1,2,3,4-


1,3,4,5-dithiadiazole

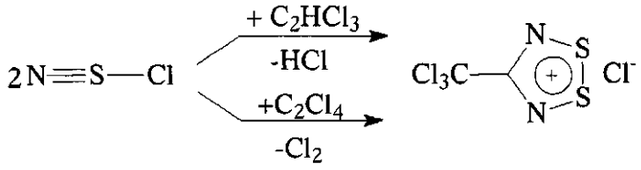
1,2,3,5-Dithiadiazolium cations (as the chloride salt), the precursor of 1,2,3,5-dithiadiazoles, were first prepared in 1977 from the reaction of thiazyl chloride with organic nitriles.[68] The yield of salt is particularly dependent on reaction conditions with best results being achieved after extended periods of heating. At lower temperature, an intermediate, dithiatriazine has been isolated, formed by cyclization of two equivalents of thiazyl chloride with RCN (Figure 2.17a).[69] Thiazyl chloride exists as a trimer in the solid state called trichlorocyclotrithiazene $(NSCl)_3$. It dissociates into the monomer on warming and so hot solutions of the trimer were reacted with the unsaturated molecules C_2HCl_3, C_2Cl_4, and CCl_3CN. In each case the main product analyzed as 1,2,3,5-dithiadiazolium chlorides (Figure 2.17b), although the mechanism of this reaction has not been established.[70]

The other way to synthesize 1,2,3,5-dithiadiazolium cations was from nitriles and tricyclotrithiazene (Figure 2.17c). The route was found to be unsatisfactory for nitriles with α-CH bonds. Thiazyl chloride probably reacts with the activated hydrogen.[71,72] Roesky et al.[73] have shown that reaction of thiazyl chloride with several alkazines RC(H)=N–N=C(H)R provides a convenient route to 1,2,3,5-dithiadiazolium cations

(Figure 2.17d), but the yield would appear to be particularly dependent on the nature of the substituent R.



(a)



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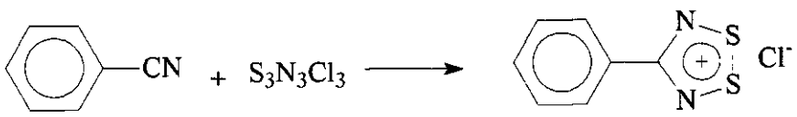

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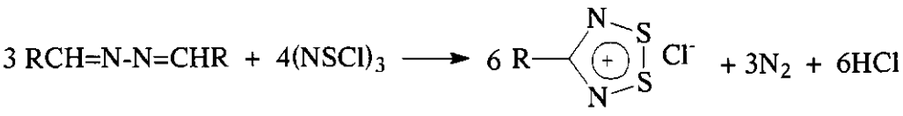
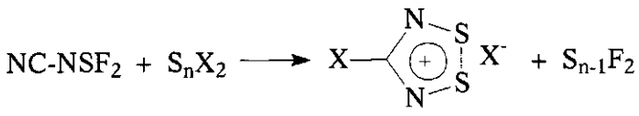


(d)



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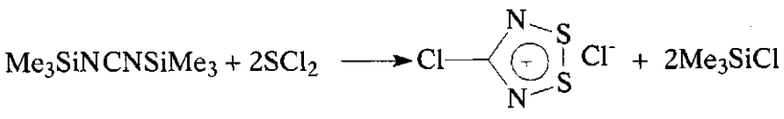


(f)

Figure 2.17 Synthetic route to 1,2,3,5-dithiadiazolium cations

The halo-substituted 1,2,3,5-dithiadiazolium salts were initially prepared in 1983 by Mews and co-workers[74] from NC—N=SF_2 and the sulfur halide SCl_2 or S_2Br_2 (Figure 2.17e). However, the chloro derivative can be more conveniently prepared from the readily accessible bis(trimethylsilyl) carbodiimide by condensation with SCl_2 at 50 °C (Figure 2.17f).[74]

The reaction of amidines $RC(NH)NH_2$ with SCl_2 to yield 1,2,3,5-dithiadiazolium chloride initially employed benzamidine hydrochloride.[72] Subsquently, other workers reported the preparation of 1,2,3,5-dithiadiazolium chloride (R = Me_2N-, *m*- and *p*-NC-C_6H_4-, furenyl and thienyl derivatives) from similar condensation reactions.[73,75-78] In many cases, yields were moderate but could be improved by using the free amidine (rather than the amidinium salt) or by the addition of a base to abstract the HCl formed. The recovered yield of 1,2,3,5-dithiadiazolium chloride can be maximized by slow addition of the amidine or its *N*-lithio salt to excess SCl_2, followed by warming to a low reflux for ~ 1 hour in an inert solvent such as CH_3CN, CCl_4, or CH_2Cl_2. This route has been used extensively in recent years for preparing aryl derivatives of 1,2,3,5-dithiadiazolium chlorides and is the most convenient route to many of these salts.[21,77,79] Condensation of silylated amidines with "$SeCl_2$" (i.e., an in situ 1:1 mixture of $SeCl_4$ and Se or $SeCl_4$ and Ph_3Sb) has also allowed the synthesis of the isostructural 1,2,3,5-diselenadiazolium salts.[21,78,79]

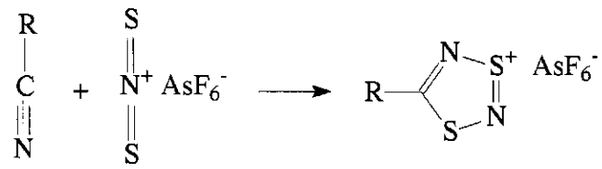
Many aryl-substituted dithiadiazolium salts are most conveniently prepared in good yield from the condensation reaction of SCl_2 with amidines, silylated amidines, or their salts. However the synthesis of alkyl-substituted salts generally requires more specific conditions.

The first 1,2,3,5-dithiadiazolyl radicals were prepared by reduction of dithiadiazolium chloride salts using sodium dust, triphenylverdazyl or tetramethyl-*p*-phenylene diamine.[80] Subsequently, other materials including zinc/copper couple, potassium, mercury, and elemental zinc were used.[81] The reductions proceed smoothly at room temperature in oxygen-donor solvents such as THF or monoglyme or in liquid SO_2. Purification of the crude product is usually carried out by vacuum sublimation. Other reducing agents that have been employed include NaNCS, KCN, LiN_3, PhMgBr, *n*BuLi, $SnCl_2$,[82] and particularly Ph_3Sb is widely used currently.[78,81]

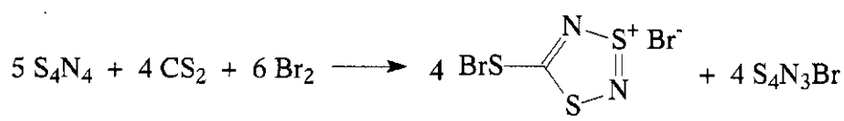
The most extensive route to 1,3,2,4-dithiadiazolium cations was carried out by the reaction of dithianitronium hexafluoroarsenate ([SNS][AsF_6]) with nitriles (Figure 2.18a). The reactions were observed by NMR, in many cases, to proceed quantitatively in liquid SO_2. Yields are commonly in excess of 80%. In a majority of cases, reaction proceeds smoothly at room temperature over 1-24 hours. All published reactions with different substituents were given by Parson[83] for R = Me, *t*Bu, I, H, Me_2N, Ph, *p*-O_2N–Ph, 3,5-$(O_2N)_2C_6H_3$, 2,5-$(Me)_2C_6H_3$, HCSNSC; Rawson[84] for R = *p*-CF_3-C_6H_4, *p*-Br-C_6H_4, *p*-Cl-C_6H_4, *p*-F-C_6H_4, *p*-MeS-C_6H_4, *p*-Me-C_6H_4, *p*-MeO-C_6H_4; and Schriver[85] for R = CF_3. Modification of the nitrile substituent R may alter the HOMO-LUMO energy gap and consequently change the relative reactivities of nitriles to [SNS][AsF_6]. Thus Me_2N-CN reacts 50 times faster than *t*Bu-CN and 100 times quicker than MeCN.[83]

The 1,3,2,4-dithiadiazolium chloride salts was first synthesized by Chivers and co-workers.[86] They examined the use of $(NSCl)_3/SO_2Cl_2$ as an *in situ* source of $NSCl_3$ and found that "$NSCl_3$" reacted with thioamides to form 1,3,2,4-dithiadiazolium chloride via a condensation reaction. Wolmershäuser and co-workers[87] found that reaction of S_4N_4

with bromine in CS_2 at ambient temperature led to dithiadiazolium bromide (Figure 2.18b).



(a)



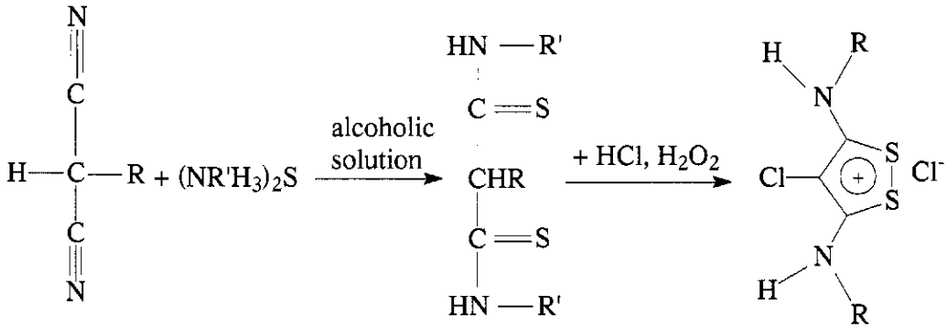
(b)

Figure 2.18 Synthetic route to 1,3,2,4-dithiadiazolium cations

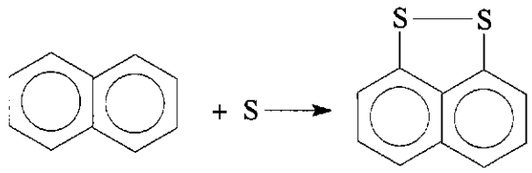
Reduction of 1,3,2,4-dithiadiazolium cations with reducing agents, such as silver powder,[88] $Ph_3Sb/[Me_4N]Cl$[85] or $Na_2S_2O_4$,[88] leads to the formation of the corresponding free radical. Purification by fractional sublimation has been used for the most radicals. The most recent review on dithiadiazoles were reported by Rawson[89] including preparation and electrochemical properities, and Boeré[15] on electrochemical properties.

2.4.4 1,2-dithioles

1,2-Dithioles, by virtue of incorporation of two sulfur atoms into the ring, have an odd electron count in the neutral form. They are normally prepared as salts of the diamagnetic cations. These preparations were carried out in two steps: first to prepare a special ligands, e.g. thioamide,[90] and second for a cyclization of the ligands (Figure 2.19a).[91]



dinitrile dithiomalonamide 3,5-diamino-4-chloro-1,2-dithiolium chloride (a)



naphthalene naphthalene 1,8-disulfide (b)

Figure 2.19 Synthetic route of 1,2-dithioles

A highly ring-fused derivative of 1,2-dithiole, naphthalene 1,8-disulfide, was first prepared by Lanfrey,[92] who used naphthalene and sulfur to interact in a hot iron tube (Figure 2.19b). Price et.al[93] and Zweig et.al[94] also reported the preparation of naphthalene 1,8-disulfide, starting with 1-aminonaphthalene-8-sulfonic acid. 1,2-dithiolyl free radicals were obtained by reduction of the corresponding salts by Ph_3Sb. Naphthalene 1,8-disulfide could be oxidized by dissolution in concentrated sulfuric acid or electrolytic oxidation to the cation radical, or reduced with sodium to the anion radical.[94]

2.5 Six-membered rings

Currently known six-membered rings can be classified as thiatriazines, 1,2,4,6-selenatriazines, dithiatriazines and dithiadiazines. The six-membered ring systems have received far less study, and are often less stable and harder to synthesize than the

numerous kinds of five-membered ring compounds. Thiatriazines and selenatriazines are seven π-electron systems in the neutral form, making them candidates for neutral radical conductors.

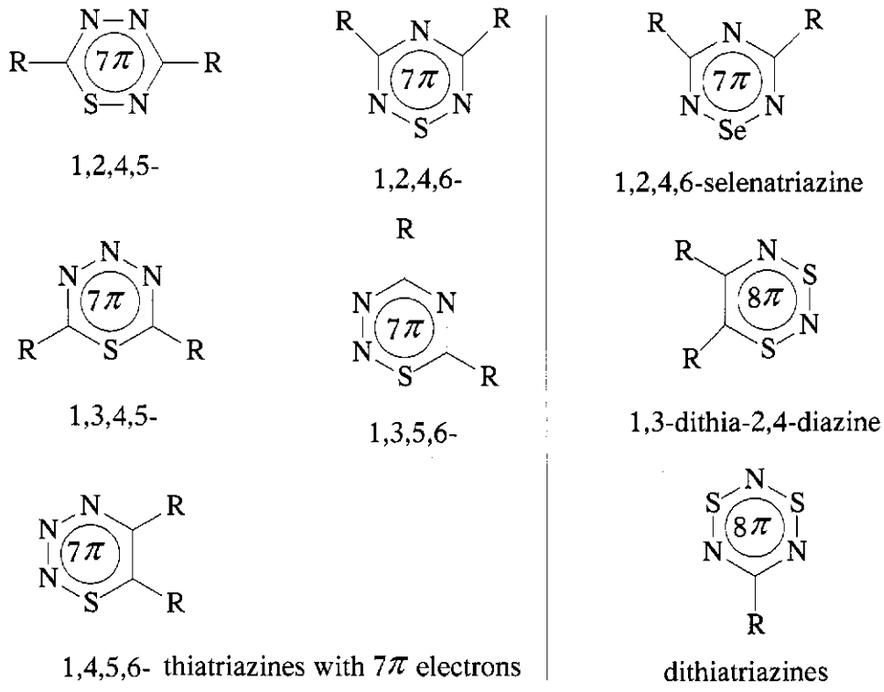


Figure 2.20 Six-membered thiazyl/selenazyl heterocycles

2.5.1 1,2,4,6-Thiatriazines

1,2,4,6-Thiatriazines are known with a wide range of substituents at sulfur and carbon. The majority of known thiatriazine derivatives are cyclic sulfonamides (an amide group attached to sulfur) or are part of fused ring systems.[95-98] As well, derivatives with alkyl or aryl groups in the 1,3,5 positions have been prepared by the reaction of *N*-haloamidines with thiolates or *N*-sulfenylamidines (Figure 2.21).[99,100]

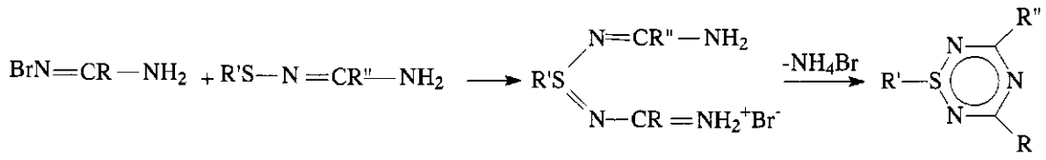
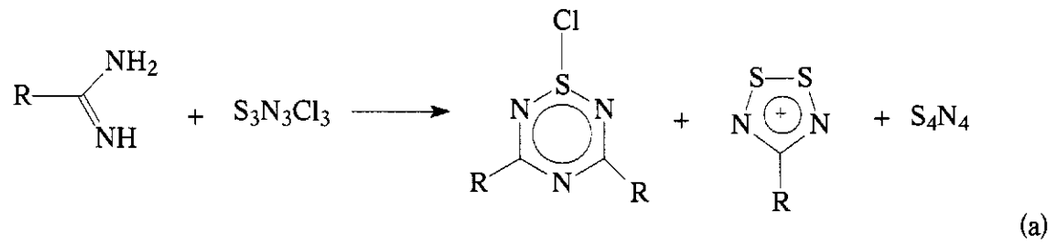
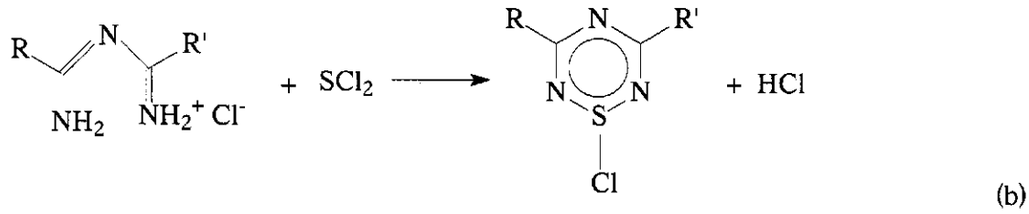


Figure 2.21 Synthesis of 1,2,4,6-thiatriazines with alkyl or aryl in 1,3,5 position

The fully chlorinated compound $Cl_3C_2N_3S$ can be prepared from reacting sodium dicyanamide with thionyl chloride.[95,101,102] Reduction of this compound to the radical was reported much later.[103] 1-Chloro-1,2,4,6-thiatriazines can be prepared in several ways. The reaction of benzamidine with $S_3N_3Cl_3$ represents a convenient but limited route to 1-chloro-3,5-diphenyl derivatives (Figure 2.22a).[104,105] The major side product of the reaction is the phenyldithiadiazolium chloride, this can be easily separated from the product by extraction with carbon tetrachloride (in which phenyldithiadiazolium chloride is insoluble). This later method provides a convenient source of quantities of 3,5-diphenyl-substituted compounds, but it is both costly and limited in scope.



(a)



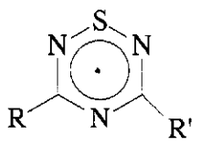
(b)

Figure 2.22 Synthetic routes to 1-chloro-1,2,4,6-thiatriazines

The most convenient way to 1-chloro-1,2,4,6-thiatriazines is the condensation of an imidoylamidine, or its hydrochloride, with excess sulfur dichloride SCl_2 (Figure 2.22b). This approach has been successfully applied in the preparation of a variety of trichloromethyl-substituted (in 1- and/or 3-positions) derivatives.[106] Some 1-chloro-selenatriazines can be obtained similarly with $SeCl_4$, although more forcing conditions are required to effect complete elimination of HCl.[107]

1,2,4,6-thiatriazines are by far the most investigated six-membered ring system, specifically the S-Cl compounds (products of Figure 2.22) because reductive elimination of chloride can lead to delocalized π-radicals that are stored as weakly dimerized species in the solid state. Such radicals are known so far for **a**,[98] **b**, **c**,[105,108] **d**, **e**, **f**,[15] and **g**[109] (Figure 2.23).

All the free radicals were made from the 1-chloro-thiatriazines through either Ph_3Sb or Zn/SO_2 reduction. The electrochemical properties of compounds **a**, **c**, **d**, **e**, **f**, and **g** have been fully characterized.[15]



a R = R' = Cl **b** R = R' = NEt_2
c R = R' = Ph **d** R = R' = 4-NO_2-Ph
e R = R' = 4-CH_3O-Ph **f** R = R' = CF_3
g R = CCl_3, R' = Ph, 4-CH_3-Ph, 4-CH_3O-Ph
4-CF_3-Ph, 4-Cl-Ph,
R = CF_3, R' = Ph, 4-CH_3-Ph, 4-CH_3O-Ph
4-CF_3-Ph, 4-Cl-Ph

Figure 2.23 Known 1,2,4,6-thiatriazine radicals with substitutes on 3,5 positions

2.5.2 1,2,4,5-Thiatriazines

1,2,4,5-Thiatriazine is one such ring whose 3,6-disubstituted derivatives satisfy the geometric requirements of calamitic (rod-like) liquid crystals.[110] The first object for 1,2,4,5-thiatriazine free radicals was reached by a series reactions (Figure 2.24).[111] The author synthesized 3,6-diphenyl-4-H-1,2,4,5-thiatriazine with good yield. The compound was treated with SO_2Cl_2 to 1-chloro-3,6-diphenyl-1,2,4,5-thiatriazine, which was then reduced by Ph_3Sb to the corresponding free radical showing weak EPR signal.

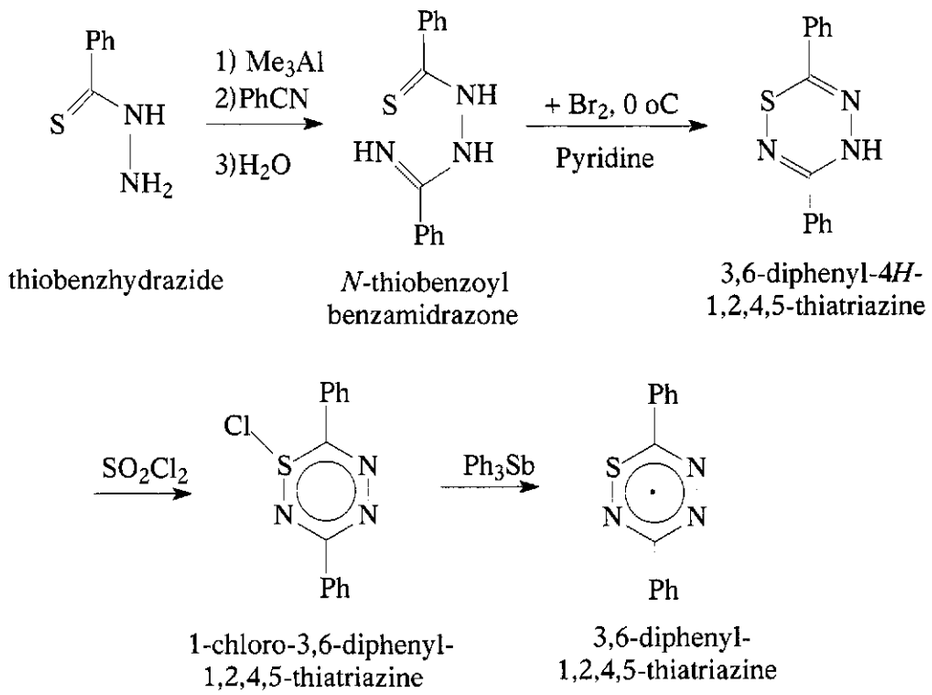
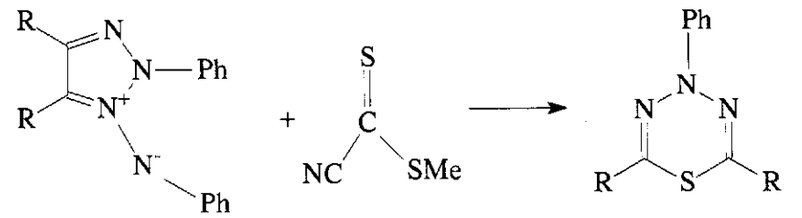


Figure 2.24 Synthetic route to 1,2,4,5-thiatriazines

2.5.3 1,3,4,5-thiatriazines

A sulphur atom was introduced into the structure when methyl cyanodithioformate was used as dipolarophile to the triazolium imide 1,3-dipole (Figure 2.25). Thus

treatment of the triazolium imide 1,3-diploes for short periods in benzene at ambient temperatures gave high yields of 1,3,4,5-thiatriazines. These are the first examples.[112-114] Structural analysis indicates that the 1,3,4,5-thiatriazines molecule is planar and the bond lengths suggest conjugation in the N—N—C—S unit.[115]



triazolium imide 1,3-dipole | methyl-cyanodithioformate | 2,4,6-substituted-1,3,4,5-thiatriazine

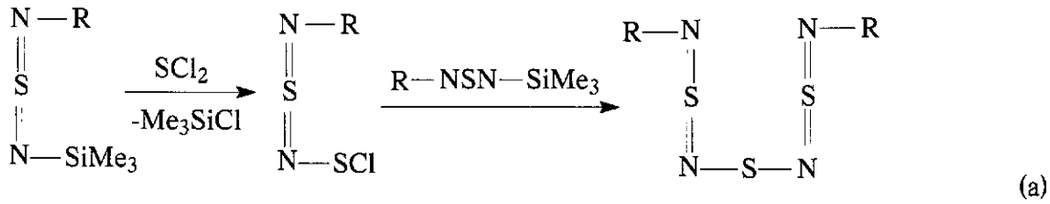
Figure 2.25 Synthetic route to 1,3,4,5-thiatriazines

2.5.4 Dithiatriazine

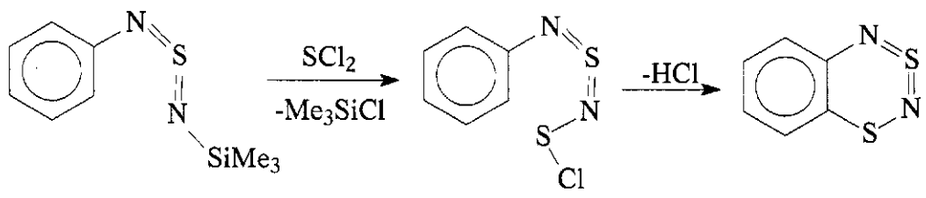
The first 8π-electron dithiatriazine was reached by the reaction of N,N-dimethylguanidinium hydrochloride with $S_3N_2Cl_2$ producing 5-(dimethylamino)-1,3-dichloro-1,3,2,4,6-dithiatriazine in low yield.[116] The corresponding 5-trifluoromethyl derivative can be isolated from the reaction of trifluoroacetonitrile with $S_3N_3Cl_3$.[117] However, neither method is generally applicable to the generation of 1,3-dichloro-1,3,2,4,6-dithiatriazines; for example, the reactions of benzamidine hydrochloride and trichloroacetonitrile with $S_3N_3Cl_3$ yield the corresponding dithiadiazolium chloride rather than a dithiatriazine.

2.5.5 Dithiadiazine

The coupling of silylated sulphur di-imide with sulphur dichloride is a widely-used method for producing conjugated sulphur-nitrogen oligomers and polymers (Figure 2.26a). However, if the R group of Figure 2.25a is an aromatic ring, electrophilic attack of the sulphenyl chloride group of R—NSN—SCl at the *ortho*-position of the aromatic ring occurs, yielding a novel six-membered 1,3-dithia-2,4-diazine ring (Figure 2.26b).[118]



(a)



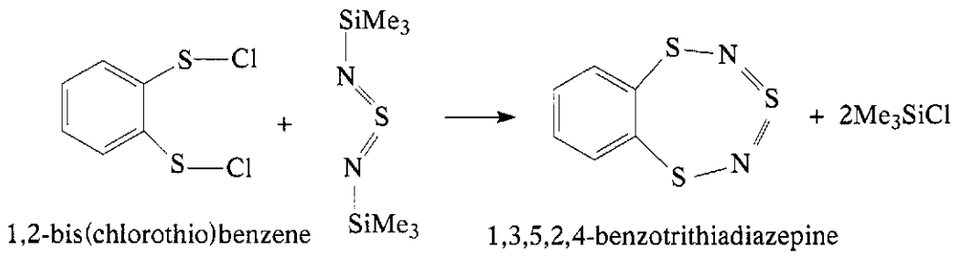
(b)

Figure 2.26 Synthetic routes to 1,3-dithia-2,4-diazine

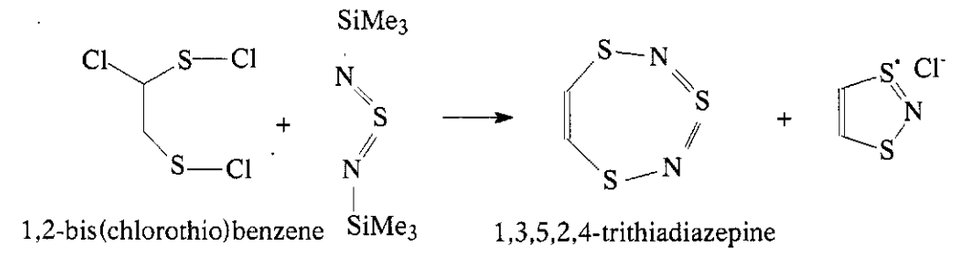
The annelation reaction (Figure 2.26b) represents the first example of a potentially general method for preparing electron-rich heterocycles based on the novel 1,3-dithia-2,4-diazine unit. Although benzo-1,3-dithia-2,4-diazine possesses a naphthalene-like framework, the π-manifold contains two extra electrons (12π *vs* 10π for naphthalene). The formation of benzo-1,3-dithia-2,4-diazine demonstrates that planar rings containing conjugated S—N units can exist with $4n$ as well as $4n+2$ π-electrons. A diverse redox chemistry for such molecules is to be expected.

2.6 Seven-membered rings

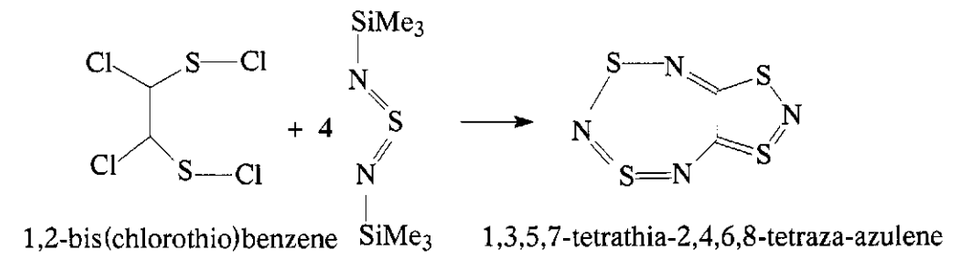
An intriguing new class of heteroaromatic compounds containing nitrogen and sulphur in seven-membered ring were synthesized independently by Rees et. al[119,120] and Oakley et.al.[121] They found an efficient route to the desired product via the coupling of $Me_3SiNSNSiMe_3$ with 1,2-bis(chlorothio)benzene (Figure 2.27a). The compound is extremely stable, with respect to both thermolysis and hydrolysis. Structural analysis shows the molecule is planar, and has a compact N—S—N unit.



1,2-bis(chlorothio)benzene 1,3,5,2,4-benzotrithiadiazepine (a)



1,2-bis(chlorothio)benzene 1,3,5,2,4-trithiadiazepine (b)



1,2-bis(chlorothio)benzene 1,3,5,7-tetrathia-2,4,6,8-tetraza-azulene (c)

Figure 2.27 Synthetic route to 1,3,5,2,4-benzotrithiadiazepine

By using 1-chloroethane-1,2-bis(sulphenyl chloride) or 1,2-dichloroethane-1,2-bis(sulphenyl chloride) instead of 1,2-bis(chlorothio)benzene, Rees et. al[121] successfully synthesized 1,3,5,2,4-trithiadiazepine and a fused 5-member-ring-7-member-ring compound, 1,3,5,7-tetrathia-2,4,6,8-tetraza-azulene (Figure 2.27b and c).

2.7 Eight-membered rings

The first eight membered ring, $C_2N_4S_2$, was synthesized by condensation reaction of an amidine with SCl_2.[122] The product was named 1,5-dithia-2,4,6,8-tetrazocine with low yield about 5%. Amidines used were benzamdine, *para*-methoxybenzamidine, *para*-(ethoxycarbonyl)benzamidine. When *N,N*-dimethylguanidine was used instead of amidine, the reaction produced 3,7-bis(dimethylamino)-1,5-dithia-2,4,6,8-tetrazocine with a pretty high yield of 54%.

New preparative routes to the 1,5-dithia-2,4,6,8-tetrazocines were reported later by Boeré in which the yields are substantially improved over previous methods.[123] In one route, reaction of O_2 with a mixture of $XC_6H_4CN_2S_2^+Cl^-$ and Ph_3Sb led to 1,5-dithia-2,4,6,8-tetrazocines with yield 40 – 60% for different substituents. In another, the reaction of the same salts with silylated amidines $XC_6H_4C\{NSiMe_3\}N(SiMe_3)_2$ in a 1:1 mol ratio led to the same compounds with yields between 18 – 65% depending on different substituents X (Figure 2.28). For aryl-substituted derivatives of dithiatetrazocines, the eight-membered ring is a planar 10π-aromatic, but for R_2N-substituted systems the ring becomes folded.

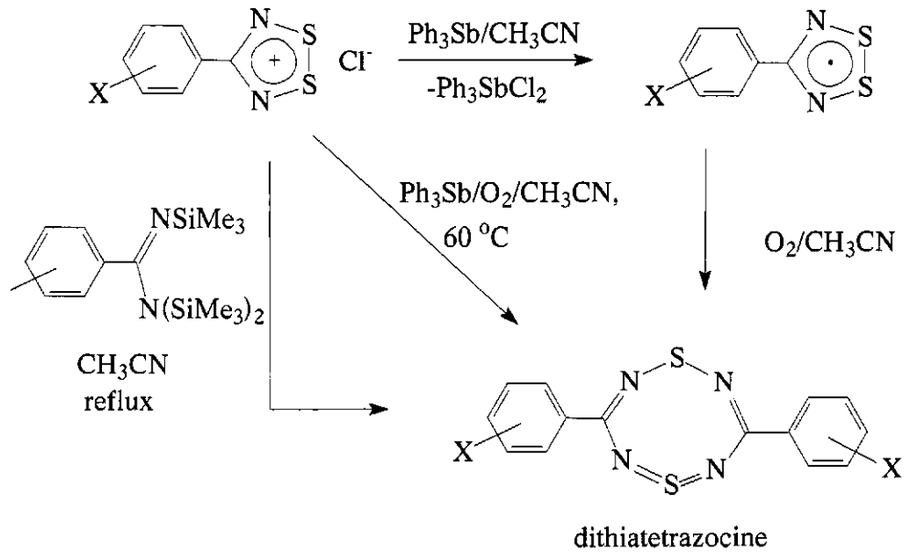


Figure 2.28 Synthetic routes to dithiatetrazocines

2.8 References

1. Jerome, D.; Mazaud, A.; Ribault, M.; Bechgaard, K. *Journal de Physique Lettres*, **1980**, *41*, L95-L98.

2. Bechgaard, K.; Carneiro, K.; Rasmussen, F. B.; Olsen, M.; Rindorf, G.; Jacobsen, C. S.; Pedersen, H. J.; Scott, J. C. *J. Am. Chem. Soc.*, **1981**, *103*, 2440 – 2442]

3. Bruce, D. W.; O'Hare, D. *Inorganic Materials*; John Wiley & Sons Ltd.; West Sussex, England, 1996.

4. Wudl, F.; Smith, G. M.; Hufnagel, E. J. *J. Chem. Soc., Chem. Commun.* **1970**, 1453.

5. Acker, D. S.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Melby, L. R.; Benson, R. E.; Mochel, W. E. *J. Am. Chem. Soc.* **1960**, 82, 6408.

6. Haddon, R. C. *Aust. J. Chem.* **1975**, *28*, 2333.

7. Haddon, R. C. *Aust. J. Chem.* **1975**, *28*, 2343.

8. Boeré, R. T.; Moock, K. H. *J. Am. Chem. Soc.* **1995**, *117*, 4755.

9. Tanner, D. B.; Jacobsen, C. S.; Garotp. A. F.; Heeger, A. J. *Phys. Rev. Lett.*, **1973**, *31*, 1311.

10. Haddon, R. C. *Nature*, **1975**, *256*, 394.

11. Garito, A. F.; Heeger, A. J. *Accounts chem.. Res.*, **1974**, *7*, 232.

12. Huheey, J.E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, Harper Collins College Publishers, **1993**, P187.

13. Zweig, A.; Hoffman, K. *J. Org. Chem.* **1965**, *30*, 3997.

14. Weast, R. C. *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, **1989**, p D-159.

15. Boére, R.T.; Roemmele, T.L. *Coord. Chem. Rev.* **2000**, *210*, 369.

16. Oakley, R.T. *Prog. Inorg. Chem.* **1988**, *36*, 299.

17. Wölmershäuser,G.; Schnauber, M.; Wilhelm, T. *J. Chem. Soc., Chem. Commun.* **1984**, 573.

18. Wölmershäuser,G.; Schnauber, M.; Wilhelm, T.; Sutcliffe, L. H. *Synth. Met.* **1986**, *14*, 239.]

19. Dormann, E.; Nowak, M. J.; Williams, K. A.; Angus, R. O.; Wudl, F. *J. Am. Chem. Soc.* **1987**, *109*, 2594.]

20. Wölmershäuser, G.; Wortmann, G.; Schnauber, M. *J. Chem. Res. Synop.* **1988**, 358.

21. Belluz, P. D. B.; Cordes, A. W.; Kristof, E. M.; Kristof, P. V.; Liblong, S. W.; Oakley, R. T. *J. Am. Chem. Soc.* **1989**, *111*, 9276.

22. Wölmershäuser, G.; Johann, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 920.

23. Becke-Goehring, M. *Inorg. Synth.*,**1960**, *6*, 123.

24. Villena-Blanco, M.; Jolly, W.L. *Inorg. Synth.*, **1967**, *9*, 98.

25. Burt, F.P. *J. Chem. Soc.*, **1910**, 1171.

26. Patton, R.L. Ph.D. Thesis, University of California, Berkeley, 1969.

27. Adkins, R.R.; Turner, A.G. *J. Am. Chem. Soc.*, **1978**, *100*, 1383.

28. Goehring, M. *Quarterly Reviews*, **1956**, *10*, 437.

29. Heal, H.G. *Inorg. Chem. Radiochem.,* **1972**, *15*, 375.

30. Labes, M.M.; Love, P.; Nichols, L. F. *Chem. Rev.* **1979**, *79*, 1.

31. Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci. Chem. Ed.* **1974**, *12*, 11.

32. Chiang, C. K.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1977**, *39*, 1098.

33. Herz, R. *Chem. Zent.* **1922**, *4*, 948.

34. Blomquist, A.T.; Diuguid, L. I. *J. Org. Chem.*, **1947**, *12*, 720.

35. Warburton, W. K. *Chem. Rev.*, **1957**, *57*, 1011.

36. Huestis, L. D.; Walsh, M. L.; Hahn, N. *J. Org. Chem.*, **1965**, *30*, 2763.

37. Hope, P.; Wiles, L.A. *J. Chem. Soc. C*, **1967**, 1642.

38. Barclay, T.M.; Cordes, A.W.; Goddard, J.D.; Mawhinney, R.C.; Oakley, R.T.; Preuss, K.E.; Reed, R.W. *J. Am. Chem. Soc.*, **1997**, *119*, 12136.

39. Rawson, J. M.; McManus, g. D. *Coord. Chem. Rev.* **1999**, *189*, 135.

40. Mayer, R.; Domschke, G.; Bleisch, S; Bartl, A. *Tetrahedron Lett.*, **1978**, *42*, 4003.

41. Hecknamm, G.; Johann, R.; Kraft, G.; Wölmershäuser, G. *Synth. Met.* **1991**, *43*, 3287.

42. Barclay, T.M.; Cordes, A.W.; George, N.A.; Haddon, R.C.; Itkis, M.E.; Mashuta, M.S.; Oakley R. T.; Patenaude, G.W.; Reed, R.W.; Richardson, J.F.; Zhang, H. *J. Am. Chem. Soc.*, **1998**, *120*, 352.

43. Barclay, T.M.; Cordes, A.W.; George, N.A.; Haddon, R.C.; Itkis, M.E.; Mashuta, M.S.; Oakley R. T.; Patenaude, G.W.; Reed, R.W.; Richardson, J.F.; Zhang, H. *J. Am. Chem. Soc.*, **1997**, *119*, 2633.

44. Hecknamm, G.; Johann, R.; Kraft, G.; Wölmershauser, G. *Synth. Met.* **1991**, *43*, 3287.

45. Barclay, T.M.; Cordes, A.W.; George, N.A.; Haddon, R.C.; Itkis, M.E.; Mashuta, M.S.; Oakley R. T.; Patenaude, G.W.; Reed, R.W.; Richardson, J.F.; Zhang, H. *J. Am. Chem. Soc.*, **1998**, *120*, 352.

46. Wolmershäuser, G.; Kaim, W.; Heckmann, G.; Lichtblau, A. *Z. Naturforsch.*, **1992**, *47*, 675.

47. Khmelnitski, L. I.; Rakitin, O. A. in : Katritsky, A. R.; Rees, C. W.; Scriven, E. F. V. (Eds.), *Comprehensive Heterocyclic Chemistry*, Vol. II, 4 and 6, Pergamon, Oxford, **1996**.

48. Pechmann, H.; Nold, A. *Ber.*, *1896*, *29*, 2588.

49. Wolff, L. *Justus Liebigs Annalen Der Chemie.*, **1902**, *325*,129.

50. Hurd, C.D.; Mori, R.I. *J. Am. Chem. Soc.*, **1955**, *77*, 5359.

51. Meir, H.; Voigt, E. *Tetrahedron,* **1972**, *28,* 187.

52. Attanasi, O.A.; De Cresscentini, L.; Filippone, P.; Mantellini, F. *Synlett*, **2001**, 557.

53. Attanasi, O.A.; De Cresscentini, L.; Favi, G.; Filippone, P.; Giorgi, G.; Mantellini, F.; Santeusanio, S. *J. Org. Chem.*, **2003**, *68*, 1947.

54. Lalezari, I.; Shafiee, A. *Tetrahedron Letters*, *1969*, **58**, 5105.

55. Carmack, M.; Weinstock, L. M.; Shew, D. Abstracts, *136th National Meeting of the American Chemical Society*, Atlantic City, N. J., September, **1959**, p.37.

56. Bertini, V.; Pino, P. *Angew. Chem. Intern. Ed. Engl.* **1966**, *5*, 514.

57. Mizsak, S. A.; Perelman, M. *J. Org. Chem.* **1966**, *31*, 1964.

58. Vest, R. D. *U.S. Patent 3115497*, **1963** and *Chem. Abstr.* **1963**, *23*, 4121.

59. Ross, J. M.; Smith, W. C. *J. Am. Chem. Soc.* **1964**, *86*, 2861.

60. Weinstock, L. M.; Davis, P. Handelsman, B.; Tull, R. *J. Org. Chem.* **1967**, *32*, 2823.

61. Hope, P.; Wiles, L. A. *J. Chem. Soc.* **1966**, 1283.

62. Weinstock, L. M.; Davis, P.; Mulvey, D. M.; Schaeffer, J. C. *Angew. Chem. Internat. Edit. Engl.* **1967**, *6*, 364.

63. Kornis, G. *1,3,4-Thiadiazoles*, in: Katritzky, A. R.; Rees, C. W. (Eds.), *Comprehensive Heterocyclic Chemistry*, vol. 6, Pergamon Press, Oxford, **1984**, pp.545, part 4B.

64. Guha, P.C. *J. Am. Chem. Soc.* **1922**, *44*, 1502 and 1510; **1925**, *47*, 385.

65. Mazzone, G.; Puglisi, G.; Bonina, F.; Corsaro, A.; *J. Heterocycl. Chem.* **1983**, *20*, 1399.

66. Wang, P. *J. Electrochem. Soc.* **2002**, *149*, A1171.

67. Tatsuma, T.; Yokoyama, Y.; Buttry, D. A.; Oyama, N. *J. Phys. Chem. B* **1997**, *101*, 7556.

68. Alange, G.G.; Banister, A.J.; Bell, B.; Millen, P.W. *Inorg. Nucl. Chem. Lett.* **1977**, *13*,143.

69. Höfs, H.-U.; Hartmann, G.; Mews, R.; Sheldrick, G.M. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 988.

70. Alange, G.G.; Banister, A.J.; Bell, B.;Millen, P.W. *J. Chem. Soc., Perkin Trans.* **1979**, 1192.

71. Alange, C.G.; Banister, A.J.; Bell, B.; Millen, P.W. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 143.

72. Alange, C.G.; Banister, A.J.; Bell, B.; Millen, P.W. *J. Chem. Soc., Perkin Trans.* **1979**, *1*, 1192.

73. Roesky, H.W.; Muller, *Chem. Ber.* **1978**, *111*,2960.

74. Höfs, H.U.; Mews, R.; Clegg, W.;Noltemeyer, M.; Schmidt, M.; Sheldrick, G.M. *Chem. Ber.* **1983**, *116*, 416.

75. Amin, M.; Rees, C.W. *J. Chem. Soc., Chem. Commun.*, **1989**, 1137.

76. Cordes, A.W.; Goddard, J.D.; Oakley, R. T.; Westwood, N.P. *J. Am. Chem. Soc.* **1989**, *111*, 6147.

77. Amin, M.; Rees, C.W. *J. Chem. Soc., Perkin Trans.* **1989**, *1*, 2495.

78. Cordes, A.W.; Haddon, R.C.; Hicks, R.G.; Oakley, R.T.; Palstra, T. T.M. *Inorg. Chem.* **1992**, *31*, 1802.

79. Cordes, A.W.; Haddon, R.C.; Hicks, R.G.; Oakley, R.T.; Palstra, T.T.M.; Schneemeyer, L. F.; Waszczak, J.V. *J. Am. Chem. Soc.* **1992**, *114*, 5000.

80. Markovski, L.N.; Polumbrik, O. M.; Talanov, V.S.; Shermolovich, Y.G. *Tetrahedron Lett.* **1982**, *23*, 761.

81. Cordes, A.W.; Chamchoumis, C.M.; Hicks, R.G.; Oakley, R.T.; Young, K.M.; Haddon, R.C. *Can. J. Chem.* **1992**, *70*, 919.

82. Banister, A.J.; Smith, N.R.M.; Hey, R.G. *J. Chem. Soc., Perkin Trans.* **1983**, *1*, 1181.

83. Parsons, S.; Passmore, J.; Schriver, M.J.; Sun, X. *Inorg. Chem.* **1991**, *30*, 3342.

84. Aherne, C.M.; Banister, A.J.; Gorrell, I.B.; Hansford, M.I.; Hauptman, Z.V.; Luke, A.W.; Rawson, J.M. *J. Chem. Soc., Dalton Trans.* **1993**, 967.

85. Burford, N.; Passmore, J.; Schriver, M.J. *J. Chem. Soc., Chem. Commun.* **1986**, 140.

86. Apblett, A.; Chivers, T. *J. chem. Soc., Chem. Commun.* **1987**, 1889.

87. Wölmershäuser, G.; Street, G.B.; Smith, R.D. *Inorg. Chem.* **1979**, *18*, 383

88. MacLean, G.K.; Passmore, J.; Rao, M.N.S.; Schriver, M.J.; White, P.S.; Bethell, D.; Pilkington, R.S.; Sutcliffe, L.H. *J. Chem. Soc., Dalton Trans.* **1985**, 1405.

89. Rawson, J. M.; Banister, A. J.; Lavender, I. *Adv. Heterocycl. Chem.* **1995**, *62*, 137.

90. Taylor, E. C.; Zoltewicz, J. A. *J. Am. Chem. Soc.* **1960**, *82*, 2656.

91. Menabue, L. Pellacani, G. C. *J. Chem. Soc. Dalton Trans.* **1976**, 455.

92. Lanfrey, M. *Compt. Rend.* **1911**, *152*, 92.

93. Price, W. B.; Smiles, S. *J. Chem. Soc.* **1928**, 2372.

94. Zweig, A. Hoffmann, A. K. *J. Org, Chem.* **1965**, *30*, 3997.

95. Schramm, W.; Voss, G.; Rembarz, G. *Z. Chem.* **1974**, *14*, 471.

96. Leonhardt, G.; Scheibe, R.; Schramm, W.; Voss, G.; Fischer, E.; Rembarz, G. *Z. Chem.* **1975**, *15*, 193.

97. Storek, W.; Schramm, W.; Voss, G; Rembarz, G.; Fischer, E. *Z. Chem.* **1975**, *15*, 104.

98. Jeroschewski, P.; Voss, G.; Fischer, E. *Z. Chem.* **1977**, *17*, 145.

99. Goerdeler, J.; Loevenich, D. *Chem. Ber.* **1954**, *87*, 1079.

100. Goerdeler, J.; Wedekind, B. *Chem. Ber.* **1962**, *95*, 147.

101. Greevers, J.; Hackmann, J.T.; Trompen, W.P. *J. Chem. Soc. C* **1970**, 875.

102. Schramm, W.; Voss, G.; Michalik, M.; Rembasz, G. *Z. Chem.* **1975**, *15*, 19.

103. Boeré, R.T.; Oakley, R.T.; Reed, R.W.; Westwood, N.P.C. *J. Am. Chem. Soc.* **1989**,*111*,1180.

104. Corde, A.W.; Hayes, P.J.; Josephy, P.D.; Koenig, H.; Oakley, R.T.; Pennington, W.T. *J. Chem. Soc., Chem. Comm.*, **1984**, 1021.

105. Hayes, P.J.; Oakley, R. T.; Cordes, A. W.; Pennington, W. T. *J. Am. Chem. Soc.* **1985**, *107*, 1346.

106. Kornuta, P.P.; Derii, L. I.; Markovskii, L.N. *Zh. Org. Khim.* **1980**, *16*, 1303.

107. Oakley, R.T.; Reed, R.W.; Cordes, A.W.; Craig, S.L.; Graham, J. B. *J. Am. Chem. Soc.* **1987**, *109*, 7745.

108. Boeré, R. T.; Cordes, A. W.; Hayes, P.J.; Oakley, R. T.; Reed, R. W.; Pennington, W. T. *Inorg. Chem. 1986*, **25**, 2445.

109. Roemmele, T. L. *M. Sci. thesis*, Univ. of Lethbridge, **2002**.

110. Demus, D. *Mol. Cryst. Liq. Cryst.* **1988**, *165*, 45.

111. Farrar, J.M.; Mahesh K.P.; kaszynski, P. *J. Org. Chem.* **2000**, *65*, 931.

112. Jarvis, B. B.; Stakly, G. P. *J. Org. Chem.* **1980**, *45*, 2604.

113. Butler, R. N.; O'Shea, P. D.; Cunningham, D.; McArdle, P. *J. Chem. Soc., Perkin Trans. 1 Commun.*, **1989**, 371.

114. Butler, R. N.; Cunningham, D.; McArdle, P.; O'Halloran, G. A. *J. Chem. Soc., Chem. Commun.* **1988**, 232.

115. Butler, R. N.; Evans, A. M.; McNeela, E. M.; O'Halloran, G. A.; O'Shea, P. D.; Cunningham, D. McArdle, P. *J. Chem. Soc. Perkin Trans.* **1990**, *1*, 2527.

116. Roesky, J.W.; Schafer, P.; Noltemeyer, M.; Sheldrick, G.M. *Z. Naturforsch., B* **1983**, *38*, 347.

117. Höfs, H. U.; Hartmann, G.; Mews, R.; Sheldrick, G.M. *Z. Naturforsch., B* **1984**, *39*, 1389.

118. Koenig, H.; Oakley R.T. *J. Chem. Soc. Chem. Commun.* **1983**, 73.

119. Morris, J. L.; Rees, C. W.; Rigg, D. J. *J. Chem. Soc., Chem. Commun.* **1985**, 55.

120. Daley, S. T. A. K.; Rees, C. W.; Williams, D. *J. Chem. Soc., Chem. Commun.* **1985**, 57.

121. Cordes, A. W.; Hojo, M.; Koenig, H.; Noble, M. C.; Oakley, R. T.; Pennington, W. T. *Inorg. Chem.* **1986**, *25*, 1137.

121. Rees, C. W.; Surtees, J. R. J. *J. Chem. Soc. Perkin Trans.* **1991**, *1*, 2945.

122. Plater, M. J.; Rees, C. W. *J. Chem. Soc. Perkin Trans.* **1991**, *1*, 301.

122. Ernest, I.; Holick, W.; Rihs, G.; Schlmburg, D.; Shoham, G.; Wenkert, D.; Woodward, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 1540.

123. Boeré, R. T.; Moock, K. H.; Derrick, S.; Hoogerdijk, W.; Preuss, K.; Yip, J. *Can. J. Chem.* **1992**, *71*, 473.

Chapter 3

Preparation of 1-chloro-1,2,4,6-selenatriazines

3.1 Introduction

This chapter focuses attention on synthetic design, execution and results. These are: (1) the preparation of 1-chloro-1,2,4,6-selenatriazines and *bis*(1-chloro-1,2,4,6-selenatriazine)benzenes; (2) a description of precursors required to synthesize selenatriazines, (3) the characterization of these selenatriazine chlorides. My synthetic approach is conceptually the conversion of: amidine→imidoylamidine→selenatriazine chloride. Before discussing any of these results, however, it is necessary to describe the synthetic work required to generate the precursors: amidines and *N*-imidoylamidines.

3.2 Synthesis of amidines

Amidines are generally prepared from nitriles, amides, thioamides and miscellaneous preparations.[1] Among these, nitriles are the most popularly used. There are three way to use nitriles: ① addition of metal amides to nitriles; ② addition of ammonia and amines to nitriles; and ③ Pinner synthesis through imido ester intermediates. All amidines used in this work are aryl substituted compounds and prepared from the corresponding nitriles.

3.2.1 Monoamidines

Most of the aryl substituted free amidines required were made by adding a lithium amide to the corresponding nitriles (Figure 3.1).[2] A nitrile reacted with lithium

bis(trimethylsilyl)amide, $LiN(SiMe_3)_2$, in ether allowed the isolation of lithiated amidine derivative. Directly hydrolyzing with four equivalents of ethanolic HCl gave amidine hydrochlorides by precipitation. Free amidines were obtained by dissolving the corresponding amidine hydrochloride salt in water and adding 5M sodium hydroxide. Addition of the base caused the amidine to precipitate out of solution. The amidines were purified by sublimation under vacuum at ~130 °C to yield white powders. Benzamidine was made by treatment of the commercial benzamidine hydrochloride salt with potassium hydroxide followed by extraction with dichloromethane. The dichloromethane extract was dried with magnesium sulfate, filtered and evaporated to yield quantitative amounts of crude benzamidine. A final purification by sublimation *in vacuo* was performed at 45 °C to yield a white powder.

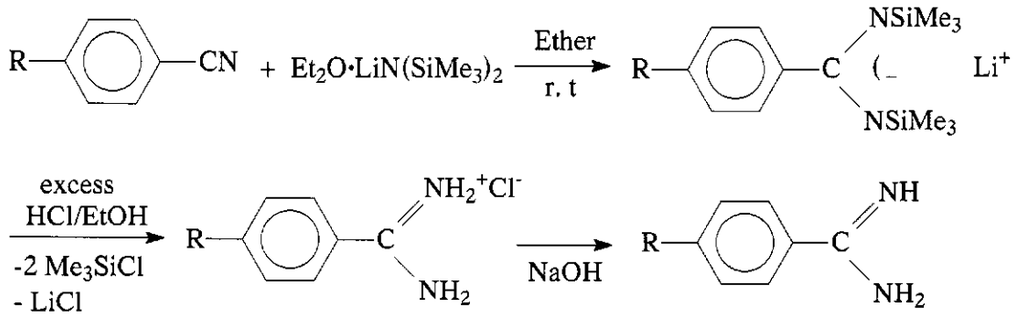


Figure 3.1 General routes to aryl substituted free amidines

2,6-Diisopropylphenylamidine (Dipp-amidine) was made from the corresponding Grignard reagent (Figure 3.2) (our lab found the corresponding nitrile did not react with $LiN(SiMe_3)_2$). Dipp-magnesium bromide reacted with TMS–N=C=N–TMS to yield a solid Mg adduct which was hydrolyzed by ethanolic HCl to give Dipp-amidine

hydrochlorides by precipitation. Dipp-amidine was obtained by treating the Dipp-amidine hydrochloride salt with 5M sodium hydroxide. Purification of Dipp-amidine was performed by subliming at 80 °C to yield a white powder.

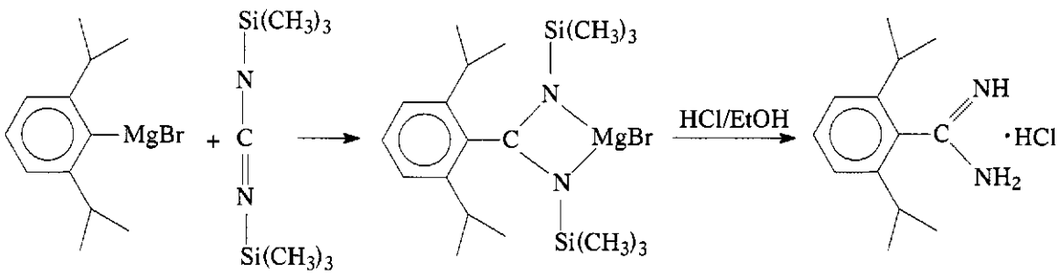


Figure 3.2 Synthesis of Dipp-amidine from Grignard reagent

Table 3.1 summarizes the amidines that have been prepared in this thesis. The melting point varies in a wide range depending on the substituent on benzene. Unsubstituted benzene rotates around C—C bond easily, hence benzamidine has the lowest melting point. The bulky Dipp group hinders C—C rotation and enhances the melting point about 3 times higher than benzamidine. The highest melting point of *para*-cyanobenzamidine most possibly comes from intermolecular N...H hydrogen bond in the solid state, as does *para*-chloro- and *para*-bromobenzamidine. The ^{1}H NMR spectra of amidines show a single broad NH signal because of H exchange. The location of the two doublets of phenyl protons appears in the 7-8 ppm range for *para*-substituted benzamidines. The *ortho* proton (H1) to the amidine group shifts downfield compared to the *meta* proton (H2). This is because of the effect from N nearby.

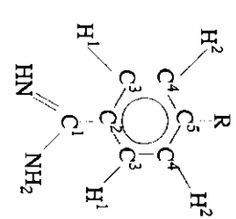
Table 3.1 Characteristics of monoamidines

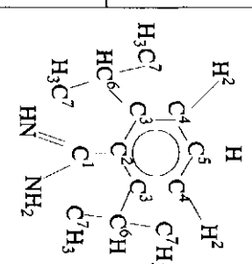
R	mp	^{1}H NMR				^{13}C NMR						
	(°C)	H1	H2	NH	II-R	C1	C2	C3	C4	C5	C_R (C6)	C7
CH_3O	114 – 116	7.57 (d)	6.92 (d)	5.0	3.85							
CH_3	104 – 106	7.50 (d)	7.22 (d)	5.3	2.39							
H	59 – 62	7.61 (d)	7.44 (d)	5.3	7.41							
Cl	155 – 157	7.49 (d)	7.32 (d)	5.1	-	161.3[a]	134.3	127.8	128.3	135.1		
		7.80 (d)[a]	7.45 (d)	6.4								
Br	176 – 178	7.56 (d)	7.49 (d)	5.11	-	164.6	135.7	128.0	132.2	125.1		
CF_3	140 – 143	7.75 (d)	7.69 (d)	5.5	-							
CN[a]	181 –183	7.95 (d)	7.88 (d)	6.5	-	160.9	140.5	127.4	131.9	112.1	118.4	
Dip	159 – 160	7.18 (d)	7.32 (t)	5.0	1.24, 3.20	166.5	136.4	129.3	123.4	145.3	(31.0)	25.0

All values are in ppm

[a] DMSO-d_6 as solvent,

all others used $CDCl_3$ as solvent





3.2.2 Diamidines

In the synthetic route shown in Figure 3.1, 1,4-dicyanobenzene reacts with one equivalent of lithium bis(trimethylsilyl)amide to afford a final *para*-cyanobenzamidine, and the reaction works well. Yet 1,4-dicyanobenzene reacted with two equivalents of lithium bis(trimethylsilyl)amide does not afford benz-1,4-diamidine, instead *para*-cyanobenzamidine is the only product. This is the same case when 1,3-dicyanobenzene is used. The result proves that once one —CN group takes part in the reaction, the other —CN group on the benzene ring is deactivated. This method is thus not applicable for the synthesis of benzdiamidines.

Instead, benzdiamidines can be prepared by Pinner's reaction (Figure 3.3)[3]. The treatment of dicyanobenzene in dry EtOH by HCl gas afforded the diiminoesters, which were isolated as white powders and characterized with ^{1}H and ^{13}C NMR. Further treatment of the latter in EtOH with gaseous NH_3 gave corresponding benzdiamidine hydrochloride salts as white powder. The associated hydrochlorides were neutralized with NaOH leaving benzdiamidines. Benz-1,3-diamidine can be purified by subliming at 130 °C, while benzene-1,4-diamidine needs a higher subliming temperature.

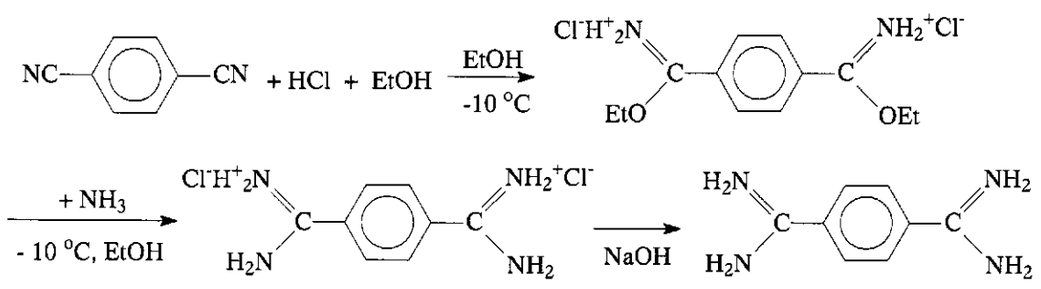
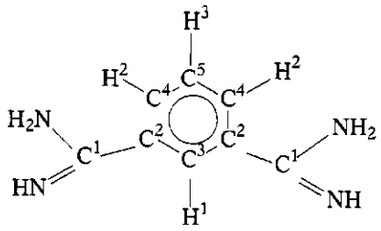


Figure 3.3 Pinner's reaction to benzdiamidines



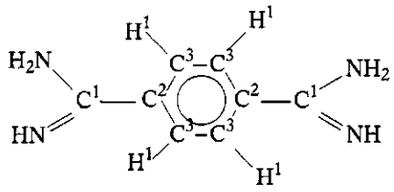


Table 3.2 Characteristics of benzdiamidines

		Benz-1,3-diamidine	Benz-1,4-diamidine
mp (°C)		152 – 154	240 – 243
Subliming temp (°C)		130	-
^{1}H NMR (ppm)	H1	8.10	7.78
	H2	7.80	-
	H3	7.41	-
	NH	6.4	6.4
^{13}C NMR (ppm)	C1	162.4	161.9
	C2	136.2	137.3
	C3	124.5	126.0
	C4	127.6	-
	C5	127.7	-
IR (cm^{-1})	NH	3387 (br), 314 (sh), 3279 (sh), 3180 (br)	3366 (br), 3168 (br)
	C–N, C=N	1643, 1684	1660, 1617

Benz-1,3-diamidine NMR in $CDCl_3$, while benz-1,4-diamidine in DMSO-d_6.

Table 3.2 lists the characteristics of benz-1,3-diamidine and benz-1,4-diamidine. Both compounds have much higher melting points than the corresponding benzamidine (59 °C, see Table 3.1). Presumably this is caused by intermolecular N---H hydrogen bonding in solid state. The typical NH signal as a single broad peak in the ^{1}H NMR integrating to > 2H is consistent with a primary amidine. Just as in monoamidines, the

proton *ortho* to the amidine group is shifted downfield compared to the *meta* proton. H1 of benz-1,3-diamidine, which is *ortho* to two amidine groups, is shifted further downfield than H2. ^{13}C NMR spectra confirmed the conversion of the C≡N group (about 118 ppm) to amidine (about 162 ppm). The infrared spectrum shows the disappearance of the C≡N group at about 2232 cm^{-1} from the starting materials, dicyanobenzenes. NH stretches appear between 3000 – 3400 cm^{-1}. The C—N and C=N stretches appear between 1600 – 1700 cm^{-1}.

3.3 Synthesis of *N*-imidoylamidines

3.3.1 Mono-imidoylamidines

N-Imidoylamidines possess the open-chain N—C—N—C—N. These are important intermediates for many reactions, but few reports describe the isolation and characterization of these compounds. The first imidoylamidines (also called diamidides) in type RN=C(Ph)—N(R')—C(Ph)=NR" (I) and RR'N—(Ph)=N—C(Ph)=NR" (II) were prepared by Ley and Müller from the appropriate imidochloride and amidine (Figure 3.4a)[4]. For example, *N*-Phenylbenzamidine and *N*-phenylbenzimidochloride afford decomposition products of the imidoylamidine HN=C(Ph)—N(Ph)—C(Ph)=NPh. In above two structures, at least one of the R, R' or R" groups was Ph, and it was concluded that the conjugated structure of the latter type is an important factor in stabilizing the molecule.

After investigating Ley and Müller's reaction, Peak[5] postulated that conjugated *N*-imidoylamidines, in which the nitrogen atoms carry no aryl or alkyl substituents, should be capable of existence. The author then prepared a number of such *N*-imidoylamidines

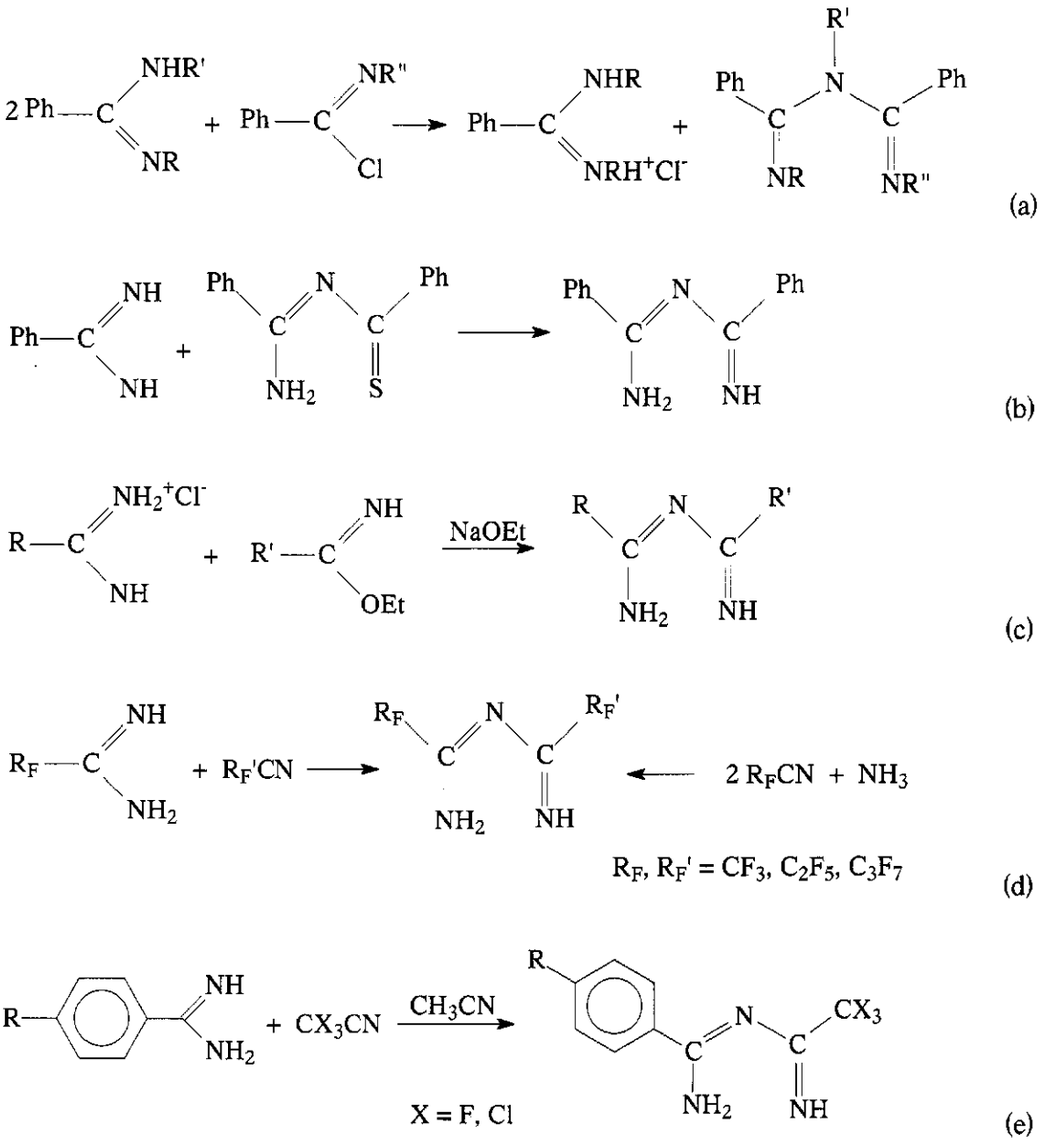


Figure 3.4 Synthetic routes to *N*-imidoylamidines

with structure of H_2N–C(Ph)=N–C(R)=NH (III) (Figure 3.4b). The method of Ley and Müller was not adaptable to the synthesis of the type III imidoylamidines owing to the instability of benzimidoyl chlorides or benzenesulphonates containing an unsubstituted

imido-group. Of alternative routes, a promising one appeared to be the desulphurising amination of *N*-thiobenzoylbenzamidines. The combination of benzamidine and *N*-thiobenzoylbenzamidine produces *N*-benzimidoylbenzamidine. The *N*-thiobenzoylbenzamidine can be prepared by the acid catalyzed condensation of benzamidine with thiobenzamide or by the sulphurization of *N*-benzoylbenzamidine. The former reaction is specific for preparing the phenyl-substituted derivative; the latter reaction was explored extensively to devise a general synthetic method.

Another route involves reacting a primary amidine hydrochloride with primary imidates in the presence of NaOEt to produce *N*-imidoylamidines with different substituents (Figure 3.4c).[6]

Special derivatives, N-(perfluoroacylimidoyl)perfluoroalkylamidines, were obtained in quantitative yields by the reaction of perfluoroalkylamidines with perfluoroalkylnitrile or by the reaction of two equivalents of perfluoroalkylnitrile with one equivalent of anhydrous ammonia (Figure 3.4d).[7]

Inspired by the reaction of amidine with nitrile on Figure 3.4d, Roemmele[8] found that the condensation reaction of free amidine with trihaloacetonitriles gave the desired imidoylamidine products in high yields (Figure 3.4e). This is a nucleophilic addition reaction, with electronegative halogen atoms drawing negative charge away from the nitrile carbon and enhancing its electrophilicity. The reaction took place in solution under nitrogen and was allowed to reflux for 2-3 hours. After cooling the solutions were evaporated to give relatively high yields of fairly pure crude solid products (between 70 – 90%). If pure amidines were used, the crude products did not show significant quantities

of impurities and can be used without purification. If necessary, materials can be purified by sublimation to give white crystals.

The imidoylamidines were characterized by ^{1}H and ^{13}C NMR (Table 3.3 and 3.4). ^{1}H NMR data showed three broad NH peaks (see Table 3.3), indicating non-equivalency of the hydrogen atom environments. The crystal structure of trichloromethyl-imidoylbenzamidine and trifluoromethyl-imidoylbenzamidine determined that N-imidoylamidines have the following forms:[8] Two hydrogen atoms (H1 and H2) are attached to one nitrogen, but one of them (H2) associates to another nitrogen by a hydrogen bond (Figure 3.5, two structures on middle and right). This makes the three hydrogens not equivalent. This pseudo ring structure extensively delocalizes charges, along with the tautomerism, to create a very stabilized structure. Each NH peak was also distinctly different in height and line width, indicating dynamic exchange of hydrogen atoms in the solution state. The specific carbon signals of imidoylamidine (C2, C3) are far downfield at 160 – 170 ppm, similar to that of amidines, while C1 signals from CCl_3 are in the normal position, far upfield at about 98 ppm. The carbons connected to and nearby fluorine (CF_3, and C—CF_3) are quartets with J_{CF} values of 281 Hz (one-bond) and 33 Hz (two-bond). All the arrangement of proton and carbon signals is consistent with Roemmele's result.[8]

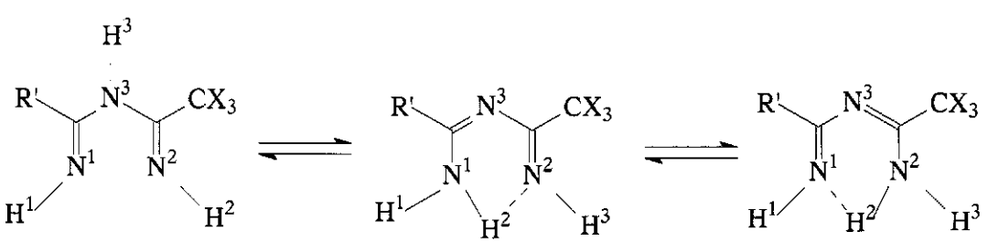


Figure 3.5 Tautomerism of *N*-imidoylamidine

Table 3.3 ^{1}H NMR of the imidoylamidines

Comp.	X	R	H^1	H^2	J_{AB} (Hz)	R	NH	NH	NH
A1	Cl	CH_3O	6.96	7.94	9.0	3.86	10.7	9.3	6.5
A2	Cl	CH_3	7.25	7.84	8.4	2.41	10.7	9.4	6.6
A3	Cl	H	7.45-7.48	7.93-7.96	-	7.42-7.56	10.7	9.4	6.6
A4	Cl	Cl	7.42	7.88	8.9	-	10.7	9.4	6.7
	Cl		7.61[a]	8.09	8.5	-	10.6	9.7	9.4
A5	Cl	Br	7.60	7.83	8.7	-	10.7	9.4	6.5
A6	Cl	CF_3	7.73	8.06	8.1	-	10.8	9.5	6.6
A7	Cl	CN	7.78	8.08	8.7	-	10.9	9.5	6.6
A8	Cl	Dip	7.18-7.21	7.32-7.39	-	1.26, 3.06	10.8	9.5	6.2
A9	F	CH_3O	6.93	7.87	9.0	3.85	11.0	9.0	6.7
A10	F	CH_3	7.26	7.81	8.1	2.41	11.0	9.1	6.7
A11	F	H	7.39-7.60	7.83-7.88	-	7.38-7.54	11.0	9.1	6.8
A12	F	Cl	7.42	7.84	8.8	-	11.0	9.2	6.7
A13	F	Br	7.61	7.80	8.5	-	11.0	9.2	6.7
A14	F	CF_3	7.73	8.02	8.1	-	11.1	9.3	6.8
A15	F	CN	7.78	8.04	8.8	-	11.1	9.3	6.8
			8.00[a]	8.17	8.4	-	10.9	10.3	9.7
A16	F	Dip	7.18-7.21	7.32-7.38	-	1.26, 2.98	11.0	9.2	6.4

Values are in ppm (except J_{AB}) with reference to TMS. [a] run in DMSO-d_6, others are in $CDCl_3$.

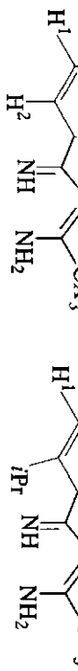


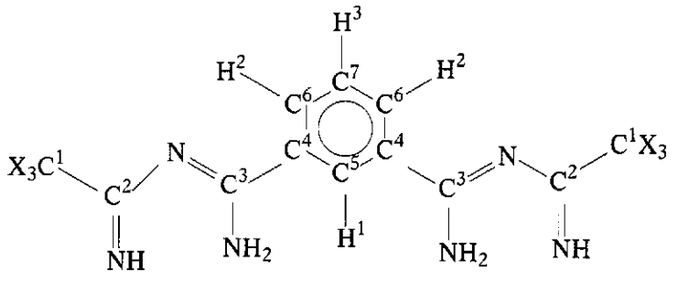
Table 3.4 ^{13}C NMR of the imidoylamidines

Comp.	X	R	C1	C2	C3	C4	C5	C6	C7	C_R (C8/C9)
A1	Cl	CH_3O	98.18	163.02	168.15	127.75	129.36	114.33	164.23	55.71
A2	Cl	CH_3	98.11	164.66	168.17	132.64	127.52	129.62	142.60	21.65
A3	Cl	H	97.99	164.72	168.17	135.48	127.56	128.97	132.07	
A4	Cl	Cl	97.78	163.59	167.94	133.83	128.90	129.17	138.39	
A5	Cl	Br	97.80	163.70	168.10	134.4	129.10	132.20	126.90	
A6	Cl	CF_3	97.62	163.39	168.03	138.90	128.03	126.00[2]	133.83[3]	123.97[4]
A7	Cl	CN	97.47	162.84	167.94	139.58	128.26	132.77	115.70	118.20
A8	Cl	Dip	97.86	166.51	168.15	129.74	145.81	123.34	135.40	(31.02/25.01)
A9	F	CH_3O	117.86[5]	163.41[6]	165.33	127.33	129.25	114.32	163.09	55.66
A10	F	CH_3	117.84[5]	163.55[6]	165.83	132.37	127.64	129.70	142.84	21.65
A11	F	H	117.80[5]	163.51[6]	165.92	135.22	127.44	129.02	132.20	
A12	F	Cl	117.70[5]	163.31[6]	164.76	133.60	128.83	129.28	138.62	-
A13	F	Br	117.72[5]	163.28[6]	164.87	134.06	128.98	132.25	127.02	
A14	F	CF_3	117.67[5]	163.23[6]	164.65	138.55	127.91	125.98[2]	133.91[3]	123.91[4]
A15	F	CN	117.61[5]	163.10[6]	164.01	139.27	128.17	132.77	115.82	118.11
A16	F	Dip	117.69[5]	163.39[6]	169.02	129.97	145.72	123.44	135.04	(31.03/24.63)

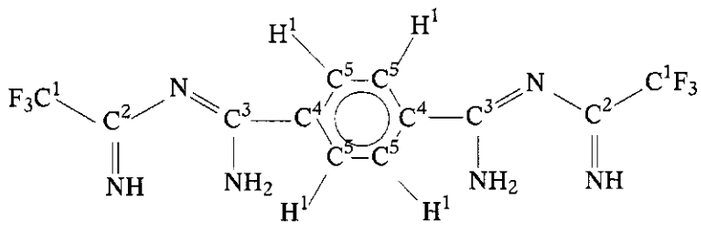
1. All values are in ppm, with reference to TMS
2. q, $^3J_{(F,C)} = 3.9$ Hz 3. q, $^2J_{(F,C)} = 33$ Hz 4. q, $^1J_{(F,C)} = 273$ Hz 5. q, $^1J_{(F,C)} = 281$ Hz

3.3.2 Diimidoylamidines

The condensation reaction for monoimidoylamidine (Figure 3.4e) is applicable to synthesize di-*N*-imidoylamidines. Two equivalents of trihaloacetonitrile were added to benz-1,3- or 1,4-diamidine. The mixture was heated up to 50 °C with stirring for one day. The solution was evaporated to give a white or pale yellow powder of di-*N*-imidoylamidine. Subliming to purify di-*N*-imidoylamidines was not successful, perhaps due to thermal instability. The fingerprint of di-*N*-imidoylamidines' ^{1}H NMR is the three broad peaks from NH, one peak is upfield of aromatic proton signals while the other two are downfield. The ^{1}H NMR in DMSO-d_6 shows all the three NH peaks are downfield to the aromatic proton signals and are closer than that tested in $CDCl_3$. The *ortho* protons (H1 and H2) to imidoylamidine groups shifted downfield compared to the *meta* proton (H3). H1 of **A17** and **A18**, which is *ortho* to two imidoylamidine groups is shifted further downfield than that of H2, because of the double influence.



A17 X = Cl
A18 X = F



A19

Table 3.5 Characteristics of diimidoylamidines

Compounds		**A17**		**A18**	**A19**
Yield		79%		63%	56%
Mp (°C)		60 – 62		74 – 76	126 – 128
^{1}H NMR	H1	8.60	7.95[a]	8.32	8.00
	H2	8.09 (d, 8Hz)	7.29 (d, 8Hz)[a]	8.00 (d, 8Hz)	
	H3	7.58 (t, 8Hz)	6.73 (t, 8Hz)[a]	7.50 (t, 8Hz)	
	NH	6.66	8.61[a]	7.00	6.86
	NH	9.47	8.79[a]	9.28	9.26
	NH	10.82	9.63[a]	11.04	11.12
^{13}C NMR	C1	97.8		117.8 (q, 281Hz)	117.7 (q, 281Hz)
	C2	163.8		163.4 (q, 33Hz)	163.3 (q, 33Hz)
	C3	168.1		165.0	164.8
	C4	136.2		135.9	138.3
	C5	126.9		126.1	130.8
	C6	130.6		130.8	-
	C7	129.4		129.6	-

[a] NMR in DMSO-d_6, all other NMR in $CDCl_3$, values are in ppm

3.4 Preparation of the 1-chloro-1,2,4,6-selenatriazines

The first and only previous 1,2,4,6-selenatriazine was synthesized in 1987 by Oakley.[9] These authors investigated the synthetic route to 1,2,4,6-thiatriazines and modified it for the synthesis of 1-chloro-3,5-diphenyl-1,2,4,6-selenatriazine. When I examined this synthetic route for other 1,2,4,6-selenatriazines, the reaction resulted in unexpected products. I report here a modified design for synthesizing 1,2,4,6-selenatriazines. Before discussing the design of this synthesis, however, it is necessary to review the previous works on thia- and selenatriazines.

3.4.1 Previous synthetic routes to 1-chloro-1,2,4,6-thiatriazines

The first 1,2,4,6-thiatriazine was prepared by Greevers[10] in 1970, from the reaction of sodium dicyanamide and thionyl chloride, but they incorrectly assigned the structure. Schramm[11] repeated Greevers's work and assigned the correct structures in 1974. An alternate synthesis of thiatriazines was discovered by Oakley and co-workers.[12] The reaction of benzamidine with trimeric thiazyl chloride produced in low yield 1-chloro-3,5-diphenyl-1,2,4,6-thiatriazine. Side products of this reaction include 4-phenyl-1,2,3,5-dithiadiazolium chloride and S_4N_4.

The most efficient method for the production of 1-chloro-1,2,4,6-thiatriazines was reported by Kornuta and coworkers.[13] The reaction involves a simple condensation of an *N*-imidoylamidine with sulphur dichloride. This approach has been successfully applied in the preparation of a variety of trichloromethyl-substituted (in 1- and/or 3-positions) derivatives. The advantages of Kornuta's method are the absence of side products and the high yield of the reaction. This is a widely used method for the preparation of 1-chloro-1,2,4,6-thiatriazines. An outline of the synthetic route is shown in Figure 3.6.

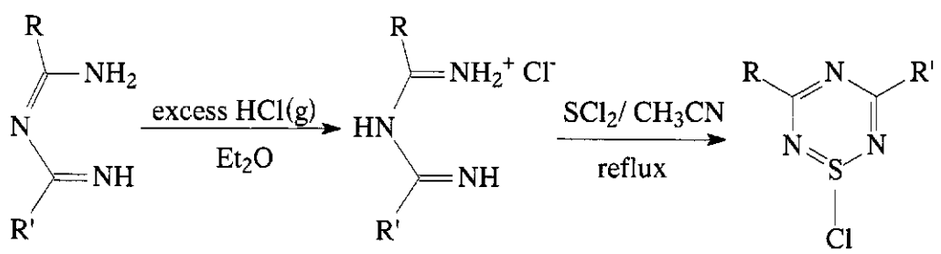


Figure 3.6 General synthetic route to 1,2,4,6-thiatriazines

3.4.2 Previous synthetic routes to 1-chloro-1,2,4,6-selenatriazines

Although the corresponding 1,2,4,6-thiatriazines are straightforwardly produced by the route in Figure 3.6,[8] the corresponding selenatriazines have not been examined previously. Extension of the above method to allow the incorporation of selenium was not a simple task. This is because of the known tendency of selenium (IV) to act as a strong acceptor to chloride ion, thus causing the reluctance of this material to eliminate HCl and condense to the desired products.

Indeed, the only previous selenatriazine was reported by Oakley and co-workers.[9] Based on the preparation of thiatriazines, the authors designed a modified synthetic route to 3,5-diphenyl-1,2,4,6-selenatriazine chloride (Figure 3.7). A number of steps, involving carefully controlled solid-state thermolyses, were required to reach the desired $Ph_2C_2N_3SeCl$. The authors chose to use selenium tetrachloride as a starting reagent; this they were able to prepare quickly and easily *in situ* by the reaction of chlorine on a slurry of elemental selenium in acetonitrile. A pale yellow slurry of $SeCl_4$ thus generated reacts rapidly with imidoylamidine hydrochloride to produce the complex *N*-chloroimidoylamidinium decachlorodiselenate, whose composition and structure has been confirmed by both chemical and crystallographic analysis.[14] The reluctance of this material to eliminate HCl and condense to the desired product was not wholly unexpected. Elimination of HCl could finally be induced by heating the decachlorodiselenate salt in the solid state at 60 °C under vacuum of 0.01 Torr, but the product, 1,1-dichloro-3,5-diphenyl-4-H-1,2,4,6-selenatriazine,[15] still contained an extra 1 mole equivalent of hydrogen chloride and a four-coordinate selenium center. The final

elimination required that 1,1-dichloro-3,5-diphenyl-4-H-1,2,4,6-selenatriazine be heated again in the solid state to 120 °C under 0.01 Torr for 48 hours.

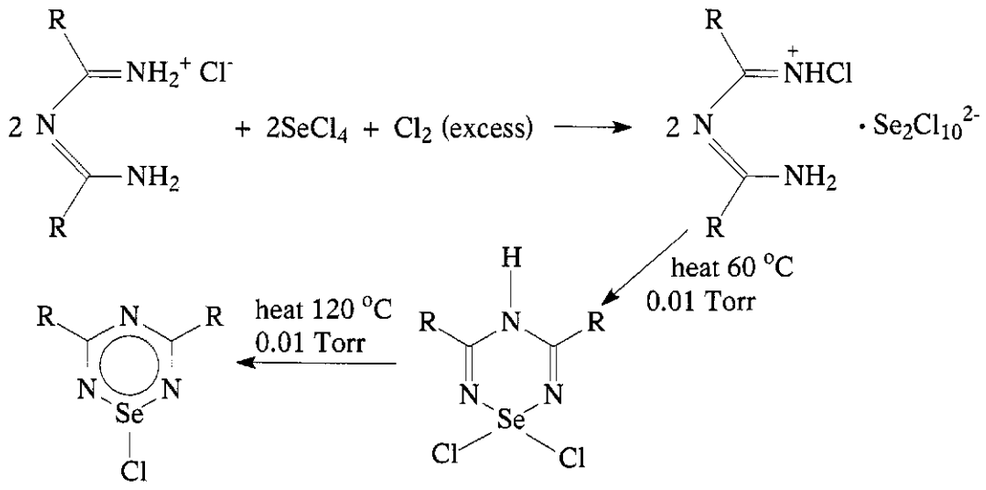


Figure 3.7 Oakley's route to prepare 1-chloro-1,2,4,6-selenatriazine

Like the corresponding 1-chlorothiatriazine $Ph_2C_2N_3SCl$, the 1-chloro-3,5-diphenyl-1,2,4,6-selenatriazine can be easily reduced by triphenylantimony.[13] When the reaction is carried out in methylene chloride, the resulting yellow solution exhibits an EPR signal whose appearance is very similar to that of the corresponding thiatriazinyl radical.

3.4.3 Initial attempts at preparing 1,2,4,6-selenatriazines with new substituents

(1) **Trichloromethyl-*p*-tolyl-imidoylamidine·HCl reacts with $SeCl_4 + Cl_2$:**

Oakley's method works well enough (60% yield) for the diphenyl selenatriazine chloride, and no side products were produced. While I examined the method for the derivatives with a more polar substituent, say trichloromethyl instead of one phenyl group, the reaction did go rapidly to produce a clear yellow solution when **A2**·HCl reacts

with $SeCl_4$ + Cl_2. Removing solvent yielded a yellow oil. Treating the product with dried chloroform yields a mixture of mostly white powder and a yellow solution. ^1H, ^{13}C NMR and infrared spectrum indicated the white powder to be starting material, **A2**·HCl. This is clearly a reversible reaction (Figure 3.8).

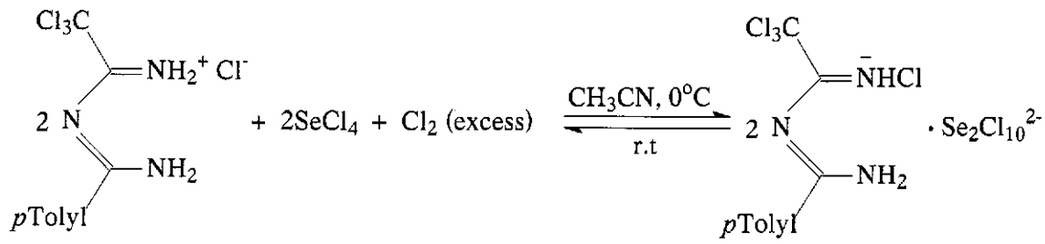


Figure 3.8 Reversible reaction by Oakley's method to new 1-chloroselenatriazines

(2) Trichloromethyl-*p*-tolyl-imidoylamidine·HCl reacts with $SeCl_4$:

Considering sulfur and selenium are in the same group (16) in the periodic table, Kornuta's method for the synthesis of thiatriazine (Figure 3.6) could be applicable for synthesis of 1-chloroselenatriazine. The idea was carried out by reacting **A2**·HCl with selenium tetrachloride in CH_3CN. The two reactants reacted rapidly at room temperature to give a possible complex salt (see Figure 3.9) as a clear yellow solution in CH_3CN. After 5 hours at reflux two products were obtained: a white precipitate, and a clear yellow solution that was evaporated to a yellow powder. ^1H, ^{13}C NMR and infrared spectrum identified the white precipitate as the starting material, **A2**·HCl. This means the complex is reversed to starting material upon reflux. The yellow powder was sublimed at 90 °C to nice yellow crystals, which were identified as 1-chloro-3-trichloromethyl-5-*p*-tolyl-selenatriazine (**D2**) by ^1H NMR and infrared spectrum. The yield of **D2** is only 9%. I

conclude that, while the reaction appears to work, the equilibrium seems to favor starting material. If anything, heating the reaction seems to disfavor product formation.

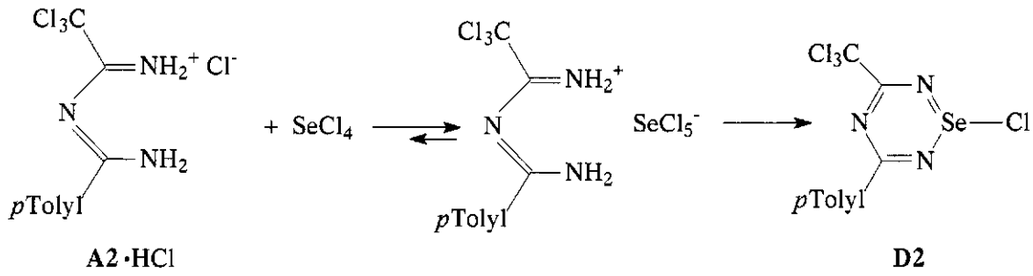


Figure 3.9 An attempt to prepare new 1-chloro-1,2,4,6-selenatriazines

3.4.4 A more versatile synthetic method for 1-chloro-1,2,4,6-selenatriazines

The question here is how the yield could be raised. When imidoylamidine hydrochloride reacted with sulfur dichloride, hydrogen chloride was eliminated easily in 2 hours to produce 1,2,4,6-thiatriazine chlorides. Oakley's method and my initial results indicated that more forcing conditions are required to effect complete elimination of HCl from selenatriazines. The fact is that hydrochloride associated with imidoylamidine does not take part in the condensation reaction. I have therefore sought a more flexible and general route that would allow for modification of the exocyclic substituents. The core idea is to use free-base imidoylamidine, not imidoylamidine hydrochloride, directly with selenium tetrachloride to form the 1-chloro-1,2,4,6-selenatriazine. For example, the ice bath cooled selenium tetrachloride suspended in CH_3CN reacts with imidoylamidine **A2** dissolved in CH_3CN rapidly to produce a clear yellow solution. The mixture was warmed to room temperature and heated to reflux for 24 hours, then cooled down and crystallized in a freezer to the corresponding 1-chloroselenatriazine **D2** as bright yellow crystals with

83% yield. The composition and structure has been confirmed by both chemical and crystallographic analysis (discussed later). The elimination of HCl and condensation to the desired product was encouraged by flowing N_2 in a "T" type facility shown as Figure 3.10.

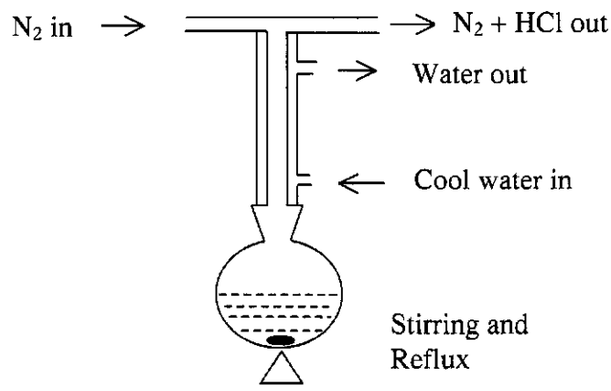


Figure 3.10 Reactor setup diagram

Compared to the first attempt based on Oakley's method, one can conclude: ① adding chlorine gas to the reaction is unnecessary; ② the synthetic route from imidoylamidine to selenatriazine can be simplified by eliminating four steps to one step reaction; ③ sublimation is necessary only for purifying product, not for reaction; ④ yield was raised greatly by using free imidoylamidine. If we use amidine as starting material to a final 1-chloroselenatriazine, the synthetic route can be outlined as in Figure 3.11.

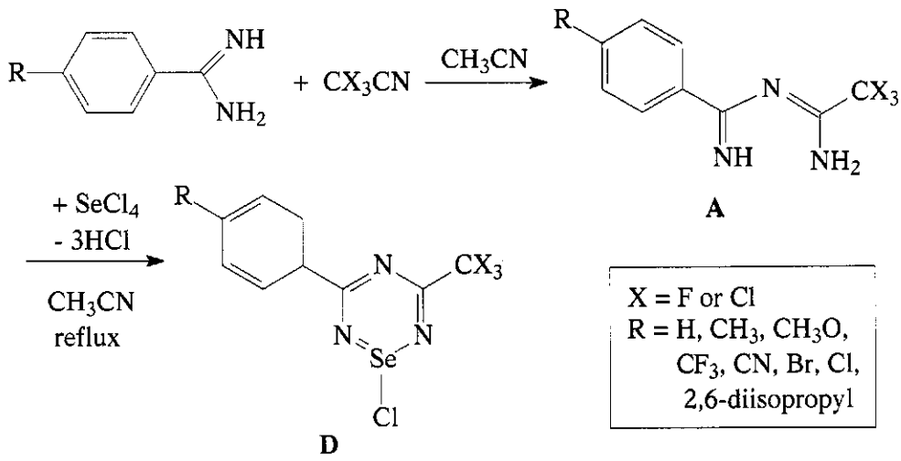


Figure 3.11 General route to 1-chloroselenatriazines

3.4.5 Reaction Intermediates

(1) **Imidoylamidine·$SeCl_4$ complexes (B)**: So far it has not been possible to identify the yellow-colored species first formed when the suspension of $SeCl_4$ reacts with imidoylamidine, **A**. On warming to room temperature, the mixture usually goes cloudy; a white precipitate of **A**·HCl forms. This indicates that the condensation reaction leading to **D** has commenced. Evidently the released HCl reacts with the initially formed species **B** to precipitate the much less-soluble **A**·HCl.

All attempts to isolate **B** as a pure compound were unsuccessful. Evaporation of the cold CH_3CN solution produced yellow powder. Analysis by NMR indicated these to be mixture of **A**·HCl and another species which presumably is responsible for the yellow color (Table 3.6).

On balance, the evidence suggests that the initial intermediate **B** (Figure 3.12) is a Lewis acid-base complex between **A** and $SeCl_4$. While **B** may be responsible for the yellow color, we cannot rule out the possibility that the known bright-yellow anion

$Se_2Cl_{10}^{2-}$ forms in solution as a minor side product. After all, a salt of this anion was isolated by Oakley[9] from a similar reaction, albeit in the presence of both Cl_2 and excess HCl.

Table 3.6 ^{1}H NMR analyses of complex **B2** and **B4**

Comp.	R/X	H1	H2	NH	NH	R
B2	CH_3/Cl	7.35 (d, 8.1Hz)	8.20 (d, 7.9Hz)	8.9	9.2	2.39
B4	Cl/Cl	7.60 (d, 8.4Hz)	8.26 (d, 8.4Hz)	8.9	9.3	-

Values are in ppm, DMSO-d_6 was used as solvent

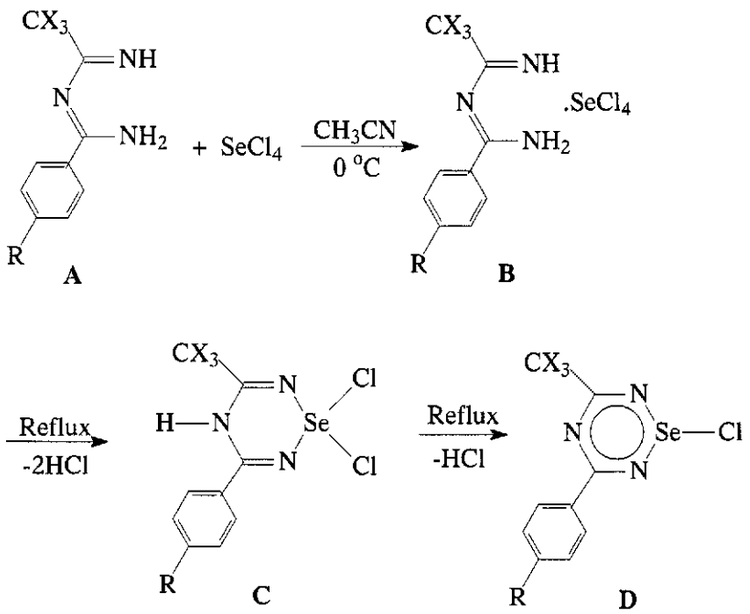


Figure 3.12 Intermediates during reaction to 1-chloroselenatriazines

(2) **1,1-dichloro-4-H-selenatriazines (C)**: On warming to room temperature, most reactions formed a precipitate of **A**·HCl. In several cases, the resulting suspension could be heated to reflux for a short period to cause the **A**·HCl to redissolve. For example, the mixture of imidoylamidine **A2** and $SeCl_4$ in CH_3CN was refluxed 2 hours to see white solid **A**·HCl disappear to a clear yellow solution. The solution was chilled in a freezer at $-10^{\circ}C$ overnight to give colorless crystals of compound **C2**. ^1H NMR showed four peaks 2.01 (s, 1H, CH_3), 7.42 (d, 2H, 8.1Hz, phenyl), 7.80 (d, 2H, 8.1Hz, phenyl), 9.2 (s, br, NH) (ppm). Only one NH peak appeared. ^{13}C NMR was not obtained due to instability of **C2** in solution. Compound **C2** did not give a molecular ion in the mass spectrum, instead, the fragments of selenatriazine **D2** cation and its chloride-free cation showed up. This is because the two chlorine atoms on selenium are easily lost on ionization. The same intermediate **C8** was well crystallized after overnight reaction of **A8** and $SeCl_4$ at reflux. ^1H NMR showed only one broad NH peak at 8.63 ppm. X-ray crystallography confirmed the structure of compound **C8** proposed in Figure 3.12. Oakley obtained a similar species as the main product of reaction (Figure 3.7).

(3) **1-chloroselenatriazines (D)**: Most reactions can reach the intermediates **C** easily under a few hours reflux. But it takes longer for **C** to convert to final products **D**. Generally, overnight refluxing is required for the completion of reaction. The time required for HCl elimination varied much even with very similar starting material. For example, *para*-bromophenyl-imidoylamidine **A5** reacted with $SeCl_4$ for only 3 hours to produce **D5** with a yield of 66%, while *para*-chlorophenyl-imidoylamidine **A4** took more than 2 days to react with $SeCl_4$ and produce **D4** in a yield of 61%.

Compounds **C** can also be transformed into **D** through pyrolysis. For example, colorless crystals **C2** were easily converted to **D2** as bright yellow crystals by subliming at 90 °C in vacuum.

(4) **^{77}Se NMR study**: Selenium has a spin –1/2 isotope (^{77}Se) with sufficient sensitivity to make their study readily accessible by Fourier transform NMR. Selenium-77 NMR has great potential as a means of exploring the chemistry of this interesting element. The large chemical shift range of ^{77}Se was demonstrated by Wood.[16] Mason[17] has summarized known ^{77}Se data and indicated that the ^{77}Se chemical shift depends on selenium oxidation state and bond polarity. For example, $SeCl_4$ has chemical shift at 1154 ppm, $MeSeCl_3$ at 890 ppm, R_2SeCl_2 between 510 – 840 ppm.

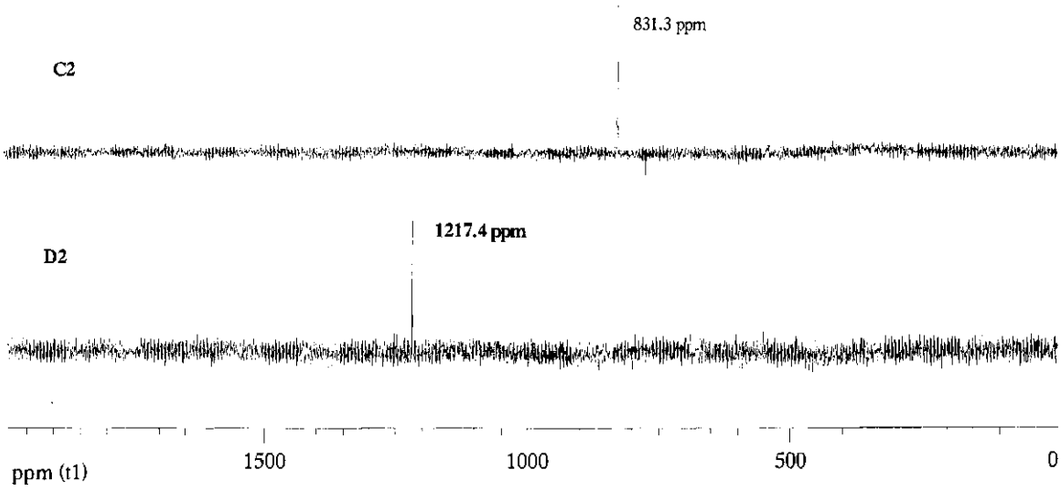


Figure 3.13 ^{77}Se NMR of **C2** (in DMSO) and **D2** (in chloroform) using SeO_2 (in H_2O) at +1306 ppm as external standard.

A solutions of **C2** prepared as described in Figure 3.13 contains a single ^{77}Se signal at +831.3 ppm. A solution of **D2** also displays one sharp ^{77}Se signal at +1217.4 ppm. Thus the two compounds have easily distinguishable ^{77}Se chemical shifts, within the

known range of Se^{+IV} species. These values may be compared with δ 1144 ppm for $Ph_3P{=}N{-}SeCl_3$ and δ 1334 for $[(Ph_3P{=}N)_2SeCl]^+SbCl_6^-$.[17] Further ^{77}Se NMR studies were frustrated by equipment failure.

3.4.6 Preparation of bis(1-chloro-1,2,4,6-selenatriazine)benzenes

Similar to **D1 – D16**, 1,3-bis(1-chloro-3-trichloromethyl-selenatriazinyl)benzene (**D17**), 1,3-bis(1-chloro-3-trifluoromethyl-selenatriazinyl)benzene (**D18**) and 1,4-bis(1-chloro-3-trichloromethyl-selenatriazinyl)benzene (**D19**) were made from diimidoylamidines **A17**, **A18** and **A19** respectively reacting with two molar equivalents of $SeCl_4$ in dried CH_3CN. All reactions immediately turned from a suspension to a clear yellow solution, indicating formation of complex-like **B**. Heating up the mixtures did not produce white precipitates. ^1H NMR monitoring indicated that no NH signal remained after two days at reflux. Because of the difficulty of purifying the precursor diamidines and diimidoylamidines, the final products formed brown solutions which were hard to crystallize. The solutions containing **D17** and **D18** were pumped dry to give dark brown solids. Subliming at high temperature yield less than 10% fine yellow crystals of diselenatriazines **D17** and **D18**. The solution containing **D19** was chilled in a freezer at –10°C to give fine yellow crystals of **D19** in 26% yield.

3.4.7 Results and Discussion

(1) **Physical properties**: After refluxing under N_2 flow, the flasks were cooled, sealed, and placed in a refrigerator overnight to allow for possible crystallization. Some solutions crystallized very well, some needed concentration to crystallize. Due either to

impurities or to good solubility, some solutions did not crystallize, which were then evaporated dry for purification by sublimation. Table 3.7 summarizes the properties of all the 1-chloroselenatriazines. The yields of the crude products were typically high (71-99%). Purified yields were from 41-91%. One reason for lower yields is impure starting materials. Some imidoylamidines such as **A1** and **A9** are thermally unstable, and decomposed when they were purified by sublimation. These imidoylamidines were used without further purification. The other reason is refluxing too long. All reactions were refluxed overnight. More refluxing time was required based on whether or not there were precipitates in the solution. For example, the reaction for **D14** was refluxed 57 hours with some solids still in solution. But on analysis, these solids appeared to be side products.

Generally yields from sublimation were lower than those from crystallization. **D8** and **D16** with Dipp group are extremely soluble in CH_3CN and reactive in many solvents. Trying to crystallize **D8** in dried CH_2Cl_2 resulted in decomposition to a white compound. **D8** and **D16** are also thermal unstable and are decomposed during sublimation with lots of black residue. The diselenatriazine chlorides could be purified by sublimation in extremely poor yield, but higher yields were obtained from crystallization (**D19**). Almost all 1-chloroselenatriazines are yellow in color. But compound **D15** was sublimed as a brown solid. Trying to crystallize **D15** in solvents was not successful (decomposed). Basically 1-chloroselenatriazines with CCl_3 substituents have high melting points than those with CF_3, hence high subliming temperatures were required.

Table 3.7 Physical properties of 1-chloroselenatriazines

Comp	X/R	Purified Yield(%)	Purifying method	Color	Mp (°C)	Subliming Temp. (°C)
D1	Cl/CH_3O	46	Sublime	Yellow	126-128	100
D2	Cl/CH_3	83	Crystallize	Yellow	136-138	100
D3	Cl/H	91	Crystallize	Orange yellow	150-154	100
D4	Cl/Cl	61	Crystallize	Yellow	148-150	110
D5	Cl/Br	66	Crystallize	Yellow	163-165	Not done
D6	Cl/CF_3	94	-	Dark yellow	123-125	100
D7	Cl/CN	58	Sublime	Yellow	135-138	110
D8	Cl/Dip	41	Sublime	Yellow	131-135	90
D9	F/CH_3O	48	Crystallize	Yellow	100-103	90
D10	F/CH_3	73	Crystallize	Green yellow	105-107	65
D11	F/H	63	Crystallize	Yellow	113-117	80
D12	F/Cl	76	Crystallize	Yellow	111-114	80
D13	F/Br	63	Sublime	Yellow	120-124	90
D14	F/CF_3	57	Sublime	Brown yellow	124-126	70
D15	F/CN	48	Sublime	Brown	135-138	110
D16	F/Dip	55	Sublime	Yellow	102-105	80
D17	Cl/	5	Sublime	Yellow	255-260	190
D18	F/	6	Sublime	Yellow	132-134	110
D19	F/	26	Crystallize	Yellow	238-242	Not done

(2) **^{1}H, and ^{13}C spectra**: All selenatriazines were fully characterized by ^{1}H and ^{13}C NMR (Table 3.8, 3.9 and 3.10). The completed HCl elimination was confirmed with the absence of NH peaks from the imidoylamidines and only the phenyl and substituent peaks appearing in the spectra. The location of the two doublets from the aromatic hydrogens was similar to that of the imidoylamidines and appeared in the 6-8 ppm range.

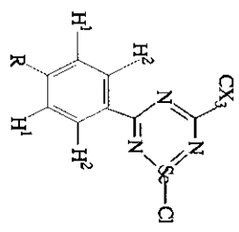
H1, which is *meta* to the selenatriazine core, has been less affected from the conversion to ring from imidoylamidine and appears only ~0.1 ppm further downfield in all cases. H2, which is *ortho* to the selenatriazine core, has a much more noticeable effect, shifting further downfield in all cases by ~0.55ppm. Such dramatic deshielding of aromatic *ortho* protons is diagnostic for aromatic heterocycles containing nitrogens. For example, the chemical shifts of the *ortho* hydrogen atoms in comparably substituted 1,5-dithia-2,4,6,8-tetrazocine heterocycles[18,19] have very similar chemical shifts to those of **D1** to **D19**. The same result was found in 1-chloro-1,2,4,6-thiatriazines.[8] The H_3 of diselenatriazines **D17** and **D18** is located *ortho* to two aromatic heterocycles, hence is doubly affected such that the shift of signal occurs further downfield by ~1.0ppm.

The ^{13}C NMR spectra (Table 3.9) of 1-chloroselenatriazines showed seven distinct carbon peaks plus that from any substituent on the benzene ring. The assignments of signals could be made using a combination of standard data compilations[20] and ^{19}F coupling in the analysis. The aromatic heterocyclization makes the carbons (C2 and C3) on the ring more uniform than those of imidoylamidine, hence the ^{13}C NMR signals of C2 and C3 are much closer than those of imidoylamidine. C2 and C3 of **D17** even overlapped each other with a relatively broad peak at 166.2 ppm. All carbon signals of **D**8 and **D**16 with Dipp group show as broad peaks after two days. ^{1}H NMR spectra showed that the compound decomposed slowly in $CDCl_3$.

Table 3.8 ^{1}H NMR of 1-chloroselenatriazines

Comp.	X	R	H1	J_{AB} (Hz)	H2	J_{AB} (Hz)	R (*i*Pr)
D1	Cl	CH_3O	7.01	9.2	8.47	9.0	3.91
D2	Cl	CH_3	7.33	7.9	8.39	8.2	2.47
D3	Cl	H	7.50-7.56	-	8.50		7.65
D4	Cl	Cl	7.51	8.8	8.44	8.8	-
D5	Cl	Br	7.68	8.7	8.36	8.8	-
D6	Cl	CF_3	7.80	8.2	8.61	8.1	-
D7	Cl	CN	7.83	8.8	8.60	8.7	-
D8	Cl	Dip	7.24	7.9	7.42	-	(1.21(CH_3), 2.68 (CH))
D9	F	CH_3O	7.00	9.2	8.42	9.2	3.91
D10	F	CH_3	7.26	8.1	8.27	8.4	2.39
D11	F	H	7.50-7.57	-	8.46	7.2	7.62-7.69
D12	F	Cl	7.50	8.7	8.39	8.5	-
D13	F	Br	7.66	8.7	8.30	8.6	-
D14	F	CF_3	7.79	8.4	8.57	8.2	-
D15	F	CN	7.83	8.5	8.56	8.6	-
D16	F	Dip	7.24	7.6	7.42	-	(1.21(CH_3),2.59(CH))

Values are in ppm with reference to TMS



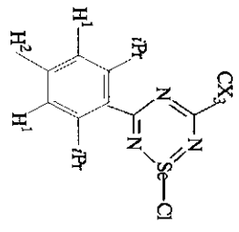


Table 3.9 ^{13}C NMR of 1-chloroselenatriazines

Comp.	X	R	C1	C2	C3	C4	C5	C6	C7	C_R (C8/C9)
D1	Cl	CH_3O	96.96	169.84	170.90	128.01	132.36	114.63	165.30	55.86
D2	Cl	CH_3	96.87	170.07	171.55	132.96	129.94	130.11	145.83	22.09
D3	Cl	H	96.79	170.20	171.61	135.60	129.13	130.00	134.52	
D4	Cl	Cl	96.65	170.28	170.70	134.05	129.51	131.23	141.23	
D5	Cl	Br	96.66	170.37	170.94	134.54	131.32	132.53	129.99	
D6	Cl	CF_3	96.54	170.54	170.54	138.82	130.20	126.06[2]	135.70[3]	123.91[4]
D7	Cl	CN	96.43	170.07	170.62	139.44	130.19	132.76	117.54	118.15
D8	Cl	Dip	91.74	164.90	173.28	125.78	141.31	118.68	131.26	(26.46/19.64)
D9	F	CH_3O	117.86[5]	162.21[6]	169.94	127.71	132.38	114.56	165.48	55.86
D10	F	CH_3	118.00[5]	162.44[6]	170.62	132.65	129.94	130.07	146.05	22.07
D11	F	H	117.98[5]	162.58[6]	170.73	135.32	129.14	129.96	134.69	
D12	F	Cl	117.88[5]	162.61[6]	169.78	133.71	129.51	131.19	141.43	-
D13	F	Br	117.86[5]	162.57[6]	169.93	134.14	131.25	132.52	130.19	
D14	F	CF_3	117.88[5]	162.83[6]	169.59	138.46	130.14	126.06[2]	135.86[3]	119.02[4]
D15	F	CN	117.78[5]	162.81[6]	169.02	139.04	130.10	132.74	117.65	118.08
D16	F	Dip	117.80[5]	161.97[6]	177.07	130.73	146.07	123.47	135.51	(31.26/24.29)

1. All values are in ppm, with reference to Chloroform
2. q, $^3J_{(F,C)}$ = 3.9 Hz
3. q, $^2J_{(F,C)}$ = 33 Hz
4. q, $^1J_{(F,C)}$ = 273 Hz
5. q, $^1J_{(F,C)}$ = 281 Hz
6. q, $^2J_{(F,C)}$ = 38 Hz

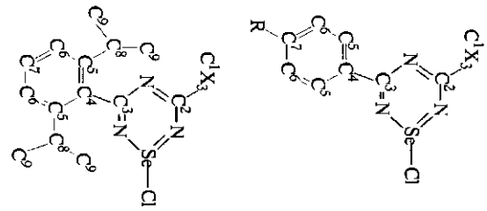
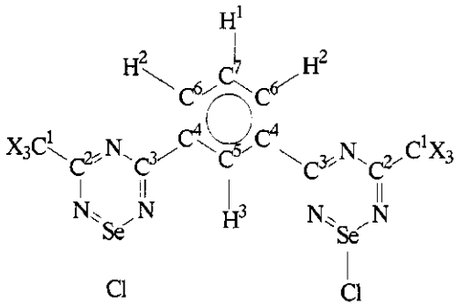


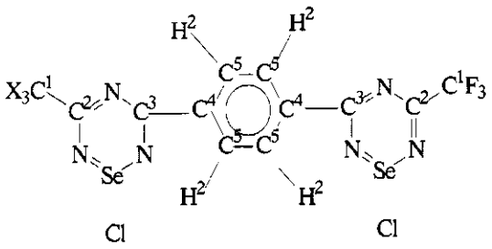
Table 3.10 ^{1}H and ^{13}C NMR of diselenatriazines

Compounds		D17	D18	D19
^{1}H NMR	H1	7.75 (t, 85.0Hz)	7.87 (t, 7.8 Hz)	
	H2	8.53 (d, 6.4Hz)	8.67 (d, 14 Hz)	8.40 (s)
	H3	9.33 (s)	9.36 (s)	
^{13}C NMR	C1	97.3		117.9 (q, 281 Hz)
	C2	166.2		157.7 (q, 38 Hz)
	C3	166.2		164.9
	C4	136.7		139.6
	C5	128.3		128.3
	C6	132.0		
	C7	129.0		

All values are in ppm using DMSO-d_6 as solvent



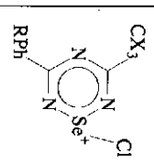
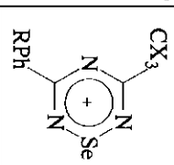
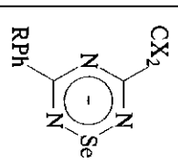
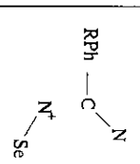
D17: X=Cl; **D18**: X = F



D19

(3) **Mass spectra**: The mass spectra of compounds **D1-D16** showed consistent fragmentation patterns. The major fragment peaks are listed in Table 3.11. All mass spectra showed a small peak from 1-chloroselenatriazine, except **D8** and **D16**. Evidently the Cl atom on Se is easily lost from the cations. Compounds **D1** to **D8** with CCl_3 groups easily lose an additional chlorine atom, while the others with CF_3 groups do not lose fluorine. Most mass spectra did not show corresponding imidoylamidine as a fragment, indicating that imidoylamidines are relatively unstable. Other common fragments that

Table 3.11 Mass spectra of 1-chloroselenatriazincs

Comp.	R/X					R-Ph-CN$^+$	SeN$^+$
D1	CH_3O/Cl	405 (5.9)	370 (40.8)	-	-	133 (100)	94 (25.0)
D2	CH_3/Cl	389 (7.90)	354 (73.1)	319 (4.0)	211 (20.5)	117 (100)	94 (86.0)
D3	H/Cl	377 (15.1)	340 (100)	305 (5.0)	195 (11.0)	103 (69.2)	94 (75.4)
D4	Cl/Cl	411 (6.1)	376 (70.5)	339 (6.2)	231 (14.2)	137 (87.1)	94 (100)
D5	Br/Cl	455 (14.9)	420 (100)	385 (3.6)	275 (9.2)	-	-
D6	CF_3/Cl	443 (7.8)	408 (100)	373 (5.3)	-	171 (21.1)	-
D7	CN/Cl	400 (2.2)	365 (90.8)	330 (8.8)	-	128 (49.4)	94 (100)
D8	Dip/Cl	-	424 (48.6)	388 (9.8)	281 (32.1)	186 (63.0)	94 (11.4)
D9	CH_3O/F	357 (21.0)	322 (84.8)	-	227 (12.1)	133 (100)	94 (38.7)
D10	CH_3/F	341 (30.0)	306 (117)	-	211 (16.0)	117 (62.9)	94 (100)
D11	H/F	327 (10.6)	292 (100)	-	-	103 (32.5)	94 (74.2)
D12	Cl/F	361 (6.8)	326 (77.3)	-	231 (5.2)	137 (63.8)	94 (100)
D13	Br/F	405 (6.9)	370 (57.6)	-	275 (4.5)	-	-
D14	CF_3/F	395 (3.8)	360 (67.8)	341 (4.4)	-	171 (36.9)	94 (100)
D15	CN/F						
D16	Dip/F	-	376 (49.7)	-	281 (14.5)	186 (69.0)	-

Values in brackets are intensity in %

appeared were R-Ph-CN_2Se^+, aromatic nitrile cation, and NSe^+. The most intensive peaks in the mass spectra of **D8** and **D16** are Dipp-CN_2^+, derivative of Dipp-amidine.

(4) **Raman and Infrared spectra**: The crystals of selenatriazine chlorides were sealed in a 2 mm diameter glass tube for Raman spectroscopy. They were also mixed with KBr and pressed to pellets for infrared spectroscopy. IR spectra of imidoylamidines presented very intense peaks between 3300 – 3500 cm^{-1}, which were from NH stretching bands. When imidoylamidines were cyclized to 1-chloroselenatriazines, the hydrogens were eliminated from nitrogen, and the NH signals disappeared. Only weak peaks appeared between 2800 – 3100 cm^{-1} from CH stretching bands (see Table 3.12). C=N stretches occurred in the range of 1610 – 1680 cm^{-1}, while aromatic C⎓C stretching vibration shows signals at about 1600, 1580, 1500, 1450, and 1000 cm^{-1}.[21] The strong IR signals between 1650 – 1700 cm^{-1} were definitely from the selenatriazine ring CN stretching vibrations, which gave strong peaks at about 1610 ± 20 cm^{-1} in the Raman spectra. The two or three weak peaks between 625 – 700 cm^{-1} were from the symmetric and asymmetric stretching vibrations of NSeN. Generally Se—Cl stretchings were assigned at the low wavenumber, because of the ionic character of this bond in the studied complexes in parallel with the comparatively long Se—Cl bond length.[22] The most intense peaks in the Raman of compounds **D** at about 300 ± 12 cm^{-1} is the contribution of the Se—Cl stretching vibration (Se—Cl ~ 2.3 Å). The Se—Cl stretching vibration of bis(thiourea)selenium dichloride was reported at 120–134cm^{-1} with a strong peak and a weak peak.[22] The lower wavenumber in this Se(II) species is possibly from the more ionic character of this compound with Se-Cl bond length of 3.2 Å. The complex cation in $(SeCl_3)^+[SbF_6]^-$ displays a Se—Cl signal in the Raman spectrum at 433 cm^{-1} as

the strongest signal.[23] IR spectra could not record the signal from Se—Cl because it is out of range of the instrument.

Table 3.12 Raman and Infrared spectra of 1-chloroselenatriazines

Comp.	Raman (cm^{-1})				Infrared (cm^{-1})		
	CH	NCN	NSeN	SeCl	CH	NCN	NSeN
D1	3084, 3055 3008	1605	661, 646 632	292	3070, 3000	1684, 1603	659
D2					3113	1684, 1631 1608	696, 673
D3	3070, 3063	1595	655, 645	290	3068	1675, 1594 1580	657, 647
D4	3078, 3059	1590	654, 641, 628	290	3109	1684, 1591	668, 652
D5	3074 3056	1584	651,634, 626	289	3091	1683, 1585	650
D6	3084 3021	1618	675, 654, 633	297	3122	1695, 1627	667
D7					3095	1684, 1620	667, 653
D8	3068, 3030, 2970, 2932 2904, 2865	1591	679 668 638	303	2963, 2926, 2867	1645, 1591	694, 680, 666
D9	3079, 3066 2935, 2844	1599	673 633	306	3081	1700, 1603	687, 655
D10	3078 3037 2923	1606	679 638	295	3064	1696, 1606	685, 667
D11					3196, 3087	1695, 1635	694, 668
D12	3087 3062	1592	680, 667 629	312	3089	1696, 1592	663, 637
D13					3091	1684, 1585	650
D14	3084	1618	675, 654 633	298	3111	1681, 1626	675, 654
D15						1684, 1620	668, 653
D16	3072, 3033 2973, 2937 2907, 2867	1592	683 655 630	298	3076, 2968, 2872	1671, 1606	685, 667

3.5 Conclusions

A general route to 1-chloro-1,2,4,6-selenatriazines was developed via the condensation of *N*-imidoylamidine and selenium tetrachloride. All 19 1-chloroselenatriazines (named **D1 – D19**) described in this work are new. The detailed reaction procedure was investigated. The reaction experienced two intermediates **B**, **C**, and side product **A**·HCl. The structure of intermediates **B** is not conclusive due to instability and difficulty of crystallization. Full spectroscopic and analytical data have been presented to support the synthetic claims. Further confirmation of the structures of one intermediate **C8**, and of five 1-chloroselenatriazines **D** have been obtained by X-ray crystallography, as described in chapter 5.

3.6 References

1. Patai, S. *The Chemistry of Amidines and Imidates*, Vol. 1, Chapter 1: *General and theoretical aspects of amidines and imidic acid derivatives*, Wiley, London, **1975**.
2. Boeré, R. T.; Oakley, R. T.; Reed, R. W. *J. Organomet. Chem.* **1987**, *331*, 161.
3. Felix, O.; Hosseini, M. W.; Cian, A. D.; Fischer, J. *New J. Chem. Commun.* **1997**, *21*, 285.
4. Ley, H.; Müller, F. *Ber.* **1907**, *40*, 2950.
5. Peak, D. A. *J. Chem. Soc.* **1952**, 215.
6. Oto, K.; Ichikawa, E. *Chem. Abs.*, **1975**, 428.
7. Brown, H. C.; Schuman, P. D. *J. Org. Chem.* **1963**, *28*, 1122.
8. Roemmele, T. L. *M.Sci. Thesis*, University of Lethbridge, **2002**.
9. Oakley, R. T.; Reed, R. W.; Cordes, A. W.; Craig, S. L.; Graham, J. B. *J. Am. Chem. Soc.*, **1987**, *109*, 7745.
10. Greevers, J.; Hackmann, T.; Trompen, W.P. *J. Chem. Soc. (C)* **1970**, 875.

11. Schramm, W.; Voss, G.; Rembarz, G.; Fischer, E. *Z. Chem.* **1974**, *14*, 471.

12. Cordes, A. W.; hayes, P. J.; Joesphy, P. D.; Koenig, H.; Oakley, R. T.; Pennington, W. T. *J. Chem. Soc., Chem. Commun.*, **1984**, 1021.

13. Kornuta, P. P.; Derii, L. I.; Markovskii, L. N. *Zh. Org. Khim.*, **1980**, *16*, 1303.

14. Privett, J. A. J.; Cordes, A. W.; Craig, S. L.; Oakley, R. T.; Reed, R. W. *Acta Crystallogr. Sect. C-Cryst. Struct. Commun.* **1987**, *43*: 2023.

15. Cordes, A. W.; Oakley, R. T.; Reed, R. W. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1986**, *42*: 1889.

16. McFarlane, W. M.; Wood, R. J. *J. Chem. Soc. A*, **1972**, 1397.

17. Mason, J. *Multinuclear NMR*, Plenum press, New York and London, **1987**, P421.

18. Boeré, R. T.; Moock, K. H.; Derrick, S.; Hoogerdijk, W.; Preuss, K.; Yip, J. *Can. J. Chem.* **1993**, *71*, 473.

19. Boeré, R. T.; fait, J.; Larsen, K.; Yip, J. *Inorg. Chem.* **1992**, *31*, 1417.

20. Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*; John Wiley & Sons, Inc.: New York, **1998**.

21. Schrader, B. *Infrared and Raman Spectroscopy*, VCH publishers Inc., New York, **1995**.

22. Alía, J. M.; Edwards, H. G. M.; Fernández, A.; García-Navarro, F. J.; Prieto, M. *J. Molecul. Struct.*, **1999**, *510*, 107.

23. Rautiainen, J. M.; Way, T.; Schatte, G.; Passmore, J. Laitinen, R. s.; Suontamo, R. J.; Walkonen, J. *Inorg. Chem.* **2005**, *44*, 1904.

Chapter 4

1,2,4,6-Selenatriazine Free Radicals

4.1 Introduction

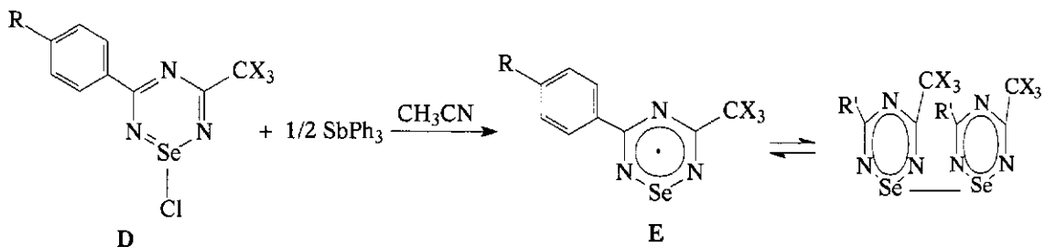
1-Chloro-1,2,4,6-selenatriazine compounds **D** were successfully reduced to their radicals **E** by the use of triphenylantimony in hot acetonitrile. Pure selenatriazinyl dimers of **E** were obtained through *in-situ* crystallization during the reduction reaction. Characterization of these radicals using EPR analysis gave insight as to the unpaired electron's spin distribution on the selenatriazine core.

4.2 Preparation of 1,2,4,6-selenatriazine free radicals

Many reducing agents have been used to prepare radicals. Silver powder, triphenyl antimony, sodium dithionite[1-3] were commonly used to reduce 1,3,2-dithiazolylium cations. 1,2,3,5-Dithiadiazolyl radicals were prepared by reduction of dithiadiazolylium chloride salts using sodium dust, triphenylverdazyl or tetramethyl-*p*-phenylene diamine.[4] Subsequently, other reducing agents including zinc/copper couple, potassium, mercury, and elemental zinc were used.[5] Triphenylantimony is of general utility in the reduction of thiazyl halides.[6-8] Other reducing agents that have been employed include sodium verdazyl,[9-10] NaNCS, KCN, LiN_3, PhMgBr, *n*BuLi, $SnCl_2$[11] and zinc in sulfur dioxide. In this work, I used triphenylantimony as reducing agent.

Oakley[6] and Roemmele[8] described the preparation of the 1,2,4,6-thiatriazinyl radical and its association, in the solid state, into the cofacial dimer. The stability of thiatriazinyl radical to both oxidation (TTA^+) and reduction (TTA^-) encouraged this species as one of

a new and rapidly growing group of heterocyclic thiazyl radicals, which form dimeric units in the solid state linked through weak (long) interannular S---S interactions. 3,5-diphenyl-1,2,4,6-selenatriazine also form dimeric units in the solid state linked through weak interannular Se---Se interaction.[12] The reduction of 1-chloroselenatriazines is shown as Figure 4.1. The prepared selenatriazinyls are in equilibrium between dimer in solid state and free radical in dilute solution.



D E

F1 - F8 (X = Cl), **F9 - F16** (X = F)
R = OCH_3, CH_3, H, Cl, Br, CF_3, CN, 2,6-diisopropyl

Figure 4.1 Reduction of 1-chloroselenatriazines by Ph_3Sb

4.2.1 First method of reducing 1-chloroselenatriazine

Like the corresponding 1-chlorothiatriazine derivatives,[8] 1-chloroselenatriazine **D** was reduced in designed glassware to prevent exposure to the atmosphere (Figure 4.2). A side arm flask was filled with compound **D**, some dried acetonitrile and a stir bar. The pear-shaped funnel was filled with ½ molar ratio of solid triphenylantimony and attached to the flask. The flask was freeze-thaw-degassed three times. The triphenylantimony was added into the flask. Reduction to the radical was immediate, as the solution turned from yellow to dark red or dark purple with a precipitate. The mixture was stirred 1 hour to

ensure reaction completion. The glass funnel was removed and replaced by a glass frit filter stick to filter the crude radical as dark red or dark purple solid.

Unlike thiatriazinyl radicals, selenatriazinyl radicals are less stable and difficult to purify, as they are essentially poorly soluble in all organic solvents and easily decompose. Several attempts were made at crystallization using a variety of solvents, but no crystals were ever created. Products decomposed in all cases. Sublimation of the crude materials using a tube furnace also failed to produce crystals.

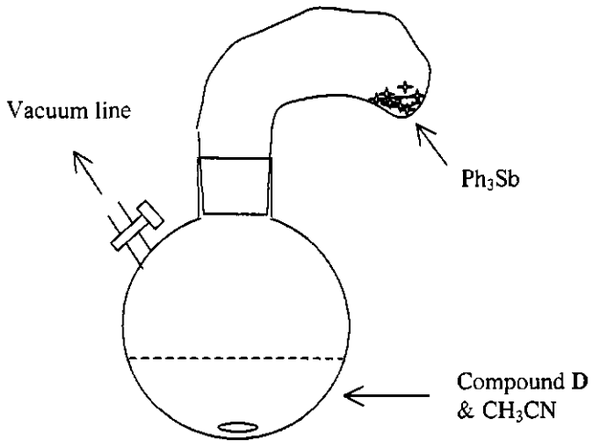


Figure 4.2 Pear-shaped solids addition funnel

4.2.2 Second method of reducing 1-chloroselenatriazine

Diffusion reactions were done using a glass H-vessel containing a central glass frit. 1-chloroselenatriazine **D** was placed in one end of the apparatus and Ph_3Sb was placed in the other. Both ends were charged with the same amount of dried CH_3CN. The apparatus was attached to the vacuum line and both ends were freeze thaw degassed three times. The apparatus was slowly turned upside down to allow the solution to diffuse for one

week. Fine red crystals were occasionally produced in low yield, but most reactions products decomposed over time.

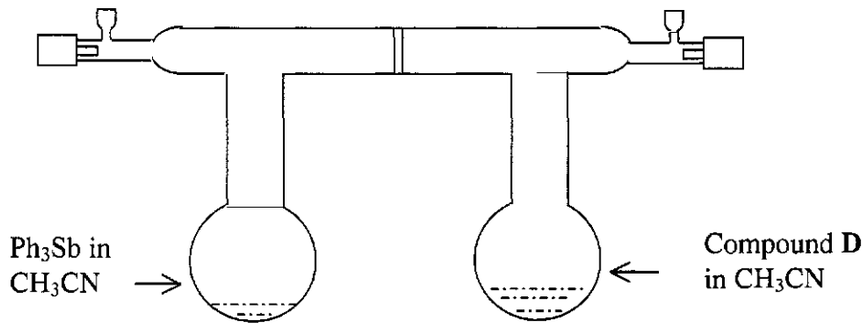


Figure 4.3 H-vessel for diffusion reaction

4.2.3 Reducing 1-chloroselenatriazine and *in-situ* crystallization

The attempts above told that triphenylantimony is a powerful agent to reduce 1-chloroselenatriazines, and pure products as crystals are sometimes obtainable, but reactions are highly sensitive to conditions. Therefore a more general method is necessary to generate pure radicals as crystals. This was carried out by using the *in-situ* apparatus shown as Figure 4.4. Ph_3Sb was charged in the flask and the apparatus was set up in a dry box before moving out for other operations. Under N_2 flow, 5 ml freshly distilled CH_3CN was charged into the flask which was then set in an oil bath with temperature stabilized at 50 – 80 °C. A clear yellow solution of 1-chloroselenatriazine in CH_3CN was transferred to the dropping funnel. Without stirring, 1-chloroselenatriazine solution was added dropwise to the hot Ph_3Sb solution in a period of one to two hours. Red or dark red solutions formed immediately. The final mixture (in hot oil bath) was

slowly cooled down to room temperature and left to stand for a few hours. Dark red or black crystals were created during the reaction.

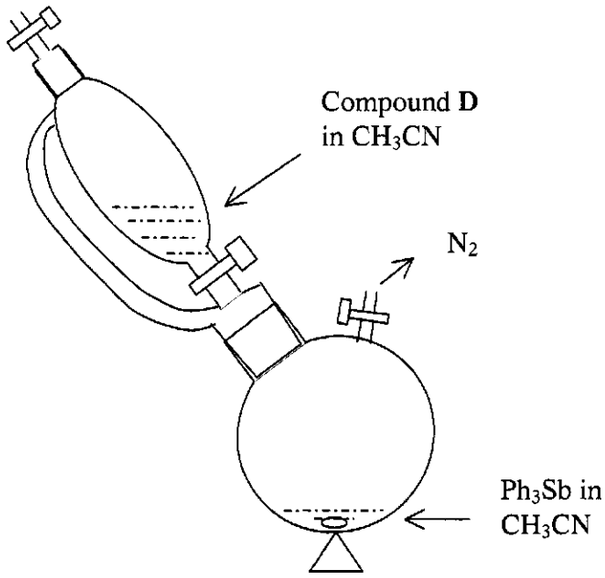


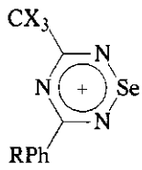
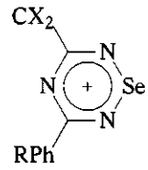
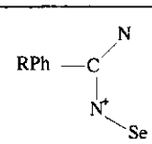
Figure 4.4 Apparatus to prepare and *in-situ* crystallize selenatriazinyl radicals

Table 4.1 summarizes the reactions and crystallizations. For these reactions, the success depends on the solubility and thermal stability of the produced radicals. Quickly adding 1-chloroselenatriazine often resulted in amorphous red solid. The radical crystals can only be created during the reaction and it is irreversible. Any attempts to recrystallize the radical through sublimation or recrystallization were not successful due to thermal and moisture instability. The melting points of **E** are higher than the corresponding starting 1-chloroselenatriazines **D** possibly due to the dimerization confirmed by X-ray crystallography. The yields of **E** are lower than the corresponding **D** compounds purified by crystallization.

Table 4.1 Summary of reduction and *in-situ* crystallization to radicals

Compound (R/X)	Reaction Temp.	Concentration for Crystallization	Color of crystal	mp (°C)	Yield (%)
E1 (*p*-CH_3O/Cl)	80 °C	0.0548 M	Black needles	140 – 142	55
E2 (*p*-CH_3/Cl)	55 °C	0.0262 M	Black needles	136 – 139	55
E3 (H/Cl)	55 °C	0.0368 M	Black plates	130 – 133	64
E9 (*p*-CH_3O/F)	80 °C	0.0832 M	Black bricks	149 – 152	33
E10 (*p*-CH_3/F)	55 °C	0.0763 M	Black bricks	155 – 157	49
E13 (*p*-Br/F)	22 °C	0.132 M	Red solid	130 – 133	64
E14 (*p*-CF_3/F)	80 °C	0.0593 M	Red plates	135 – 138	26

Table 4.2 Mass spectra of selenatriazinyl radicals

Comp.				R-Ph-CN^+	SeN^+
E2	354 (50.4)	319 (5.09)	211 (23.1)	117 (88.3)	94 (100)
E3	340 (57.5)	305 (8.10)	195 (13.8)	103 (84.8)	94 (100)
E10	306 (88.3)	-	-	117 (46.8)	94 (100)
E13	370 (50.8)	-	275 (3.6)	181 (18.2)	94 (100)

All the mass spectra of **E** are very clean and display fewer fragments than compounds **D**. There are clearly no signals of 1-chloroselenatriazines. The selenatriazinyl cation peaks are of higher intensity compared to the mass spectra of **D**. SeN^+ is the most intense signal as for **D**. The other major fragments are the nitrile cations.

4.3 Electron paramagnetic resonance (EPR)

The science of Electron Paramagnetic Resonance (EPR) spectroscopy is very similar in concept to the more familiar nuclear magnetic resonance (NMR) technique. Both deal with the interaction of electromagnetic radiation with magnetic moments; in the case of EPR, the magnetic moments arise from electrons rather than nuclei. In most systems electrons occur in pairs such that the net moment is zero. Species that contain one or more unpaired electrons possess the net spin moment necessary for suitable interaction with an electromagnetic field. To obtain an EPR spectrum having appreciable intensity requires the presence of a large number of unpaired-electron species in the sample. On the other hand, if the spin concentration in the sample is too high, the spins interact appreciably with each other, and this alters the nature of the EPR spectrum observed.

EPR has matured into a powerful, versatile, nondestructive, and nonintrusive analytical method. Unlike many other techniques, EPR yields meaningful structural and dynamical information, even from ongoing chemical or physical processes, without influencing the process itself. Therefore, it is an ideal complementary technique for other methods in a wide range of studies and application areas. The uses of EPR vary from characterization of various conducting materials and polymers to magnetic resonance imaging.

It is known that when a magnetic field B_0 is applied, an unpaired electron can assume two different spin orientations along the field's direction. The equation $\Delta E = h\nu = g\mu_B B_0$ is used to determine the size of the energy gap between these two spin orientations (h = 6.626076×10^{-34} J s Planck constant, v: resonant frequency). Constant g

is called the Landé splitting energy or the "g value". For a free electron this value is 2.0023, and can be used for comparison between the magnetic environments of measured spectra versus that of the free electron. μ_B is the Bohr magneton and B_0 is the applied magnetic field. The size of the energy gap corresponds to photon energies in the microwave region of the electromagnetic spectrum when magnetic fields of 1 – 10 Tesla are used.

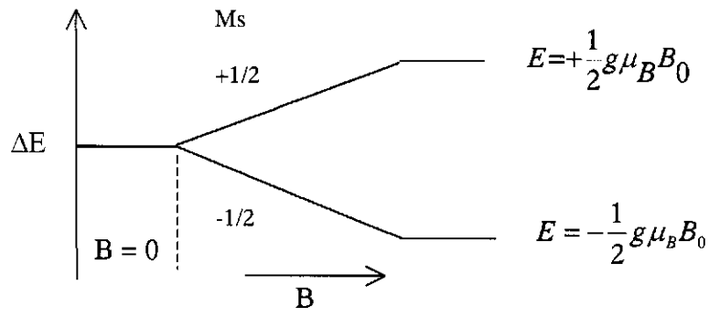


Figure 4.5 Energy gap between the +1/2 and –1/2 spin orientations

Since the electron magnetic moment is much larger than that of nuclei, electron-electron dipolar interactions are usually very strong and dominate the spectral features. Lines or bands in an EPR spectrum represent transitions between energy levels of the absorbing species. EPR spectra are traditionally recorded as the first derivative of the absorption peak (dispersion mode), and the electron spin energy levels are often split into multiplets called their hyperfine structure. These are due to the interaction of the nuclear spins of attached nuclei where a magnetic nucleus of spin quantum number I can adopt $2N \cdot I + 1$ different orientations and hence give rise to $2N \cdot I + 1$ different contributions to

the local field. N is the number of equivalent nuclei the electron couples to, and I is the nuclear spin.

4.4 Result and discussion

Selenatriazinyls **E1** – **E19** each have three kinds of N atom, the two in the formal —N=Se=N— linkage (identified as N1 and N3) and the single atom of the —C=N=C— unit (N2). Hence the dominant hyperfine coupling constants (hfc) are likely to come from the ^{14}N (I = 1), ^{77}Se (I = 1/2), ^{13}C (I = 1/2) and ^{37}Cl (I = 3/2)/^{19}F (I = 1/2) nuclei (I is nuclei spin number). The formula $2N{\cdot}I + 1 = 7$ predicts 7 lines if the nitrogen atoms are considered to be equivalent,. The unequal spacing observed in the experimental spectra of selenatriazinyls **E** is due to the nonequivalence of nitrogen atoms (e.g. **E4** in Figure 4.6).

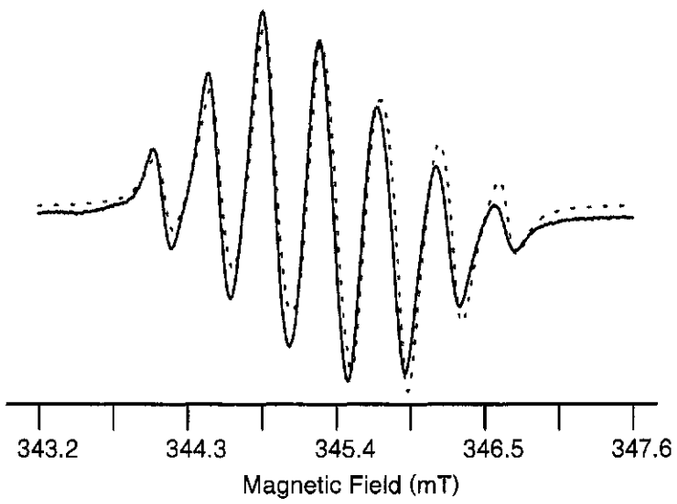


Figure 4.6 EPR spectrum and its simulation of radical **E4**.
Solid line is experimental curve and the broken line is the simulation
With nitrogen coupling of a_{N2} = 3.86, a_{N4} = 4.05, a_{N6} = 4.67 Gauss

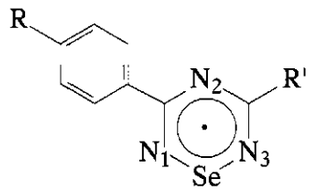
The spectra of **E** were successfully simulated using WINEPR SimFonia software (Bruker), and WinSim (NIH) was used for the lineshape fitting. The excellent match to the experimental trace is evident. Spectral simulation yields the hfc a_N with nonequivalent values (e.g 3.86, 4.05, 4.67 Gauss for **E4**). In order to assign the hfc constants to the individual nitrogen nuclei in the selenatriazine ring, it was necessary to perform quantum mechanical calculations. UB3LYP/6-31G(d) geometry optimizations were therefore performed on **E4** and theoretical hyperfine coupling constants were calculated. The EPR results (summarized in Table 4.3) suggest that the spin orbital in which the unpaired electron resides is distributed unequally over the N1, N3 and N2 nitrogens. The a_N values are larger than those of the corresponding thiatriazinyl **TTA4**. Oakley[14] compared a series 1,2,4,6-thia and 1,2,4,6-selenatriazinyl radicals, and concluded that "sulfur appears to be a better acceptor of spin density than selenium; as a result, the coupling constants a_N for nitrogen adjacent to selenium are raised relative to the a_N values found in the corresponding sulfur-based radicals". This is consistent with the results in Table 4.3.

The sum of the hyperfine coupling to nitrogen in all four rings is highly consistent. The distribution of the coupling changes with substituent, but the total is almost invariant and slightly larger than that of **PhPhSeTA** (Table 4.3). The relatively complicated EPR spectra of thiatriazinyl radicals are contributed not only from nitrogen hfc, but also from carbon and fluorine hfc. There is no resolvable hfc to selenium, chlorine, fluorine, carbon and phenyl protons for radical **E**.

The deviation of the *g* value of **E4** (2.018) from the free-electron figure (2.0023) is indicative of a substantial spin density on the selenium atom (the only atom which is sufficiently heavy to induce a spin-orbit coupling effect). There are some systematic

variations in signal intensity, *g* value, and line width as a function of electronic structure. The replacement of sulfur by selenium leads to increasing line widths and *g* values. Oakley[13] compared naphthalene-1,2,3-dithiazolyl and its selenium-containing variants and revealed a steady increase in *g*-value with increasing selenium content, as well as a general loss of resolution. Both effects can be attributed to the expected greater spin – orbit contribution of selenium. A similar trend is observed between the selenatriazinyl and corresponding thiatriazinyl radicals (Table 4.3).

Table 4.3 Hyperfine coupling constants of EPR data based on simulation



Radical	R/R'	a_{N1}	a_{N2}	a_{N3}	g-factor	linewidth
E2	*p*-CH_3/CCl_3	4.792	4.029	3.837	2.0174	1.381
E4	*p*-Cl/CCl_3	4.673	4.052	3.861	2.0180	1.256
(DFT Calc.)	*p*-Cl/CCl_3	4.606	4.009	3.995	-	-
E6	*p*-CF_3/CCl_3	4.588	4.040	3.951	2.0179	1.162
E10	*p*-CH_3/CF_3	4.750	4.042	3.754	2.0171	1.524
PhPhSeTA[12]	H/Ph	4.3	3.8	4.3	2.0169	-
TTA2[8]	*p*-CH_3/CCl_3	4.370	4.374	3.240	-	-
TTA4[8]	*p*-Cl/CCl_3	4.227	4.446	3.260	-	0.38
TTA6[8]	*p*-CF_3/CCl_3	4.100	4.560	3.350	-	-
TTA10[8]	*p*-CH_3/CF_3	4.370	4.375	3.200	-	-

1. All a_N values are in Gauss.
2. Calculated hfc in Gauss from UB3LYP-DFT calculations, multiplied by a scaling factor of 0.82. DFT calculation was done by T. Roemmele.

4.5 Conclusions

Selenatriazinyls **E** are synthesized through reduction of 1-chloroselenatriazine by triphenylantimony and purified by *in-situ* crystallization. These compounds crystallize as dimers in the solid-state (Chapter 5), they dissociate in solution to free radical although the extent of this dissociation has not been measured. The EPR spectra for compounds **E** are highly diagnostic as to the structure of the selenatriazine radicals in solution. DFT calculation was done to assign the hfc constants to the individual nitrogen nuclei in the selenatriazine ring. The EPR spectra of compounds **E** are simulated by WINEPR SimFonia and WINSIM software; thus the g-factors, linewidth and $a_{(N)}$ values are calculated. Comparing with thiatriazinyl radicals, the replacement of sulfur by selenium leads to increasing coupling constants $a_{(N)}$, line widths and g values as well as general loss of resolution. These effects can be attributed to the expected greater spin – orbit contribution of selenium. There is no resolvable hfc to ^{77}Se, ^{37}Cl and phenyl protons.

Reference

1. Wölmershäuser,G.; Schnauber, M.; Wilhelm, T. *J. Chem. Soc., Chem. Commun.* **1984**, 573.

2. Barclay, T.M.; Cordes, A.W.; George, N.A.; Haddon, R.C.; Itkis, M.E.; Mashuta, M.S.; Oakley R. T.; Patenaude, G.W.; Reed, R.W.; Richardson, J.F.; Zhang, H. *J. Am. Chem. Soc.*, **1997**, *119*, 2633.

3. Hecknamm, G.; Johann, R.; Kraft, G.; Wölmershauser, G. *Synth. Met.* **1991**, *43*, 3287.

4. Markovski, L.N.; Polumbrik, O. M.; Talanov, V.S.; Shermolovich, Y.G. *Tetrahedron Lett.* **1982**, *23*, 761.

5. Cordes, A.W.; Chamchoumis, C.M.; Hicks, R.G.; Oakley, R.T.; Young, K.M.; Haddon, R.C. *Can. J. Chem.* **1992**, *70*, 919.

6. Hayes, P. J.; Oakley, r. T.; Cordes, A. W.; Pennington, W. T. *J. Am. Chem. Soc.* **1985**, *107*, 1346.

7. Cordes, A. W.; Hayes, P. J.; Josephy, P. D.; Koenig, H.; Oakley, R. T.; Pennington, W. W. *J. Chem. Soc., chem. Commun.* **1984**, 1021.

8. Roemmele, T. L. *M. Sci. thesis*, Univ. of Lethbridge, **2002**.

9. Kornuta, P. P.; Deril, L. I.; Markovski, L. N. *Zh. Org. Khim.* **1980**, *16*, 1308.

10. Markovskii, L. N.; Kornuta, P. P.; Katchkovskaya, L. S.; Polumbrik, P. M. *Sulfur Lett.* **1983**, *1*, 143.

11. Banister, A.J.; Smith, N.R.M.; Hey, R.G. *J. Chem. Soc., Perkin Trans.* **1983**, *1*, 1181

12. Oakley, r. T.; Reed, R. W.; Cordes, A. W.; Craig, S. L.; Graham, J. B. *J. Am. Chem. Soc.* **1987**, *109*, 7745.

13. Oakley R. T.; Reed, R. W.; Robertson, C. M.; Richardson, J. F. *Inorg. Chem.* **2005**, *44*, 1837.

14. Bestari, K.; Cordes, A. W.; Oakley, R. T.; Young, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 2249.

Chapter 5 Crystal structures

5.1 Introduction

This chapter will describe the X-ray structures of 1,2,4,6-selenatriazinyl dimer (**E9** and **E10**), 1-chloro-1,2,4,6-selenatriazines **D2**, **D7**, **D8**, **D10**, **D16**, and the intermediate **C8**.

Crystal structures are usually determined by the technique of X-ray crystallography. This technique relies on the fact that the atomic spacings in crystals are of the same order of magnitude as the three-dimensional diffraction grating to a beam of X-rays. Single crystal X-ray diffraction is used to measure both the position and intensity of the X-ray diffraction patterns of a crystal, to determine the space group as well as the precise atomic positions, and therefore the bond lengths and angles of molecules within the crystal. These reflections are collected and measured by an automatic diffractometer, and the intensities of the indexed reflections are stored and then corrected from geometric and polarization effects.

Crystal structures are solved by creating a set of trial phases for the structure factors. There are two main methods for doing this. The first is known as the **Patterson** method, and relies on the presence of at least one, but not many, heavy atoms in the unit cell. The heavy atoms in a structure determine most of the phases, and so once they have been located these phases can be used to calculate a preliminary electron density map, and this usually then shows the positions of the other lighter atoms in the unit cell. The second way is to use so-called **direct methods** and this is used when there are no heavy atoms in the cell, for example, in solving the structures of organic, biological and cluster compounds. Direct methods use the facts that the electron density in a structure cannot

take any value but must always be positive, and that the structure consists of discrete spherically symmetric atoms, to calculate mathematical probabilities for the phase values and thus to calculate an electron density map of the unit cell. Theoreticians have worked on the mathematics of these methods for many years and have produced accessible computer programs that employ them – two of the best known are MULTAN and SHELX.

The diffraction intensities as a function of lattice geometry are termed 'structure factors'. Once all atoms have been located, refinement of atomic positions is done until optimum agreement between calculated and observed structure factors is obtained. The R (residual) factor gives an overall measure of the difference between the two and therefore of how correct the structure is.

The final objective of the synthetic work in this project was to obtain a series of selenatriazine derivatives with varying substituents on the attached phenyl ring. A crystal structure of the similar diphenylselenatriazine ring was already known.[1-3] We have been able to isolate X-ray quality crystals from a series of compounds containing selenatriazine rings.

5.2 Data Refinement

All structures were solved by direct methods, using the SHELXS97 computer program and refined by a full-matrix least-squares method. The structure factor F was refined against all reflections. Goodness-of-fit (GooF) is based on F^2

$$GooF = \sqrt{\frac{\sum\left[w\left(F_0^2 - F_c^2\right)\right]}{(n-p)}} \qquad (5.1)$$

where n = number of reflections, p = number of refined parameters.

The weighted R-factor is also based on F^2

$$wR_2 = \sqrt{\frac{\sum\left[w\left(F_0^2 - F_c^2\right)^2\right]}{\sum\left[w\left(F_0^2\right)^2\right]}} \qquad (5.2)$$

and the conventional R_1 is based on the observed F values larger than $4\sigma(F_0)$.

$$R_1 = \frac{\sum\left||F_0| - |F_c|\right|}{\sum|F_0|} \qquad (5.3)$$

R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on all data will be even larger.

5.3 1,1-dichloro-3-trichloromethyl-4-H-5-Dipp-selenatriazine (**C8**)

5.3.1 Experimental

Crude product 0.40 g from the condensation reaction of **A8** and $SeCl_4$ in 10 ml CH_2Cl_2 was chilled at –10 °C for one week. **C8** crystallized as colorless bricks. Crystals were sent to the University of Alberta for collection of X-ray intensity data using a Mo *Kα* radiation source (0.71073 Å).

5.3.2 Data Collection and Space Group Determination

A suitable colorless crystal with dimensions 0.44 x 0.21 x 0.17 mm was selected. Data were collected between θ = 1.77 to 26.40° at –80 °C. From the 24187 collected reflections, 8385 independent reflections were found and used to determine 433 unit cell parameters. The structure was solved by direct methods, and refined by a full-matrix least-squares approach. Refinement converged with unweighted and weighted agreement factors of R = 0.037 and wR = 0.076 respectively, and goodness-of-fit (on F^2) S = 1.02.

The Laue symmetry gave this molecule in the monoclinic system with space group $P2_1/n$ belong to point group $2/m$. **C8** is at the general positions and the multiplicity for the general positions in this particular space group is four (x, y, z), (-x, y+1/2, -z), (-x, -y, -z), and (x, -y+1/2, z). The Z value of 8 indicated that there are 2 molecules per motif and 4 motifs in the general positions of the unit cell in this space group. Two independent molecules were determined to form the repeating motif in the crystal structure. Each motif is related to the other by a inversion or 2_1 screw axis.

The only known analogue of **C8**, 1,1-dichloro-3,5-diphenyl-4H-1,2,4,6-selenatriazine was independently reported by Fenske[2] and Oakley[3] respectively. Both reported the crystals in monoclinic $P2_1/n$, but with Z value as 2 and 4.

5.3.3 Discussion on Structure

The SeNCNCN ring is in a boat conformation (Figure 5.1) with the Se atom displaced 0.127 Å and the opposite N atom (which is bonded to an H atom) displaced 0.059 Å from the mean plane of the boat bottom (coplanar N11C11C12N13 within 0.001 Å). The planar phenyl ring intersects with the boat bottom with 79.31° dihedral angle. The Cl-Se-Cl bond angle 179.22(4) indicated that Cl-Se-Cl is almost linear and perpendicular to the SeNCNCN boat bottom plane (86.69° intersection). The bond lengths of N11=C11 (1.284(4) Å) and N13=C12 (1.277(4) Å), close to the average C=N double bond (~1.270(15) Å),[4] are definitely double bonds. Known C—N single bond lengths vary between 1.30 – 1.49 Å depending on the structure[5]. The bond lengths of N12–C12 (1.360(4) Å) and N12–C11 (1.387(4) Å) are longer than a typical heterocyclic C=N bond length of ~1.352(5) Å,[5] and thus can be determined as single bonds. The result is

consistent with the expected structure **C** shown on Figure 3.12 of Chapter 3. The Se-N bonds 1.828(3) and 1.840(2) Å correspond well to Pauling's Se-N single bond length of 1.86 Å,[6] and are much longer than the other ring bonds, because of the big atomic radius of selenium. The two Se–Cl bond lengths 2.3540(9) and 2.3936(9) of **C8** are consistent with the general Se–Cl single bond length, which varies between 1.8~2.8 Å depending on the tendency of ionic character and Se coordinating environment.[7,8] The more ionic, the longer the Se–Cl bond is. Because of the asymmetrical environment as well as the short intermolecular contact, the two Se–Cl bond lengths are slightly different.

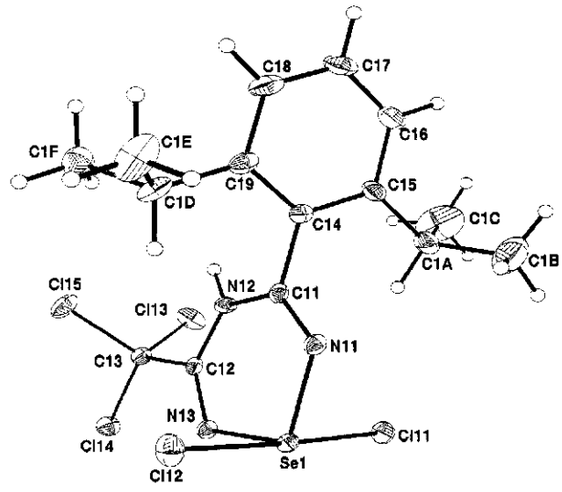
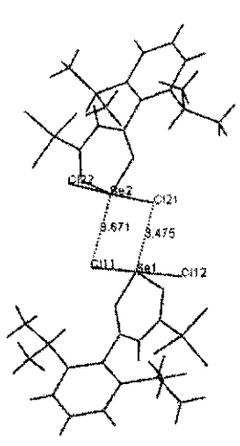


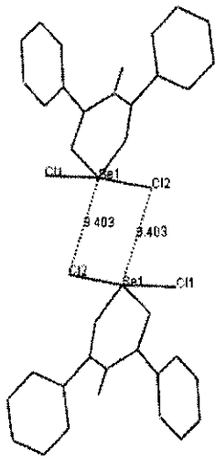
Figure 5.1 ORTEP drawing (25% probability ellipsoids) showing atom numbering of **C8**

As expected, an intermolecular hydrogen bond exists between Cl and H (Se—Cl---H—N), at 2.613 Å. Every two molecules in a unit cell were hydrogen bonded to each other, and extended to those in neighboring unit cells. The intermolecular short contacts are complicated and notable. There are Se---Cl—Se (3.475 Å), H_2C—H---Cl—Se (2.902 Å). They are closer than the sum of van der Waals radii. Fenske[2] reported that the

compound 1,1-dichloro-3,5-diphenyl-4-H-1,2,4,6-selenatriazine forms centrosymmetric dimeric molecules with $SeCl_2Se$ bridges. The lengths of two Se---Cl short contacts are 3.403 Å, less than the sum of van der Waals radius (1.90 Å for Se and 1.75 Å for Cl). Surprisingly Oakley[1] reported the same compound without dimeric character by $SeCl_2Se$ bridges. Compound **C8** has only one Se---Cl short contact at 3.475 Å. The other Se----Cl distance (3.671 Å) is more than the sum of van der Waals radii. Figure 5.2 directly compares the difference of Se---Cl short contacts between the two compounds. **D8** has a highly unsymmetric $SeCl_2Se$ bridge compared to that found in 1,1- dichloro-3,5-diphenyl-4-H-1,2,4,6-selenatriazine. The possible reason is steric hinderance from the bulky DIPP group twisted the heterocycle, hence the chlorines are displaced. The intermolecular hydrogen bonds and short contacts cross-linked all molecules to one another in a network pattern. This may be the reason the compounds **C** have much higher melting points than that of compounds **D**.



D8



1,1-dichloro-3,5-diphenyl-4-H-1,2,4,6-selenatriazine

Figure 5.2 A comparison of two crystals by Se...Cl short contact.

5.4 1-Chloro-1,2,4,6-selenatriazines

5.4.1 Experimental

Yellow crystals of **D2** were recrystallized by sublimation (100°C) in a three zone tube furnace using Pyrex sublimation tubes under dynamic vacuum. Yellow plates of **D2** were collected. Crude powders of compound **D7**, **D8**, **D10**, **D16** were sublimed using the above tubes at 110, 90, 65 and 80 °C respectively. Yellow bricks of **D7**, yellow needles of **D8** and **D16**, and yellow plates of **D10** were collected for X-ray crystallography. Crystals were sent to the University of Alberta for collection of X-ray intensity data using a Mo Kα radiation source (0.71073 Å).

5.4.2 Data Collection and Space Group Determination

Suitable yellow crystals of **D2**, **D7**, **D8**, **D10**, **and D16** were selected. All data were collected between θ ~ 1.3 to 26.5° at –80 °C. The structures were solved by direct methods, using the SHELXS97 computer program and refined by a full-matrix least-squares method. Refinement converged with unweighted and weighted agreement factors of R_1 and wR_2 as listed in Table 5.1 along with other pertinent crystal data.

The Laue symmetry gave **D2** in monoclinic system with space group $P2_1/n$ belonging to point group $2/m$. **D2** is at the general positions and the multiplicity for the general positions in this particular space group is two. The Z value of 4 indicated that there were 4 molecules in the general positions (x ,y, z), (-x, y+1/2, -z+1/2), (-x, -y, -z), and (x, -y+1/2, z+1/2) in the unit cell in this space group. They are related by inversion and 2_1 screw axis. Only one independent molecule was determined to form the repeating motif in the crystal structure. The unit cell dimensions recorded β= 95.8977(10)°, close to

orthorhombic system of reported crystal, 1-chloro-3.5-diphenylselenatriazine[3]. From 8976 reflections collected, 2724 independent reflections were found, offering 16x oversampling of the 164 parameters to refine.

D10 is in the monoclinic system with space group $P\ 2_1/c$ belonging to point group $2/m$. The multiplicity of position is 4. The Z value of 4 tells that there is 1 molecule in a motif and 4 motifs in a unit cell. The molecules are located at (x, y, z), (-x, y, -z+1/2), (-x, -y, -z) and (x, -y, z+1/2). They are related by inversion or *c* glide operation. From 5775 collected reflections, 100% were used as independent reflections, offering 35x oversampling of the 165 parameters to refine. Correspondingly a low final R-factor 0.0320 and Goodness-of-fit 0.932 are contributed, consistent with low standard deviations of bond lengths upto ±0.002 Å and bond angles upto ±0.2°.

D7 is in the triclinic system with space group $P\bar{1}$ belonging to point group $\bar{1}$. $P\bar{1}$ has two general positions at (x, y, z) and (-x, -y, -z). The Z value of 2 indicates that both molecules are at the general positions of the unit cell. They are related to each other by inversion only. Of 5203 collected reflections, 54% independent reflections (2724) were used, offering 16x oversampling of the 172 parameters to refine. High quality crystals contribute to a low final R-factor of 0.0248 and Goodness-of-fit 1.045, consistent with low standard deviations of bond lengths up to ±0.0019 Å and bond angles up to ± 0.19°.

D8 is in the orthorhombic system with space group *Fdd*2 belonging to point group *mm*2. The multiplicity of position is 16. The Z value of 16 means 1 molecule in a motif and 16 motifs in a unit cell. There are 4 molecules in general positions (x, y,z), (-x, -y, z), (x+1/4, -y+1/4, z+1/4), (-x+1/4, y+1/4, z+1/4). They are related by inversion and *d* glide. The other 12 molecules are created by multiplying by the face-centring coordinates (0,

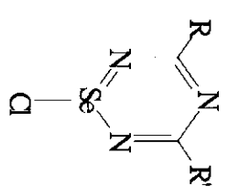
1/2, 1/2), (1/2, 0, 1/2), and (1/2, 1/2, 0). From 14973 collected reflections, only 3898 independent reflections (26%) were found. The high R-factor predicted higher standard deviation of molecular bond lengths and bond angles up to ±0.016 Å and ± 0.9°, due to relatively poor crystal quality.

D16 is in the monoclinic system with space group *I* 2/*a* belonging to point group 2/*m*. The multiplicity of positions is 8. The Z value of 8 means 1 molecule per motif and 8 motifs per unit cell. Four molecules are in general position (x, y, z), (-x, -y, -z), (1/2-x, y, -z), and (x+1/2, -y, z). The other 4 positions were created by translating (1/2, 1/2, 1/2) of above general positions. Reasonably low R-factor and Goodness-of-fit demonstrate the reliability of the crystal structure, but needle-like crystals limit the data collection hence induced relatively high standard deviation on the atom positions, bond distances, and bond angles.

Table 1 compares the data collection and refinement parameters of compounds **D** and a known analogue **Ref3**. Data of **D** were collected between wide θ ranges, hence abundant independent reflections were found. High data to parameter ratios contribute to the structures of **D** having good agreement factors of R_1 and excellent Goodness-of-fits. In contrast data of **Ref3** were collected only between 20 – 24° and found only 1083 independent reflections. The lower ratio of data to parameters (6x) results in an artificially low R_1 factor as well as poor Goodness-of-fit.

Table 5.1 Space group determination and refinement of 1-chloro-selenatriazines

Compound	**D2**	**D10**	**D7**	**D8**	**D16**	**Ref3**
R/R'	CH_3Ph/CCl_3	CH_3Ph/CF_3	$CNPh/CCl_3$	$Dipp/CCl_3$	$Dipp/CF_3$	Ph/Ph
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P\,2_1/c$	$P\bar{1}$	$Fdd2$	$I2/a$	$P2_12_12_1$
Z	4	4	2	16	8	4
Density (Mg/m^3)	1.930	1.862	1.925	1.599	1.560	1.63
θ range for data collection	1.31 – 26.21°	2.27 – 26.45°	1.95 – 26.37°	1.67 – 26.41°	1.45 – 26.41°	20 - 24°
Reflection collected	8976	5749	5203	14973	12024	2274
Independent reflection	2724 [R(int) = 0.0293]	5775 [R(int) = 0.0000]	2813 [R(int) = 0.0214]	3898 [R(int) = 0.0727]	3581 [R(int0 = 0.0624]	1083
Data/restraints/ parameters	2724 / 0 / 164	5775 / 0 / 165	2813/ 0 /172	3898/ 1 /208	3581/ 0 /236	1083/ 0 /172
Goodness-of-fit on F^2	1.265	0.932	1.045	1.059	1.023	1.55
Final R indices [I>2signa(I)]	$R_1 = 0.0323$ $wR_2 = 0.0909$	$R_1 = 0.0329$ $wR_2 = 0.0717$	$R_1 = 0.0248$, $wR_2 = 0.0596$	$R_1 = 0.0709$, $wR_2 = 0.1819$	$R_1 = 0.0446$, $wR_2 = 0.1012$	$R_1 = 0.054$, $wR_2 = 0.061$



5.4.3 Discussion of Structures

D2: The heterocycle is twisted (Figure 5.3). The four atoms C1, N1, N3, and C2 deviate from their mean plane of C1N1N3C2 by a displacement of -0.041, 0.041, -0.050, and 0.050 Å respectively. Se and N2 were displaced 0.299 and 0.085 Å from the mean plane. The phenyl ring intersects with the C1N1N3C2 mean plane by a dihedral angle of 19.62°. The Se—Cl bond is about 100° (Cl—Se—N angles are 100.42° and 98.07°) from the N—Se—N plane. The bond lengths of Se—N (1.764(2) and 1.774(3) Å) are shorter than those of **C8** (1.828(3) and 1.840(2) Å), and agree well with reported Se⋯N lengths.[3,10] C—N bonds (1.326(4), 1.315(4), 1.352(4), 1.330(4) Å) tend to be more uniform than those of **C8** and close to the typical heterocyclic C⋯N bond length of ~1.352(5) Å[5]. This result indicates the heterocycle has a delocalized electronic structure (based on geometric considerations), as with all other derivatives **D**.

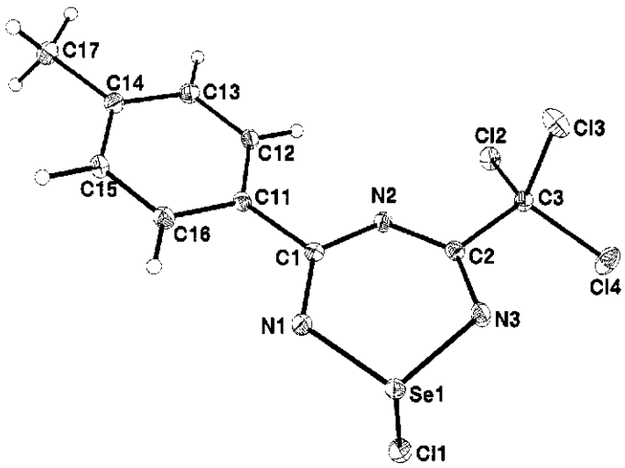


Figure 5.3 ORTEP drawing of **D2**, showing atom-numbering scheme (25% probability ellipsoids)

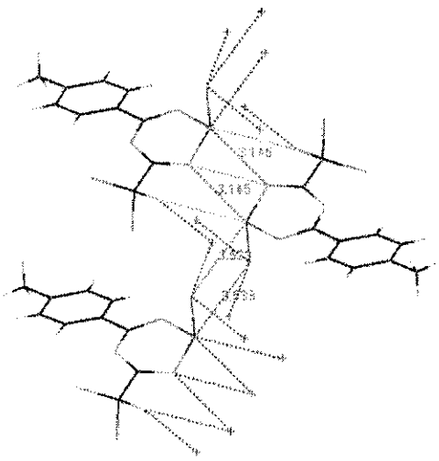


Figure 5.4 Diagram of intermolecular short contacts of **D2.**

As expected, no hydrogen bond exists. However, the intermolecular short contacts closer than the sum of van der waals radii are noticeable. There are Se---Cl, Se---N, N---N, Cl---Cl short contacts. The very important contacts were between Se and Cl (bonded to the other Se), at 3.538 Å, forming centrosymmetric $SeCl_2Se$ bridges. Furthermore, the closest inter-ring contacts are between Se and N, at 3.145 Å, forming another SeN_2Se bridge. The two bridges intersect at a dihedral angle of 88.29°. The two kinds of short contacts link molecules to a close network, hence give the crystals high density to 1.930 Mg/m^3. Correspondingly, close crystal packing effects results in the twisted heterocycle.

D10: **D10** is different from **D2** by replacing CCl_3 with CF_3. The C_2N_3Se ring is in a shallow boat conformation (Figure 5.5). This is a common conformation for six-membered ring with less ring strain. Se atom is displaced 0.202 Å and the opposite N2 atom displaced 0.053 Å from the mean plane of the boat bottom (coplanar by N1C1C2N3 within 0.005 Å). The phenyl ring intersects with the C1N1N3C2 mean plane by a dihedral angle of 8.77°, much smaller than that of **D2**. N1—C1—N2—C2—N3 bond

lengths are the same as those of **D2** in standard deviation. Se—N3 is lengthened and Se-N1 shortened compared to those of **D2**.

The intermolecular short contacts are simpler than those of **D2**. There are Se---N, Se---C, Se---F, H---Cl. The most noticeable short contact is Se---N (3.048 Å). Compound **D10** forms centrosymmetric dimeric molecules with SeN_2Se bridges (See Figure 5.6). There is no Se---Cl as in **E10**, so that the shallow boat conformation may be the result of few intermolecular contacts.

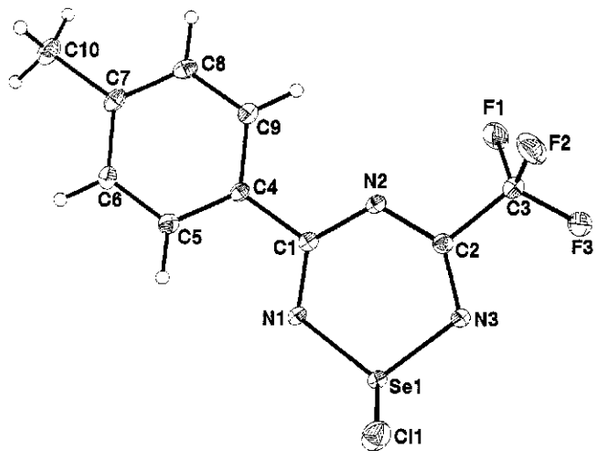


Figure 5.5 ORTEP drawing of **D10**, showing atom-numbering scheme (25% probability ellipsoids)

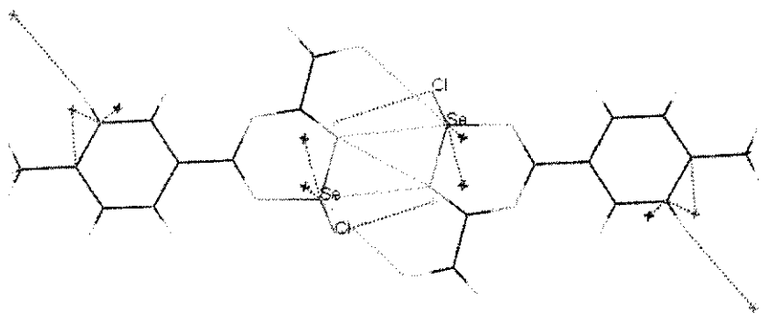


Figure 5.6 Diagram of intermolecular short contacts of **D10**.

D7: The SeNCNCN ring of **D7** was less twisted than that of **D2** (Figure 5.3) The four atoms C1, N1, N3, and C2 deviate their mean plane of C1N1N3C2 by a displacement of -0.029, 0.035, -0.034, and 0.028 Å respectively. Se and N2 were displaced 0.398 and 0.121 Å from the mean plane, more than in **D2**. The phenyl ring intersects with the C1N1N3C2 mean plane by a dihedral angle of 26.29° The bond lengths of the heterocycle are slightly different from those of **D2**, specially the Se—N bonds being longer, which may be due to intermolecular short contacts. The unsymmetric character of the heterocycle is almost a copy from **D2**.

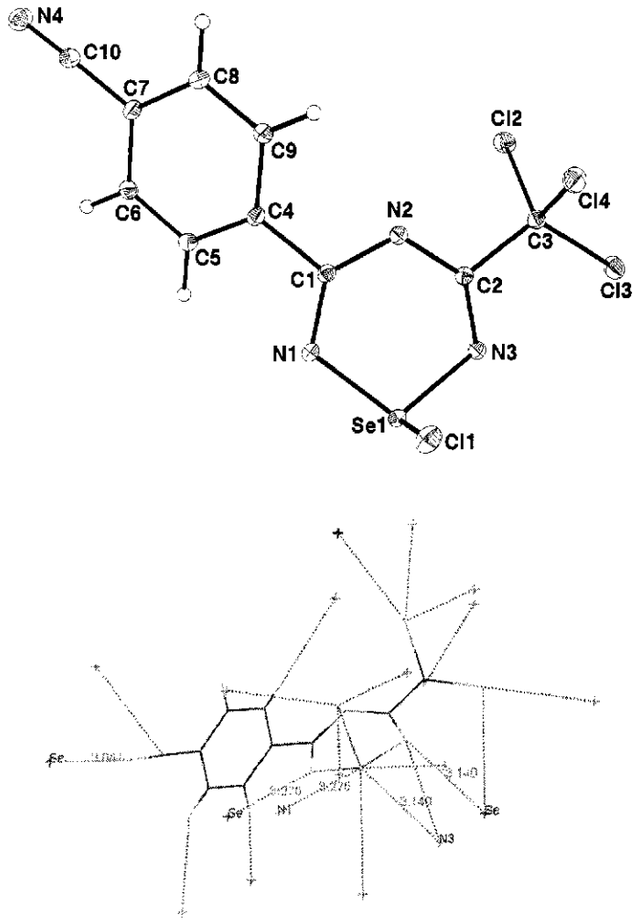


Figure 5.7 ORTEP diagram of **D7**, showing atom-numbering scheme, and intermolecular contacts less than the sum of van der Waals radii.

The crystal of **D7** does not show hydrogen bonding, as expected. There is no short contact between the two molecules in the unit cell. However, the intermolecular short contacts to neighboring unit cells are rich. The linear structure of the *para*-cyanophenyl group orients the lattice by a strong contact to Se in a neighboring molecule. The molecules are arrayed in lines with head to tail contacts of CN---Se, at 3.041 Å, a common feature between CN and Se or S.[11,12] These molecular lines are cross-linked by two SeN_2Se bridges (3.140 Å and 3.275 Å) which intersect at dihedral angle of 72.32°. These close links contribute to the crystals high density and the twisted heterocycle.

D8: Like crystals **D10**, heterocycle **D8** has a boat conformation (Figure 5.8) with the Se atom displaced 0.353 Å and the opposite N2 atom displaced 0.085 Å from the mean plane of the boat bottom (coplanar by N11C11C12N13 within 0.005 Å). The phenyl ring intersects with the C1N1N3C2 mean plane by a dihedral angle of 70.29°, much larger than those of **D2**, **D10** and **D7**. This alignment is due to steric hinderance from the two

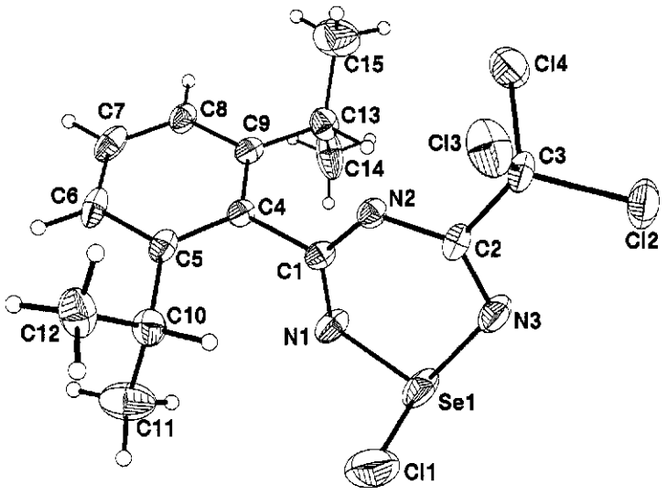


Figure 5.8 ORTEP drawing of **D8**, showing atom-numbering scheme (25% probability ellipsoids)

bulky isopropyl groups. The bond lengths of heterocycle are unsymmetric due to the unequal substituents on C1 and C2. Short contacts are Se---N, Cl---Cl, Se---C and Cl---H. The bulky aryl group keeps molecules away from each other, correspondingly a lower density. Remarkably, no $SeCl_2Se$ and SeN_2Se bridges are found as short contacts. Instead single intermolecular Se---N2 short contacts forms between Se and the opposite N2.

D16: The heterocycle also has a boat conformation with Se atom displaced 0.314 Å and the opposite N2 atom displaced 0.10 Å from the mean plane of the boat bottom (coplanar by N11C11C12N13 within 0.004 Å) (Figure 5.9). The phenyl ring intersects with the C1N1N3C2 mean plane by a dihedral angle of 75.18°, even bigger than that of **D8**. Despite unequal substituents on C1 and C2, the heterocycle is surprisingly symmetric about the Se-----N2 line.

Rotational disorder was found in the CF_3-group, a well-known feature of molecular CF_3 structures, due to their low affinity for other atoms. Two sets of fluorine atoms were located (labeled FA and FB). The same disorder was found in the crystal structure of 5-phenyl-3-trifluoromethyl-1,2,4,6-thiatriazine radical.[13]

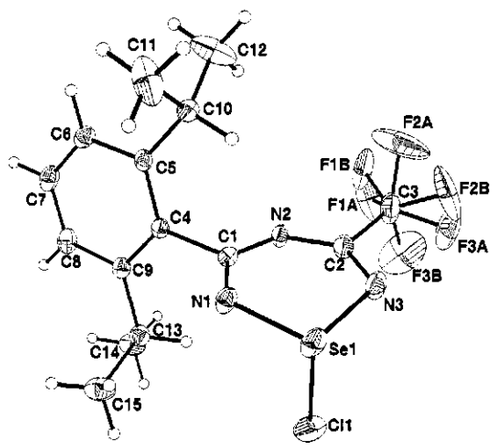


Figure 5.9 ORTEP drawing of **D16**, showing atom-numbering scheme (25% probability ellipsoids)

Overall, heterocycles of **D10**, **D8** and **D16** have boat conformations, while **D2** and **D7** are twisted. Due to different R and R' group, the heterocycles are unsymmetric except **D16**. The crystal with R = R' = Ph is symmetric about the Se-------N2 line. The N1⋯C1⋯N2 bonds are shortened comparing to N2⋯C2⋯N3 because of the proximity of the electron withdrawing CX_3 group. Correspondingly, the N1⋯C1⋯N2 angles are larger than those of N2⋯C2⋯N3. The heterocycles have aromatic ring character.

Table 5.2 compares the derived geometric partners with the known structure of 1-chloro-3,5-diphenyl-1,2,4,6-selenatriazine (**Ref3**). The unsymmetric substitution pattern in **D2**, **D7** and **D10** is clearly visible in the bond lengths. There is a tendency for the N⋯C⋯N bonds to shorten at the carbon of attachment of a CX_3 group, and lengthen at the carbon of attachment of a substituted aryl group, as with the Se⋯N bonds. These are apparently due to the proximity of electron withdrawing CX_3 group. Correspondingly, the N⋯C⋯N angles at the carbon attached to a CX_3 group are larger than those at the carbon attached to an aryl group.

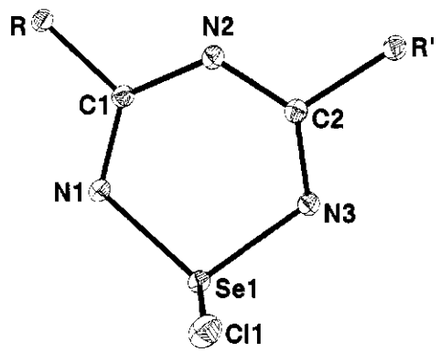


Table 5.2 Bond distances and angles of heterocycles in 1-chloro-selenatriazines

R/R'	Se—N1	N1—C1	C1—N2	N2—C2	C2—N3	N3—Se
Ph/Ph	1.759(7)	1.337(12)	1.343(12)	1.358(11)	1.320(11)	1.754(8)
Tolyl/CCl_3	1.764(2)	1.330(4)	1.352(4)	1.315(4)	1.326(4)	1.774(3)
Tolyl/CF_3	1.7554(16)	1.333(2)	1.347(2)	1.325(3)	1.321(2)	1.7884(17)
CNPh/CCl_3	1.7813(17)	1.331(3)	1.340(3)	1.332(3)	1.311(3)	1.7927(19)
Dipp/CCl_3	1.769(7)	1.318(10)	1.334(10)	1.338(9)	1.284(9)	1.789(8)
Dipp/CF_3	1.773(3)	1.316(4)	1.338(4)	1.321(4)	1.310(5)	1.768(3)

R/R'	<N1SeN3	<SeN1C1	<N1C1N2	<C1N2C2	<N3C2N2	<C2N3Se
Ph/Ph	105.4(4)	115.5(7)	130.0(9)	121.4(8)	127.1(1)	117.9(7)
Tolyl/CCl_3	104.95(12)	116.8(2)	128.0(3)	120.3(3)	132.0(3)	113.4(2)
Tolyl/CF_3	105.55(7)	117.60(14)	128.19(17)	120.12(17)	133.5(2)	113.43(14)
CNPh/CCl_3	104.42(8)	114.97(14)	129.43(29)	119.27(18)	132.5(2)	112.53(14)
Dipp/CCl_3	104.2(3)	115.7(5)	129.1(7)	120.2(7)	132.0(8)	114.1(6)
Dipp/CF_3	104.91(14)	115.8(2)	129.4(3)	119.0(3)	133.4(3)	113.3(2)

D2: Tolyl/CCl_3, **D10**: Tolyl/CF_3, **D7**: CNPh/CCl_3, **D8**: Dipp/CCl_3, **D16**: Dipp/CF_3
All bond lengths are in angstrom and angles are in degree.

5.5 1,2,4,6-Selenatriazinyl Dimers

5.5.1 Experimental

1-Chloroselenatriazine **D10** (0.78g, 2.29 mmol) was well dissolved in 25 ml dried CH_3CN. Some solid impurity in solution was filtered off. The yellow filtrate was warmed up and stabilized at about 55 °C. 0.445g (1.26 mmol) Ph_3Sb in 5 ml dried CH_3CN was added to the filtrate dropwise in a period of 2.5 hours without stirring. Black spots appeared while adding Ph_3Sb. The mixture was then allowed to cool down slowly to room temperature, then to ice for 5 hours for further crystallization. After filtering, the solid was dried under vacuum to yield shiny black blocks of bis(3-trifluoromethyl-5-*p*-tolyl-1,2,4,6-selenatriazine) (**E10**).

1-Chloroselenatriazine **D1** (0.78 g 1.92 mmol) in 30 ml dried CH_3CN (well dissolved, trace amount of solid was filtered) was added to the hot solution (80 °C) of 0.37 g (0.96 mmol) Ph_3Sb in 5 ml CH_3CN in 5 minutes without stirring. The solution turned dark red instantly. Crystallization started at about 70 °C when slowly cooled down. After being filtered and dried, black crystals of **E1** were collected. Crystals were sent to the University of Alberta for collection of X-ray intensity data using a Mo Kα radiation source (0.71073 Å).

5.5.2 Data Collection and Space Group Determination

All X-ray intensity data of compound **E9** and **E10** were collected at $\theta \sim 1.51$ to 26.40° and 1.95 to 26.37° at –80 °C respectively. The structures were solved by direct methods, using the SHELXS97 computer program and refined by a full-matrix least-

squares method. Refinement converged with unweighted and weighted agreement factors of R_1 and wR_2.

Table 3 lists the crystal data comparing **E9** and **E10** with known structures of selenium derivative **Ref3**, bis(3,5-diphenyl-1,2,4,6-selenatriazine) and sulfur derivative **Ref13**, bis(3-phenyl-5-trifluoromethyl-1,2,4,6-thiatriazine). All four crystals are in the triclinic system and the $P\bar{1}$ space group.

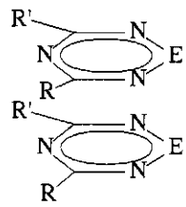


Table 5.3 Comparison of four radical dimers on space group determination

Compound	**E9**	**E10**	**Ref3**	**Ref13**
R/R'/E	MeOPh/CF_3/Se	Tolyl/CF_3/Se	Ph/Ph/Se	Ph/CF_3/S
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	2	4	2	2
Density Mg/m^3	1.954	1.886	1.59	1.677
θ range for data collection	1.51 to 26.40°	1.54 to 26.42°	8 to 22°	2.62 to 28.11°
Reflection collected	8126	16096	3492	13901
Independent reflections	4424 [R(int) = 0.0409]	8761 [R(int) = 0.0301]	1496	4269 [R(int) = 0.0399]
Data / restraints / parameters	4424 / 0 / 325	8761/ 0 /617	1496 / 0 / 337	4269/ 60 /309
Goodness-of-fit on F^2	1.044	1.018	1.55	1.048
Final R indices [I>2signa(I)]	R_1=0.0397, wR_2= 0.0815	R_1=0.0363, wR_2= 0.0811	R_1=0.050, wR_2 = 0.058	R_1=0.0412, wR_2= 0.1309

E10 is at the general positions and the multiplicity for the general positions in this particular space group is two. The Z value of 4 indicated that there were 2 dimers per motif and 1 motif in the general positions of the unit cell in this space group. A packing diagram is given in Figure 5.10. Two independent molecules (dimer 1 and dimer 2) were determined to form the repeating motif in the crystal structure. Therefore the parameters are twice that of one independent molecule. The other two molecules (dimer 3 and dimer 4) are related to dimer 1 and dimer 2 respectively by an inversion. There are no glide planes, screw axis, mirror planes, etc.

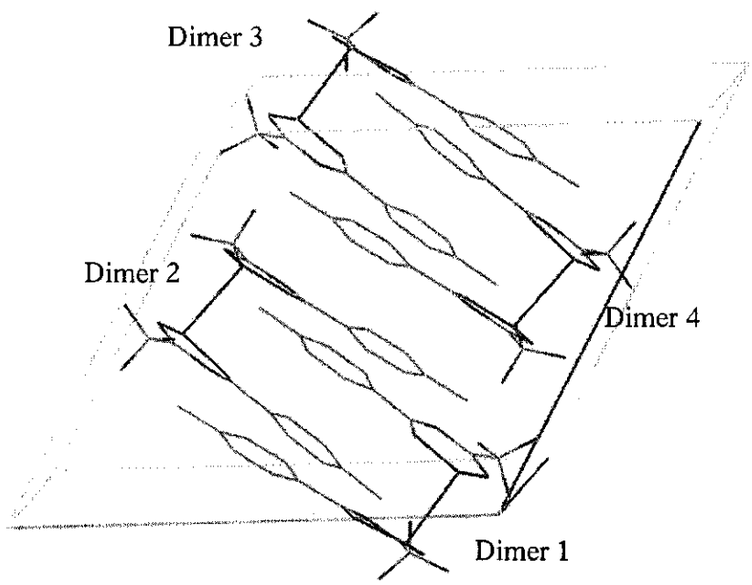


Figure 5.10 Diagram of **E10** Molecules' location in a unit cell

All **E9**, **Ref3** and **Ref13** have Z value 2, meaning two dimers are in the general positions. They are related to each other by an inversion. Only one dimer is determined, therefore the parameters are half of those of **E10**. A packing diagram of **E9** is given in

Figure 5.11. **E9**, **E10** and **Ref13** are tested in a wide theta range for data collection, but **Ref3** is in a narrow theta range with a paucity of observed data. The ratios of data to parameters are 13.6 (**E9**), 14.2 (**E10**), 4.4 (**Ref3**) and 13.8 (**Ref13**) respectively. The high ratio of data to parameters and high quality of crystal contributed to **E9** and **E10** giving very reliable crystal data with low R-factors 0.0397, 0.0363 and Goodness-of-fit on F^2 1.044, 1.018.

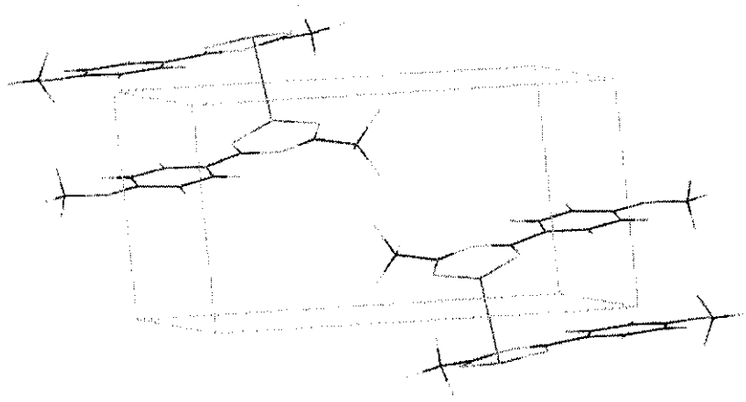


Figure 5.11 Diagram of **E9** Molecules' location in a unit cell

5.5.3 Discussion on Structure

E10: E10 has two independent dimers. The two SeNCNCN rings of first dimer are different (Figure 5.12). Se1 ring is almost planar with Se1 displaced 0.022 Å and N12 displaced only 0.008 Å from the mean plane of the central four atoms (N11, C11, C12, and N13), which are coplanar to within 0.005 Å. While Se2 ring is in slightly folded form along the N21-----C22 line. Se2 and N22 are displaced 0.060 Å and 0.022 Å from the mean plane of the central four atoms (N21, C21, C22, and N23), which are coplanar to 0.029 Å. The two mean planes intersect with a dihedral angle of 11.69 °. The two benzene rings are twisted 9.29° and 17.15° from their connected heterocycles (mean planes)

respectively. Two benzene rings intersect in an angle of 6.23°. Just as the S···S separation in 1,2,4,6-thiatriazinyl dimer (2.666 Å) is clearly longer than in a normal disulfide linkage, so too is the Se1---Se2 contact in **E10** (2.8091 Å) longer than a typical diselenide distance (2.1 – 2.5 Å)[5, 14, 15]. Similar results were found in 3,5-diphenyl-1,2,4,6-selenatriazinyl dimer (2.792 Å)[14], Se_4N_4 (2.75 Å)[16] and $Se_2I_4^{2+}$ (2.841 Å)[17]. However, it is substantially shorter than the interannular Se---Se contacts observed in 1,2,3,5-diselenadiazolyl dimer (3.311 Å) [15] and the dimer of the radical cation $SN_2Se_2^{\cdot+}$ (3.12 – 3.18 Å in its AsF_6^- and SbF_6^- salts).[18]

The heterocycles of the second dimer are slightly different from the first. Se3 ring is almost planar with Se3 displaced 0.016 Å and N32 displaced only 0.005 Å from the mean plane of the central four atoms (N31, C31, C32, and N33), which are coplanar within 0.001 Å. Se4 ring is highly twisted with Se4 and N42 displaced 0.118 Å and 0.039 Å from the mean plane of N41C41C42N43 (coplanar within 0.024 Å). The Se3---Se4 contact (2.772 Å) is shorter than Se1---Se2 (2.809 Å).

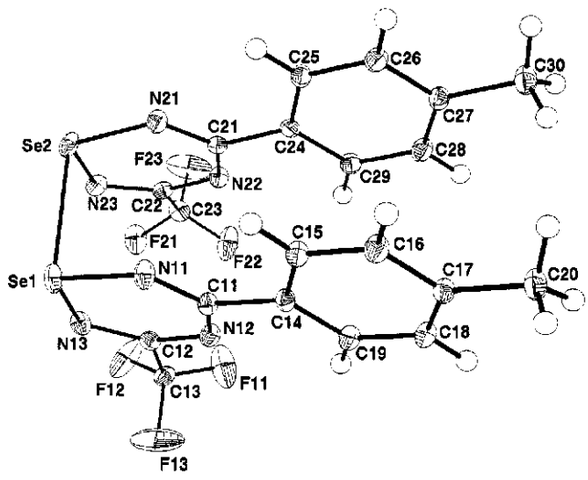


Figure 5.12 **E10** ORTEP drawing of first dimer, showing atom-numbering scheme (25% probability ellipsoids)

Within the C_2N_3Se ring of **E10**, the C—N and Se—N bonds show notable unsymmetry as those of compounds **D**. That is a tendency for the N···C···N bonds to shorten at the side of attachment of a CX_3 group, and lengthen at the carbon of attachment of an aryl group, as with the Se···N bonds. These are due to the proximity to the electron withdrawing CX_3 group and the steric hinderance aryl group. Correspondingly, the N···C···N angles at the carbon attached to a CX_3 group are larger than those at the carbon attached to an aryl group.

E9: Both SeNCNCN rings of **E9** dimer are twisted. Se1 and N2 were displaced 0.053 Å and 0.029 Å from the mean plane of N1C1C2N3 (coplanar within 0.014 Å). Se2 and N5 were displaced 0.095 Å and 0.006 Å from the mean plane of N4C4C5N6 (coplanar within 0.023 Å). The two mean planes are intersected in a dihedral angle of 10.82°.

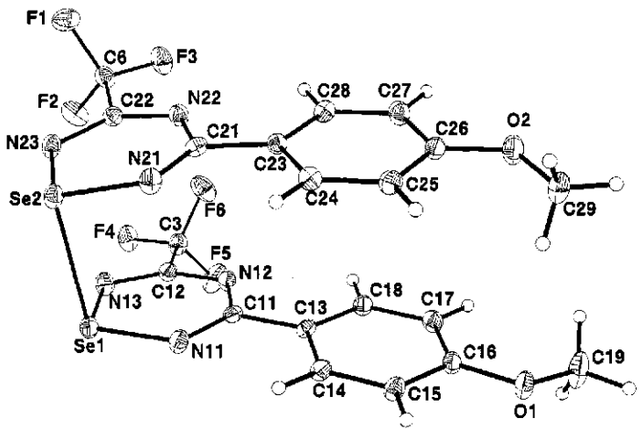


Figure 5.13 ORTEP drawing of **E9** dimer, showing atom-numbering scheme (25% probability ellipsoids)

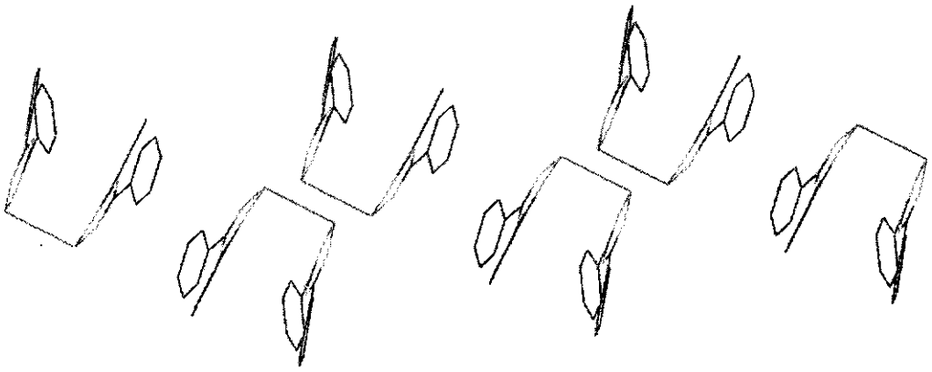
Table 5.4 Bond distances and angles of heterocycles in selenatriazinyl dimers

Compound	**E9**	**E10**		**Ref3**
R/R'	*p*-MeOPH/CF_3	*p*-Tolyl/CF_3		Ph/Ph
Se1—N11	1.773(4)	1.778(3)	1.781(3)	1.761(10)
N11—C11	1.331(6)	1.328(4)	1.325(4)	1.33(1)
C11—N12	1.358(6)	1.363(4)	1.371(4)	1.38(1)
N12—C12	1.339(5)	1.328(4)	1.317(4)	1.35(1)
C12—N13	1.312(6)	1.313(4)	1.329(4)	1.35(1)
N13—Se1	1.800(4)	1.798(3)	1.809(3)	1.794(9)
Se1—Se2	2.7914(8)	2.8091(6)	2.7717(6)	2.792(3)
Se2—N21	1.792(4)	1.784(3)	1.779(3)	1.769(10)
N21—C21	1.323(6)	1.335(4)	1.336(4)	1.34(1)
C21—N22	1.352(6)	1.361(4)	1.354(4)	1.33(1)
N22—C22	1.333(5)	1.325(4)	1.324(4)	1.34(1)
C22—N23	1.324(6)	1.318(4)	1.329(4)	1.32(1)
N23—Se2	1.791(4)	1.807(3)	1.804(3)	1.805(9)
<Se1N11C11	118.8(3)	118.3(2)	117.8(2)	118.2(8)
<N11C11N12	127.6(4)	128.4(3)	128.6(3)	127(1)
<C11N12C12	120.2(4)	119.4(3)	120.4(3)	121(1)
<N12C12N13	134.0(5)	134.8(3)	134.0(3)	132(1)
<C12N13Se1	114.0(3)	113.9(2)	113.8(2)	113.7(7)
<N13Se1N11	105.20(18)	105.12(13)	105.32(13)	107.2(4)
<Se2N21C21	117.9(3)	117.9(2)	117.0(2)	115.9(8)
<N21C21N22	128.4(4)	128.1(3)	128.2(3)	130.4
<C21N22C22	120.6(4)	120.3(3)	120.7(3)	121(1)
<N22C22N23	132.8(4)	134.0(3)	134.0(3)	129.9
<C22N23Se2	114.9(3)	114.1(2)	113.3(2)	115.7(8)
<N23Se2N21	104.67(17)	105.07(13)	105.94(13)	105.2(5)

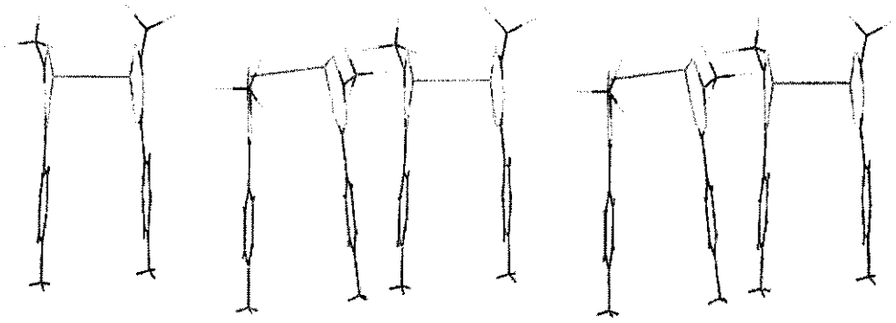
All bond lengths are in angstrom and angles are in degree.

Table 5.4 compares the selenatriazinyl heterocycles structure of **E9** with **E10** and **Ref3**. All the heterocycles have bond lengths with aromatic π bonding character Se⋯N, C⋯N. The bond lengths inherit the tendency of 1-chloro-selenatriazines. That is N⋯C⋯N bonds shorten at the carbon of attachment of a CF_3 group, and lengthen at the carbon of attachment of a substituted aryl group, due to the proximity of the electron withdrawing CF_3 group and the steric hinderance aryl group. All heterocycles have highly consistent bond lengths and angles. The weak interannular Se---Se contacts are close to each other between 2.77 Å – 2.81 Å.

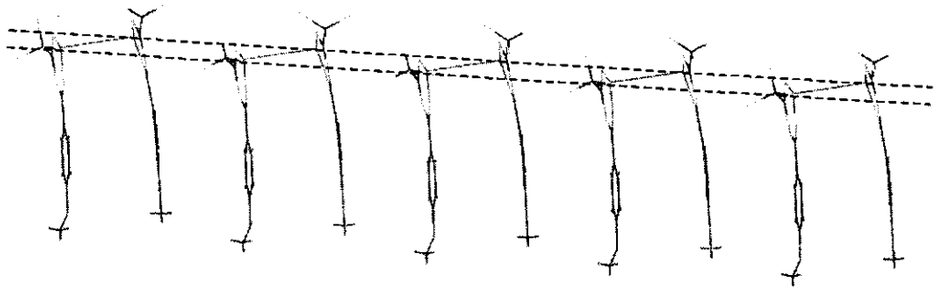
The three dimers **E9**, **E10** and **Ref3** have quite different intermolecular short contact. The main short contact from known crystal **Ref3**[3] is Se---N. The NSeSeN bridge makes every two dimers connect head to head. Therefore the packing arrangement (Figure 5.14a) does not exhibit the desired ordered stacking as Figure 5.14d. Dimers of **E10** have short contacts not only by Se---N, but also by Se---Cl. The Se---Cl short contacts arrange the dimers to line up regularly as shown in Figure 5.14b, but the dimers have the Se---Se side alternatively facing-out and back-in. The neighboring heterocycles are repeated by inversion. This packing arrangement is still not at, but closer to the desired ordered stacking than that of **Ref3**. Dimers of **E9** have Se---N, Se---Cl and C---C (between phenyl groups) short contacts, which line up the dimers regularly as Figure 5.14c. The dimers are repeated by sliding in a line with Se---Se facing the same direction. Every other Se-ring is in the line exhibiting the desired ordered stacking arrangement. This is the six-membered-ring most close to the ideal stacking arrangement. Comparing the three crystal packing arrangements, one can expect that it is very hopeful to find some selenatriazinyl radicals with a stacking arrangement as shown in Figure 5.14d.



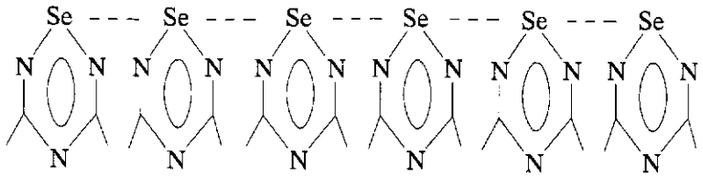
(a)



(b)



(c)



(d)

Figure 5.14 Packing arrangement for three selenatriazinyl dimers
(a **Ref3**, b **E10**, c **E9**, d desired ordered packing arrangement)

5.6 Conclusions

Eight new crystal structures are reported. The SeNCNCN ring of intermediate **C8** is in a boat conformation with two C=N double bonds, two C—N single bonds and two Se—N single bonds. Intermolecular hydrogen bond between Cl and H (Se—Cl---H—N) and short contact Se---Cl cross-link all molecules to one another in a network pattern. This may be the reason the compounds **C** have much higher melting points than the corresponding compounds **D**. Five new 1-chloro-selenatriazines are structurally determined by X-ray crystallography. **D2**, **D10**, **D16** are in monoclinic system, **D7** and **D8** are in triclinic and orthorhombic system respectively. Heterocycles of **D10**, **D8** and **D16** have boat conformation, while **D2** and **D7** are twisted. Due to unsymmetric substituents on 3 and 5 position, the aromatic heterocycles are unsymmetric. Two selenatriazinyl radicals are identified as dimers in solid state. Both **E10** and **E9** display interstack contacts between two dimers. Packing between dimers of **E9** is unique, very close to desired stacking required for metallic conductivity. The result demonstrates that the essential interstack contacts can form. This raises hopes that future crystal engineering will lead to infinitely stacked selenatriazinyl radicals.

5.7 References

1. Cordes, A. W.; Oakley, R. T.; Reed, R. W. *Acta Crystallograph. C*, **1986**, 1889.

2. Fenske, D.; Ergezinger, C.; Dehnicke, K. *Z. Naturforsch.* **1989**, *44*b, 857.

3. Oakley, R. T.; Reed, R. W.; Cordes, A. W.; Craig, S. L.; Graham, J. B. *J. Am. Chem. Soc.*, **1987**, *109*, 7745.

4. Patai, S. *The Chemistry of Amidines and Imidates.*; John Wiley and Sons: New York, **1975**.

5. *CRC Handbook of Chemistry and Physics, 70th Edition*; Weast, R. C.; CRC Press: Boca Raton, FL, **1989**; p F-188.

6. Pauling, L. *The Nature of the Chemical Bond*, 3rd ed. Cornell University Press; Ithaca, NY, **1960**; Chapter 7.

7. Hevmodsson, Y. *Acta Cryst.* **1960**, *13*, 656.

8. Barnes, N. A.; Godfrey, S. M.; Halton, R. T. A.; Pritchard, R. G. *Dalton Trans. Commun.* **2005**, 1759.

9. Björgvinsson, M.; Roesky, H. W.; Fauer, F.; Stalke, D.; Sheldrick, G. M. *Inorg. Chem.* **1990**, 29, 5140.

10. Cordes, A. W.; Haddon, R. C.; Oakley, R. T.; Schneemeyer, L. F.; Waszczak, J. V.; Young, K. M.; Zimmerman, N. M. *J. Am. Chem. Soc.* **1991**, *113*, 582.

11. Alberola, A.; Pask, C. M.; Rawson, J. M.; McInnes, E. J. L.; Wolowska, J.; Mkami, H. E.; Smith, G. *J. Phys. Chem. B*, **2003**, *107*, 14158.

12. Banister, A. J.; Bricklebank, N.; Clegg, W.; Elsegood, M. R. J.; Gregory, C. I.; Lavender, I.; Rawson, J. M.; Tanner, B. K. *J. Chem. Soc. Chem. Commun.*, **1995**, *6*, 679.

13. Roemmele, T. L. *B.Sci. Thesis*, University of Lethbridge, **2002**.

14. Doert, T.; Graf, C. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1101.

15. Cordes, A. W.; Bryan, C. D.; Davis, W. M.; de Laat, R. H. Glarum, S. H.; Goddard, J. D.; Haddon, R. C.; Hicks, R. G.; Kennepohl, D. K.; Oakley, R. T.; Scott, S. R.; Westwood, N. P. C. *J. Am. Chem. Soc.*, **1993**, *115*, 7232.

16. Baernighausen, H.; Volkmann, T. V.; Jander, J. Acta Crystallogr. 1966, 21, 571.

17. Nandana, W. A. S.; Passmore, J.; White, P. S.; Wong, C. M. *J. Chem. Soc., Chem. Commun*, **1982**, 1098.

18. Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Inorg. Chem.* **1981**, *20*, 4053.

Chapter 6 General Conclusions and Future Work

6.1 General Conclusions

1,2,4,6-selenatriazinyl radicals are considered to be potential neutral radical conductors as are 1,2,4,6-thiatriazinyl radicals in the context of molecular metal design. Literature investigation found they were completely ignored in favor of other prospective ring systems. A general route to 1-chloro-1,2,4,6-selenatriazines was developed via the condensation of *N*-imidoylamidine and selenium tetrachloride. All 19 1-chloro-selenatriazines (named **D1 – D19**) described in this work are new. The detailed reaction procedure was investigated. The reaction experienced two intermediates **B**, and **C**. The structure of intermediates **B** is not conclusive due to its reactivity and difficulty in crystallization. Full spectroscopic and analytical data have been presented to support the synthetic claims. Further confirmation of the structures of one intermediate **C8** and five 1-chloro-selenatriazines **D** have been obtained by X-ray crystallography.

Selenatriazinyls **E** are synthesized through reduction of 1-chloro-selenatriazines by triphenylantimony and purified by *in-situ* crystallization. These compounds crystallize as dimers in the solid-state, they dissociate in solution to free radicals. The EPR spectra for compounds **E** are highly diagnostic and display coupling to three unique nitrogen atoms. The EPR spectra of compounds **E** are simulated by WINEPR SimFonia and WINSIM software; thus the g-factors, linewidth and $a_{(N)}$ values are calculated. One DFT calculation was done to assign the hfc constants to the individual nitrogen nuclei in the selenatriazinyl ring. Comparing with thiatriazinyl radicals, the replacement of sulfur by selenium leads to increasing coupling constants $a_{(N)}$, line widths and *g* values as well as

general loss of resolution. These effects can be attributed to the expected greater spin–orbit contribution of selenium. There is no resolvable hfc to ^{77}Se, ^{37}Cl and phenyl protons.

Eight new crystal structures are reported. The SeNCNCN ring of intermediate **C8** is in a boat conformation with two C=N double bonds, two C—N single bonds and two Se—N single bonds. Intermolecular hydrogen bonds between Cl and H (Se—Cl---H—N) and short contacts Se---Cl cross-link all molecules to one another in a network pattern. This may be the reason the compounds **C** have much higher melting points than the corresponding compounds **D**. Five new 1-chloro-selenatriazines are structurally determined by X-ray crystallography. **D2**, **D10**, **D16** are in monoclinic system, **D7** and **D8** are in triclinic and orthorhombic system respectively. Heterocycles of **D10**, **D8** and **D16** have boat conformation, while **D2** and **D7** are twisted. All heterocycles of **D** have aromaticity, consistent with π electron on each of the 6 atoms to form big π bond. Two selenatriazinyl radicals are identified as dimers in solid state. No crystal packing diagram shows ordered stacking, but **E9** are very close to desired stacking required for metallic conductivity.

6.2 Future Work

The condensation reaction to 1-chloro-1,2,4,6-selenatriazines reported in this thesis encountered side reactions with byproducts. The first formed intermediate **B** as clear yellow solutions were not yet identified. The structure of intermediate **B** and beginning reaction mechanism are not conclusive. Further efforts will be required to analyze and

track the reaction *in-situ* by and ^{77}Se NMR. Structural confirmation of byproduct will be very helpful to investigate the reaction mechanism.

The synthesis of 1,2,4,6-selenatriazinyl radicals as crystalline solids remains challenging. Significant efforts will be required to crystallize 1,2,4,6-selenatriazinyl radicals with appropriate substituents in order to maximize inter-stack contacts which play a major role in overcoming distortion. The inter-dimer contacts observed in the crystal structure of **E9** and **E10** provide hope that the desired ordered stacking can be realized someday.

Chapter 7 Experimental

7.1 Introduction

Experimental work in this study consisted of synthetic chemical work completed and previously discussed in this thesis, as well as all crystallographic data. All procedures were performed under an atmosphere of purified N_2 using a drybox, Schlenkware, and vacuum-line techniques, unless otherwise indicated.

Solvents were reagent-grade or better and rigorously dried before use. Anhydrous diethyl ether (ACS grade) was distilled from lithium aluminum hydride. Acetonitrile (HPLC grade) was doubly distilled from diphosphoruspentoxide and calcium hydride. Dichloromethane was distilled from calcium hydride.

Ethanol purification: Place 2.5 g of clean dry magnesium turnings and 0.25g of iodine in a 1L flask, followed by 30ml of 99% ethanol; warming the mixture until a vigorous reaction occurs. When this subsides, heating is continued until all the magnesium is converted to magnesium ethoxide. Up to 500 ml of 99% ethanol is added. After an hour's reflux, anhydrous alcohol is distilled off.

The majority of reagents used were obtained from commercial sources and used as received without further purification. *Para*-substituted benzonitriles, 1,3- and 1,4-dicyanobenzene, trichloroacetonitrile (kept under refrigeration), benzamidine hydrochloride hydrate, selenium, and triphenylantimony were from Aldrich. Trifluoroacetonitrile (gas) was from PCR Inc. HCl (g), Cl_2 (g) and NH_3 (g) were from Praxair.

NMR spectra were acquired at 250.13 (^{1}H) and 62.90 (^{13}C) MHz on a Bruker Tecmag/AC250-F spectrometer using $CDCl_3$ (referenced to TMS), DMSO-d_6 or D_2O as solvents at room temperature. Infrared spectra were recorded on a BOMEM MB102 Fourier transform spectrometer, and are KBr pellets unless otherwise specified. Mass spectra were recorded by the Mass Spectrometry Center, University of Alberta, Edmonton. Melting points were determinded on an electrothermal melting point apparatus and are uncorrected. EPR spectra (X band) for radicals were recorded on an Bruker EMX10 spectrometer as solutions in dichloromethane in 4 mm Pyrex glass tubes sealed under vacuum.

7.2 Synthesis of Benzdiiminoester Hydrochloride

Benz-1,4-di(iminoester hydrochloride): In a 250ml side arm round bottom flask, a suspension of 1.52g (11.86mmol) 1,4-dicyanobenzene in 150 ml dried ethanol was freeze thawed to remove any gas in the flask. The flask was warmed up to and stabilized at –10°C before filling with HCl gas connected via a rubber balloon for 6 hours. The suspension was stirred at r. t overnight, again treated with HCl gas for 8 hours (via a rubber balloon, -10 °C), then stirred at r.t overnight. The mixture was evaporated and dried under vacuum, affording the 1,3-bis(iminoester)benzene as a white solid 3.05 g, 88%. ^{1}H NMR (δ, DMSO-d_6) ppm: 1.48 (t, 6H, 7Hz, -CH_3), 3.42 (br, 4H, NH_2^+), 4.58 (q, 4H, 7Hz, -CH_2-), 8.24 (s, 4H, phenyl), consistent with the reported result.[1]

Benz-1,3-di(iminoester hydrochloride): Prepared by the same method reported for Benzene-1,4-di(iminoester hydrochloride) using 1,3-dicyanobenzene.

7.3 Synthesis of Benzdiamidine Hydrochloride

Benz-1,4-di(amidine hydrochloride): A suspension of 3.05 g (10.38 mmol) benzene-1,4-di(iminoester hydrochloride) in 150 ml dried ethanol was freeze thawed to degas twice to remove any gas in the flask. After warming up to and stabilized at –10 °C, the flask was filled with NH_3 gas via a rubber balloon for 6 hours. The suspension was stirred at r.t overnight. Again treated with NH_3 gas 8 hour at –10 °C, then stirred at r.t 12 hours. The resulting white suspension was left to stand 4 hours before been filtered and dried leaving a white powder 2.05 g (84%) of 1,4-bis(amidine hydrochloride)benzene. ^{1}H NMR (δ, D_2O) ppm: 7.95 (s, 4H, phenyl). ^{13}C NMR (δ, D_2O): 127.0 (s, CH, phenyl), 131.2 (s, C, phenyl), 164.2 (s, C, amidine).

Benz-1,3-di(amidine hydrochloride): Prepared by the same method reported for benzene-1,4-di(amidine hydrochloride) using benzene-1,3-di(iminoester hydrochloride). ^{1}H NMR (δ, D_2O) ppm: 7.81 (t, 1H, 8Hz, phenyl), 7.90 (d, 2H, 8Hz, phenyl), 8.16 (s, 1H, phenyl). IR 3443 (s), 3357 (s), 3251 (s), 3072 (s), 1690 (s), 1660 (m), 1616 (w), 1522 (m), 1471 (m), 1423 (w), 1193 (w), 1104 (m), 929 (w), 826 (m), 737 (m), 668 (m), 590 (w), 538 (m), 476 (w), 407 (m) cm^{-1}.

7.4 Synthesis of Amidines

Para-substituted phenyl amidines were prepared according to literature methods.[2] Benzamidine was liberated from benzamidine hydrochloride hydrate by treatment with 1.0M sodium hydroxide and extraction into dichloromethane and was sublimed in vacuo prior to use.

7.4.1 Monoamidine

(1) ***p*-Bromobenzamidine**: Purification was reached by subliming at 90 °C, mp 176 – 178 °C. ^{1}H NMR (δ, $CDCl_3$) ppm: 5.13 (br, 3H, NH), 7.49 (d, 2H, 8.7Hz), 7.56 (d, 2H, 8.5Hz). ^{13}C NMR (δ, $CDCl_3$) ppm: 125.1 (s, C-Br), 128.0 (s, CH-phenyl), 132.2 (s, CH-phenyl), 135.7 (s, C-phenyl), 164.6 (s, amidine). IR

(2) ***p*-Cyanobenzamidine**: Subliming at 100 °C, mp 181 –183 °C. ^{1}H NMR (δ, DMSO-d_6) ppm: 6.6 (br, 3H, NH), 7.88 (d, 2H, 8.7Hz), 7.95 (d, 2H, 8.1Hz). ^{13}C NMR (δ, DMSO-d_6) ppm: 112.1 (s, C-phenyl), 118.4 (s, CN), 127.4 (s, CH-phenyl), 131.9 (s, CH-phenyl), 140.5 (s, C-phenyl), 160.9 (s, amidine). IR 3396 (s), 3333 (w), 3274 (w), 3054 (s, br), 2234 (s), 1668 (s), 1599 (s), 1554 (m), 1508 (m), 1452 (s), 1310 (w), 1289 (w), 1212 (m), 1180 (w), 1118 (w), 1099 (w), 1018 (w), 967 (w), 860 (s), 765 (w), 747 (w), 668 (w), 633 (w), 562 (m), 542 (m), 494 (w) cm^{-1}.

(3) **2,6-Diisopropylbenzamidine** (**Dipp**-amidine): Dipp-amidine was made by reacting Dipp-magnesium bromide with TMS–N=C=N–TMS to yield Mg adduct which was hydrolyzed by ethanolic HCl. Dipp-amidine was purified by subliming at 70 °C, mp 159 – 160 °C. ^{1}H NMR (δ, $CDCl_3$) ppm: 1.24 (d, 12H, 6.9Hz, CH_3), 3.14 (br, 3H, NH), 3.19 (m, 2H, CH), 7.18 (d, 2H, 8.4Hz, CH-phenyl), 7.33 (t, 1H, 7.7Hz, CH-phenyl). ^{13}C NMR (δ, $CDCl_3$) ppm: 25.0 (s, CH_3), 31.0 (s, CH), 123.4 (s, CH-phenyl), 129.3 (s, C-phenyl), 136.4 (s, C-phenyl), 145.3 (s, CH-phenyl), 166.5 (s, amidine). IR 3428 (s), 3323 (m), 3246 (w), 3050 (s, br), 2968 (s), 2869 (w), 2753 (w), 1653 (s), 1599 (s), 1588 (s), 1559 (w), 1506 (w), 1464 (s), 1419 (m), 1382 (m), 1362 (m), 1328 (m), 1306 (w), 1251 (m), 1187 (s), 1128 (m), 1084 (w), 1059 (m), 1038 (w), 936 (w), 834 (w), 813 (m), 738 (s), 725 (m), 668 (m), 586 (m), 572 (w), 532 (m), 474 (m) cm^{-1}.

7.4.2 Diamidines

(1) Benz-1,4-diamidine: A saturated solution of 1.27 g (5.40 mmol) benzene-1,4-di(amidine hydrochloride) in 30 ml hot distilled water was set in an ice bath, to which was immediately added 10ml 5M NaOH cooled solution with vigorous stirring for 3 minutes. The white precipitate was filtered and rinsed by cold water twice with 5 ml each. The resulting white powder was dried in air & by vacuo yielding 0.83 g (94%) benz-1,4-diamidine, mp = 240 – 243 °C. ^{1}H NMR (δ, DMSO-d_6) ppm: 6.37 (br, 6H, NH), 7.78 (s, 4H, phenyl). ^{13}C NMR (δ, DMSO-d_6) ppm: 126.0 (s, CH-phenyl), 137.3 (s, C-phenyl), 161.9 (s, C-amidine). IR 3366 (s), 3168 (s), 1660 (s), 1617 (s), 1559 (w), 1512 (w), 1457 (w), 1409 (s), 1387 (s), 1298 (m), 1160 (m), 1129 (m), 1015 (m), 865 (m), 802 (m), 734 (m), 628 (m), 527 (m), 483 (w), 418 (m) cm^{-1}.

(2) Benz-1,3-diamidine: A saturated solution of 2.55g (10.84 mmol) benzene-1,3-di(amidine hydrochloride) in 10 ml hot distilled water was set in an ice bath, to which was immediately added 10 ml of 10 M NaOH cooled solution. The mixture was stirred 2 minutes in ice bath before filtering off solvent and rinse with 5 ml cooled distilled water twice. The resulting white powder was dried in air and by vacuo yielding 1.78 g (99%) benzene-1,3-diamidine, mp = 152 – 154 °C. The product was purified by subliming at 130 °C. ^{1}H NMR (δ, DMSO-d_6) ppm: 6.37 (s, 6H, NH), 7.41 (t, 1H, 8Hz, phenyl), 7.80 (d, 2H, 8Hz, phenyl), 8.10 (s, 1H, phenyl). ^{13}C NMR (δ, DMSO-d_6) ppm: 124.5 (s, CH-phenyl), 127.6 (s, CH-phenyl), 127.7 (s, CH-phenyl), 136.2 (s, C-phenyl), 162.4 (amidine). IR 3387 (s), 3314 (s), 3280 (s), 3180 (s), 1684 (m), 1643 (s), 1617 (m), 1576

(s), 1600 (m), 1576 (s), 1464 (s), 1322 (w), 1222 (s), 1200 (w), 1174 (w), 1140 (m), 1091 (w), 873 (w), 852 (w), 816 (m), 750 (m), 710 (m), 642 (m) cm^{-1}.

7.5 Synthesis of Imidoylamidines

7.5.1 Mono-imidoylamidines

Trichloro(fluoro-)methyl imidoyl-substituted benzamidines were prepared according to literature methods[3] by reacting trichloromethyl acetonitrile or trifluoromethyl acetonitrile with amidines. The reaction took place under nitrogen. Liquid trichloromethyl acetonitrile was added dropwise to the solution of free amidine in dried acetonitrile at room temperature. The mixture was then allowed to heat up and reflux for 2-3 hours. Once cooled down, the solution was rotary evaporated to give a white or pale yellow powder of corresponding *N*-imidoylamidine.

A different approach was used in making the substituted trifluoromethyl imidoylamidines, because trifluoroacetonitrile is a gas at room temperature. This approach involved adding a quantified amount of the substituted aryl amidine and solvent to a heavy-wall Pyrex tube fitted with a rotaflow stopcock. The Pyrex tube was then attached to a vacuum line and the contents were freeze-thaw-degassed once. The aryl amidine and solvent were refrozen and the trifluoroacetonitrile was transferred into the vacuum line quantitatively in 1:1 stoichiometry. The trifluoroacetonitrile was then added into the vessel, which was warmed to room temperature, or slightly warmer, with stirring about 1 hour to ensure reaction completion. The solution was then transferred to a round bottom flask and rotary evaporated to dryness. In some cases oil remained, but these

would solidify if left in the refrigerator overnight. All the products can be purified by subliming at 90 – 110 °C.

Imidoylamidine hydrochloride salts were prepared by reacting the corresponding imidoylamidine in Et_2O with excess HCl gas at room temperature.

(1) **Trichloromethyl-*p*-methoxyphenyl-imidoylamidine (A1)**: 94% yield, mp 90 - 92 °C. The product can be purified by subliming at 90 °C. ^{1}H NMR (δ, $CDCl_3$) ppm: 3.86(s,CH_3), 6.51 (s, NH), 6.97 (d, 2H, 9.0Hz, phenyl), 7.94 (d, 2H, 9.0Hz, phenyl), 9.27 (s, NH), 10.73 (s, NH). IR 3389 (s), 3318 (m), 3170 (m), 1652 (m), 1646 (m), 1635 (w), 1616 (s), 1606 (s), 1570 (s), 1560 (w), 1539 (w), 1516 (w), 1506 (w), 1490 (m), 1465 (w), 1457 (w), 1449 (w), 1440 (w), 1422 (m), 1394 (m), 1328 (m), 1312 (m), 1254 (s), 1177 (m), 1162 (w), 1143 (m), 1116 (w), 1034 (w), 1024 (m), 943 (w), 848 (w), 835 (m), 822 (m), 805 (w), 786 (w), 764 (m), 668 (w), 652 (w), 634 (w), 599 (m), 562 (m), 523 (m), 501 (w), 484 (w), 458 (w), 419 (w) cm^{-1}.

(2) **Trichloromethyl-*p*-tolyl-imidoylamidine (A2)**: 99% yield, mp 62 - 64 °C.; ^{1}H NMR (δ, $CDCl_3$) ppm: 2.41 (s, CH_3), 6.59 (s, NH), 7.25 (d, 2H, 8.4Hz, phenyl), 7.84 (d, 2H, 8.4Hz, phenyl), 9.40 (s, NH), 10.69 (s, NH). IR 3442 (m), 3315 (m), 3127 (w), 3056 (w), 1628 (s), 1600 (s), 1584 (s), 1561 (s), 1506 (m), 1469 (vs), 1401 (w), 1327 (s), 1302 (w), 1180 (w), 1158 (s), 1126 (w), 1086 (m), 1025 (m), 1014 (s), 970 (w), 934 (w), 849 (s), 813 (s), 803 (m), 762 (s), 742 (m), 734 (m), 676 (w), 648 (m), 623 (m), 576 (m), 529 (m), 477 (w), 458 (w), 439 (m) cm^{-1}.

(3) **Trichloromethyl-phenyl-imidoylamidine (A3)**: 95% yield, mp. 68 – 70 °C. The product was purified by subliming at 60 °C ^{1}H NMR (δ, $CDCl_3$) ppm: 6.58 (s, NH), 7.45-7.48 (m, 3H, phenyl), 7.93-7.96 (m, 2H, phenyl), 9.42 (s, NH), 10.70 (s, NH). IR 3320

(s), 3284 (m), 3135 (w), 1629 (s), 1589 (m), 1574 (s), 1559 (w), 1539 (w), 1507 (s), 1482 (s), 1447 (s), 1327 (s), 1298 (w), 1180 (sh), 1161 (m), 1074 (w), 1038 (m), 1001 (w), 928 (w), 844 (m), 821 (s), 803 (w), 780 (m), 765 (w), 713 (s), 694 (s), 652 (m), 616 (w), 575 (s), 521 (w), 457 (w), 419 (w) cm^{-1}.

(4) **Trichloromethyl-*p*-chlorophenyl imidoylamidine (A4)**: 99% yield, mp 104 – 107 °C. ^1H NMR (δ, $CDCl_3$) ppm: 6.50 (s, NH), 7.42 (d, 2H, 8.9Hz, phenyl), 7.88 (d, 2H, 8.9Hz, phenyl), 9.43 (s, NH), 10.79 (s, NH). ^1H NMR (δ, DMSO-d_6) ppm: 7.61 (d, 2H, 8.6Hz, phenyl), 8.09 (d, 2H, 8.5Hz, phenyl), 9.39 (s, NH), 9.74 (s, NH), 10.56 (s, NH). IR 3442 (m), 3314 (s), 3122 (w), 3056 (w), 1628 (s), 1600 (s), 1584 (s), 1561 (s), 1506 (m), 1483 (sh), 1470 (s), 1401 (w), 1326 (s), 1301 (w), 1179 (w), 1158 (s), 1126 (w), 1085 (m), 1025 (m), 1014 (s), 970 (w), 934 (w), 849 (s), 813(s), 803 (m), 762 (s), 742 (s), 734 (m), 675 (w), 648 (m), 629 (m), 623 (m), 576 (m), 529 (m), 476 (w), 458 (w), 440 (w) cm^{-1}.

(5) **Trichloromethyl-*p*-bromophenyl-imidoylamidine (A5):** 96% yield, mp 98-99 °C. The product was purified by subliming at 90 °C. ^1H NMR (δ, $CDCl_3$) ppm: 6.5 (s, NH), 7.60 (d, 2H, 8.7Hz, phenyl), 7.83 (d, 2H, 8.7Hz, phenyl), 9.4 (s, NH), 10.7 (s, NH). ^{13}C NMR (δ, $CDCl_3$) ppm: 97.8 (s, CCl_3), 126.9 (s, C-Br, phenyl), 129.1 (s, CH, phenyl), 132.2 (s, CH, phenyl), 134.4 (s, C, phenyl), 163.7 (s, amidine), 168.1 (s, amidine). IR 3427 (m), 3312 (s), 3095 (w), 3040 (w), 1626 (s), 1603 (s),1583 (s), 1559 (s), 1501 (m), 1465 (vs), 1394 (w), 1323 (s), 1301 (w), 1180 (w), 1156 (s), 1127 (w), 1108 (sh), 1068 (m), 1024 (m), 1010 (m), 843 (s), 812 (s), 803 (m), 763 (s), 736 (m), 726 (s), 674 (w), 646 (m), 628 (w), 611 (m), 603 (m), 581 (m), 525 (m), 449 (m), 411 (m), 404 (w) cm^{-1}.

(6) **Trichloromethyl-*p*-trifluoromethylphenyl-imidoylamidine (A6)**: 94% yield, mp 91 – 92 °C. ^{1}H NMR (δ, $CDCl_3$) ppm: 6.59 (s, NH), 7.73 (d, 8.1Hz, phenyl), 8.06 (d, 8.1Hz, phenyl), 9.50 (s, NH), 10.83 (s, NH). IR 3469 (m), 3322 (m), 3101 (w), 1619 (s), 1587 (s), 1576 (m), 1521 (s), 1485 (s), 1411 (w), 1325 (s), 1312 (m), 1165 (s), 1154 (s), 1120 (s), 1067 (s), 1033 (m), 1016 (m), 932 (w), 859 (s), 833 (w), 814 (m), 799 (m), 760 (s), 748 (m), 709 (s), 679 (m), 647 (w), 601 (m), 589 (w), 510 (m), 493 (m), 458 (m), 420 (m), 406 (w) cm^{-1}.

(7) **Trichloromethyl-*p*-cyanophenyl-imidoylamidine (A7)**: 84% yield, mp 113 – 116 °C. ^{1}H NMR (δ, $CDCl_3$) ppm: 6.64 (br, NH), 7.78 (d, 2H, 8.7Hz, phenyl), 8.08 (d, 2H, 8.7Hz, phenyl), 9.55 (br, NH), 10.88 (br, NH). ^{13}C NMR (δ, $CDCl_3$) ppm: 97.5 (s, -CCl_3), 115.7 (s, C-phenyl), 118.2 (s, -CN), 128.2 (s, CH-phenyl), 132.8 (s, CH-phenyl), 139.6 (s, C-phenyl), 162.8 (s, -CN_2), 167.9 (s, -CN_2). IR 3378(s), 3293 (m), 3174 (w), 2232 (s), 1635 (s), 1586 (w), 1576 (w), 1560 (m), 1521 (s), 1506 (w), 1496 (s), 1457 (w), 1437 (w), 1405 (w), 1337 (s), 1197 (w), 1182 (w), 1168 (m), 1138 (w), 1113 (w), 1035 (w), 1018 (w), 931 (w), 853 (m), 844 (w), 817 (m), 804 (w), 767 (m), 698 (w), 677 (w), 668 (w), 646 (m), 615 (w), 560 (w), 548 (w), 514 (w), 487 (w), 443 (w), 420 (w) cm^{-1}.

(8) **Trichloromethyl-Dipp-imidoylamidine (A8)**: 78% yield, mp 140-141 °C. ^{1}H NMR (δ, $CDCl_3$) ppm: 1.26 (d, 12H, 6.8Hz, CH_3), 3.06 (m, 2H, CH), 6.14 (s, NH), 7.20 (d, 2H, 7.6Hz, phenyl), 7.35 (t, 1H, 7.7Hz, phenyl), 9.49 (s, NH), 10.7 (s, NH). ^{13}C NMR (δ, $CDCl_3$) ppm: 24.7 (d, 39.1Hz, CH_3), 31.0 (s, CH), 97.9 (s, CCl_3), 123.3 (s, CH, phenyl), 129.7 (s, C, phenyl), 135.4 (s, CH, phenyl), 145.8 (s, C, phenyl), 168.0 (s, amidine), 168.1 (s, amidine). IR 3400 (m), 3318 (m), 3065 (w), 2962 (s), 2927 (m), 2869 (m), 1591 (s), 1514 (s), 1467 (s), 1384 (m), 1363 (m), 1306 (s), 1252 (w), 1178 (w), 1146

(m), 1118 (w), 1058 (w), 1039 (w), 1024 (m), 930 (w), 839 (s), 824 (s), 806 (s), 757 (s), 734 (m), 696 (w), 655 (m), 576 (w), 555 (m), 470 (w), 455 (w) cm^{-1}.

(9) **Trifluoromethyl-*p*-methoxyphenyl-imidoylamidine (A9)**: 90% yield, mp 38 – 40 °C. ^1H NMR (δ, $CDCl_3$) ppm: 3.94 (s, CH_3), 6.64 (s, NH), 6.93 (d, 2H, 9.0Hz, phenyl), 7.87 (d, 2H, 9.0Hz, phenyl), 9.06 (s, NH), 10.98 (s, NH). IR 3385 (m), 3325 (m), 3174 (w), 2967 (w), 2941 (w), 2843 (m), 1600 (s), 1573 (s), 1483 (s), 1439 (m), 1424 (w), 1399 (w), 1310 (m), 1261 (s), 1234 (m), 1220 (m), 1175 (s), 1144 (s), 1113 (w), 1094 (w), 1030 (s), 998 (m), 848 (w), 837 (s), 816 (m), 786 (m), 759 (w), 745 (w), 729 (w), 708 (w), 690 (w), 668 (w), 643 (w), 613 (m), 588 (w), 567 (m), 514 (w), 480 (w), 434 (w) cm^{-1}.

(10) **Trifluoromethyl-*p*-tolyl-imidoylamidine (A10)**: 93% yield, mp 50 – 51 °C. ^1H NMR (δ, $CDCl_3$) ppm: 2.41 (s, CH_3), 6.69 (s, NH), 7.26 (d, 2H, 8.1Hz, phenyl), 7.81 (d, 2H, 8.1Hz, phenyl), 9.11 (s, NH), 11.04 (s, NH). IR 3455 (m), 3345 (m), 3330 (m), 3172 (w), 2922 (w), 1612 (s), 1571 (s), 1524 (s), 1485 (s), 1398 (w), 1231 (s), 1175 (s), 1154 (s), 1111 (m), 1018 (m), 997 (m), 954 (w), 867 (w), 853 (m), 842 (s), 831 (m), 820 (m), 781 (m), 754 (w), 734 (m), 687 (m), 672 (w), 588 (w), 544 (m), 512 (m), 466 (w), 443 (w) cm^{-1}.

(11) **Trifluoromethyl-phenyl-imidoylamidine (A11)**: 94% yield, mp 56 – 58 °C. ^1H NMR (δ, $CDCl_3$) ppm: 6.63 (s, NH), 7.39-7.60 (m, 3H, phenyl), 7.84-7.88 (m, 2H, phenyl), 9.19 (s, NH), 10.06 (s, NH). IR 3322 (s), 3299 (s), 3117 (m), 1636 (s), 1600 (s), 1578 (s), 1512 (s), 1473 (s), 1450 (s), 1419 (w), 1318 (w), 1300 (w), 1225 (s), 1191 (s), 1167 (s), 1141 (s), 1030 (m), 1009 (s), 1001 (s), 931 (m), 882 (m), 831 (m), 789 (m), 752 (w), 716 (s), 696 (s), 617 (w), 603 (m), 582 (m), 518 (w), 444 (w), 413 (w) cm^{-1}.

(12) **Trifluoromethyl imidoyl-*p*-chlorobenzamidine (A12)**: 81% yield, mp 46 – 48°C. ^{1}H NMR (δ, $CDCl_3$) ppm: 6.69 (s, NH), 7.42 (d, 2H, 8.8Hz, phenyl), 7.84 (d, 2H, 8.8Hz, phenyl), 9.11 (s, NH), 11.02 (s, NH). IR 3332 (s), 3257 (m), 3102 (m), 1644 (m), 1599 (s), 1572 (w), 1515 (s), 1476 (s), 1428 (w), 1395 (w), 1300 (w), 1228 (s), 1194 (w), 1179 (w), 1167 (s), 1146 (m), 1088 (m), 1017 (s), 950 (w), 882 (w), 857 (m), 836 (s), 794 (m), 732 (m), 674 (w), 646 (w), 625 (w), 592 (w), 519 (w), 486 (w), 458 (w), 428 (w) cm^{-1}.

(13) **Trifluoromethyl-*p*-bromophenyl-imidoylamidine (A13)**: 96% yield, mp 59 – 60 °C. ^{1}H NMR (δ, $CDCl_3$) ppm: 6.69 (s, NH), 7.61 (d, 2H, 8.5Hz, phenyl), 7.80 (d, 2H, 8.5Hz, phenyl), 9.20 (s, NH), 11.00 (s, NH). ^{13}C NMR ($CDCl_3$) ppm: 117.7 (q, 281 Hz, CF_3), 127.0 (s, C-Br, phenyl), 129.0 (s, CH, phenyl), 132.2 (s, CH, phenyl), 134.1 (s, C, phenyl), 163.3 (q, 33 Hz, triazine), 164.9 (s, triazine). IR 3317 (s), 3096 (w), 1624 (m), 1593 (s), 1565 (w), 1539 (w), 1506 (m), 1462 (s), 1426 (w), 1389 (m), 1302 (w), 1272 (w), 1231 (s), 1224 (s), 1196 (s), 1180 (m), 1161 (s), 1142 (s), 1107 (w), 1069 (m), 1012 (s), 955 (w), 878 (m), 840 (s), 791 (m), 736 (m), 724 (s), 682 (w), 657 (m), 627 (m), 590 (m), 518 (m), 450 (m), 400 (m) cm^{-1}.

(14) **Trifluoromethyl-*p*-trifluoromethylphenyl-imidoylamidine (A14)** 96%, mp 82 – 84 °C. ^{1}H NMR (δ, $CDCl_3$) ppm: 6.77 (s, NH), 7.73 (d, 8.1Hz, phenyl), 8.02 (d, 8.1Hz, phenyl), 9.29 (s, NH), 11.11 (s, NH). IR 3330 (m), 3244 (m), 3080 (w), 1653 (w), 1635 (w), 1606 (s), 1582 (w), 1558 (w), 1539 (w), 1526 (m), 1496 (m), 1457 (w), 1436 (w), 1419 (w), 1405 (m), 1325 (s), 1299 (w), 1229 (s), 1202 (s), 1152 (s), 1130 (s), 1111 (m), 1067 (s), 1019 (s), 962 (w), 886 (m), 852 (s), 830 (w), 760 (m), 713 (s), 691 (w), 668 (m), 630 (m), 602 (m), 519 (m), 472 (w), 458 (w), 419 (w), 409 (m) cm^{-1}.

(15) **Trifluoromethyl-*p*-cyanophenyl-imidoylamidine (A15)**: 88% yield, mp 155 - 159 °C, ^{1}H NMR (δ, $CDCl_3$) ppm: 6.81 (br, NH), 7.78 (d, 2H,8.8Hz, phenyl), 8.04 (d, 2H, 8.8Hz, phenyl), 9.32 (br, NH), 11.11 (br, NH). ^{1}H NMR (δ, DMSO-d_6) ppm: 8.01 (d, 2H, 8.5Hz, phenyl), 8.17 (d, 2H, 8.4Hz, phenyl), 9.68 (br, NH), 10.34 (br, NH), 10.89 (br, NH). ^{13}C NMR (δ, $CDCl_3$) ppm: 117.6 (s, C, phenyl), 117.8 (q, 280Hz, CF_3) 118.1 (s, CN), 130.1 (s, CH, phenyl), 132.7 (s, CH, phenyl), 139.0 (s, C, phenyl), 162.8 (q, 38Hz, triazine). IR 3397 (s), 3306 (s), 3159 (w, br), 2238 (s), 1638 (s), 1594 (m), 1566 (m), 1516 (s), 1490 (s), 1445 (w), 1424 (w), 1397 (w), 1293 (w), 1227 (s), 1188 (w), 1166 (S), 1139 (W), 1112 (W), 1095 (W), 1020 (M), 1003 (S), 858 (M), 846 (W), 837 (w), 811 (w), 792 (w), 748 (w), 724 (w), 707 (m), 671 (m), 594 (w), 550 (w), 521 (w), 437 (w), 403 (w) cm^{-1}.

(16) **Trifluoromethyl-Dipp-imidoylamidine (A16)**: 94% yield, mp 146 – 148 °C. The product was purified by subliming at 80 °C. ^{1}H NMR (δ, $CDCl_3$) ppm: 1.26 (d, 6.7Hz, CH_3), 2.98 (m, CH), 6.35 (s, NH), 7.19 (d, 2H, 7.3Hz phenyl), 7.35 (t, 1H, 7.7Hz, phenyl), 9.24 (s, NH), 11.00 (s, NH). IR 3323 (s), 3131 (m), 3059 (w), 2980 (m), 2964 (s), 2929 (m), 2872 (m), 1598 (vs), 1506 (vs), 1470 (s), 1460 (m), 1443 (m), 1420 (w), 1384 (m), 1362 (s), 1329 (w), 1301 (w), 1221 (vs), 1194 (vs), 1159 (vs), 1127 (s), 1107 (w), 1094 (w), 1057 (m), 1042 (m), 1004 (s), 965 (w), 958 (w), 940 (w), 877 (m), 849 (s), 820 (w), 804 (m), 795 (w), 757 (s), 731 (m), 696 (m), 662 (m), 590 (w), 573 (m), 557 (w), 519 (w), 467 (w), 440 (m) cm^{-1}.

7.5.2 Diimidoylamidines

(1) **1,3-Bis(trichloromethyl imidoylamidinyl)benzene (A17)**:

Trichloroacetonitrile (2.46g, 17.02 mmol) was added dropwise to the white suspension of benz-1,3-diamidine (1.38g, 8.51 mmol) in 60 ml dried acetonitrile at room temperature. The mixture was heated at reflux 20 hours till no solid remained, then cooled, pumped off solvent to leave a yellowish-white solid of **A17** after drying (3.02g, 79%), mp 60 – 62 °C;

^{1}H NMR (δ, $CDCl_3$) ppm: 6.66 (s, NH), 7.58 (t, 1H, 8Hz, phenyl), 8.09 (d, 2H, 8Hz, phenyl), 8.60 (s, 1H, phenyl), 9.47 (s, NH), 10.82 (s, NH). 1H NMR (δ, DMSO-d_6): 6.73 (t, 1H, 8Hz, phenyl), 7.29 (d, 2H, 8Hz, phenyl), 7.95 (s, 1H, phenyl), 8.61 (s, NH), 8.79 (s, NH), 9.63 (NH).

^{13}C (δ, CDCl3): 97.8 (s, -CCl_3), 126.9 (s, CH, phenyl), 129.4 (s, CH, phenyl), 130.6 (s, CH, phenyl), 136.2 (s, C, phenyl), 163.8 (s, amidine), 168.1 (s, amidine).

IR 3401 (m), 3306 (m), 2923 (w), 2852 (w), 1653 (w), 1629 (s), 1581 (s), 1559 (w), 1539 (w), 1503 (s), 1465 (m), 1419 (w), 1332 (m), 1279 (w), 1262 (m), 1152 (w), 1097 (w), 1037 (m), 810 (s), 751 (m), 682 (w), 668 (w), 646 (w), 564 (w) cm^{-1}.

(2) **1,3-Bis(trifluoromethyl imidoylamidinyl)benzene (A18)**: The reaction was performed in a 300x25 mm heavy-wall Pyrex tube fitted with a Rotaflow stopcock, containing a magnetic stirring bar. The reaction tube was evacuated to remove air, followed by charging 1.53 g (9.43 mmol) benz-1,3-diamidine and 20 ml acetonitrile. Trifluoroacetonitrile (1.79 g, 18.86 mmol) was metered on a vacuum line and added to the tube. This was weighed frozen under vacuum to ensure an accurate measurement of the gas. The mixture was allow to warm up to room temperature, and then heated to 60 °C with stirring for 30 hours to ensure completion of the reaction. After cooling down to

room temperature and standing for 1 hour, the white precipitate was filtered off. The filtrate was rotary evaporated to remove solvent and dried leaving an oily product, which stood in a freezer (–10 °C) overnight to solidify yielding 2.08g (63%) **A18**, mp 74 – 76 °C.

^{1}H NMR (δ, $CDCl_3$) ppm: 7.00 (br, NH), 7.50 (t, 1H, 8Hz, phenyl), 8.00 (d, 2H, 8Hz, phenyl), 8.32 (s, 1H, phenyl), 9.28 (br, NH), 11.04 (br, NH).

^{13}C NMR (δ, $CDCl_3$): 117.8 (q, 281 Hz, -CF_3), 126.1 (s, CH, phenyl), 129.6 (s, CH, phenyl), 130.8 (s, CH, phenyl), 135.9 (s, C, phenyl), 163.4 (q, 33 Hz, amidine), 165.0 (s, amidine).

IR 3487 (w), 3334 (s, br), 3130 (w, br), 1624 (s), 1506 (s), 1476 (w), 1379 (w), 1228 (s), 1192 (s), 1147 (s), 1015 (s), 937 (w), 895 (w), 866 (w), 846 (m), 816 (w), 788 (w), 731 (w), 707 (m) 668 (w), 650(w), 581 (m), 517 (w), 448 (w) cm^{-1}.

(3) **1,4-Bis(trifluoromethyl imidoylamidinyl)benzene (A19)**: Prepared by the same method as reported for 1,3-bis(trifluoromethyl imidoylamidinyl)benzene by using 1.23 g (7.60 mmol) benz-1,4-diamidine and 1.44g (15.15 mmol) trifluoroacetonitrile. The mixture was allowed to react 3 days at 60 °C. After cooling to room temperature, the white precipitate was filtered off. The filtrate was rotary evaporated to remove solvent and dried to leave 1.51 g (56%) pale yellow powder of **A19**, mp = 126 – 128 °C. ^{1}H NMR (δ, $CDCl_3$) ppm: 6.86 (s, 1H, NH), 8.00 (s, 4H), 9.26 (s, 1H, NH), 11.12 (s, 1H, NH). ^{13}C NMR (δ, $CDCl_3$) ppm: 117.7 (q, 281 Hz, CF_3), 130.8 (s, phenyl), 138.3 (s, phenyl), 163.3 (q, 33 Hz, amidine), 164.8 (s, amidine).

7.5.3 Imidoylamidine Hydrochloride

(1) **Trichloromethyl-*p*-tolyl-imidoylamidine hydrochloride** (**A2**.HCl): ^{1}H NMR (δ, DMSO-d_6) ppm: 2.41 (s, 3H, CH_3), 3.39 (s, 2H, NH_2^+), 7.43 (d, 2H, 7.6Hz, phenyl), 7.88 (d, 2H, 7.9Hz, phenyl), 9.06 (s, br, NH), 10.91 (s, br, NH). IR 3175 (s), 3115 (s), 3006 (s), 1686 (s), 1637 (w), 1610 (m), 1508 (w), 1437 (m), 1406 (m), 1338 (w), 1263 (w), 1190 (w), 1153 (w), 1118 (w), 1031 (w), 1019 (w), 934 (w), 829 (m), 796 (m), 745 (w), 727 (w), 677 (w), 644 (w), 626 (w), 553 (w), 530 (w), 460 (w) cm^{-1}. Raman: 3067 (w), 3040 (w), 2924 (w), 1686 (w), 1610 (s), 1523 (m), 1436 (m), 1380 (w), 1215 (w), 1192 (w), 1158 (m), 1122 (w), 1026 (w), 1016 (w), 854 (w), 825 (m), 808 (w), 728 (w), 680 (w), 634 (w), 555 (w), 526 (w), 467 (w), 432 (m), 392 (w), 341 (w), 288 (w), 201 (w), 133 (w), 96 (s), 85 (s) cm^{-1}.

(2) **Trichloromethyl-*p*-chlorophenyl-imidoylamidine hydrochloride** (**A4**·HCl): ^{1}H NMR (δ, DMSO-d_6) ppm: 3.42 (s, 2H, NH_2^+), 7.74 (d, 2H, 8.5Hz, phenyl), 7.98 (d, 2H, 8.7Hz, phenyl), 9.3 (s, br, NH), 11.0 (s, br, NH).

7.6 Synthesis of Selenium tetrachloride

A flask charged with element selenium powder (black) was emptied of air by vacuum and cooled down in ethanol/dry ice bath. Dry chlorine gas was filled in the flask through a rubber balloon to control the pressure. After the chlorine was liquefied (in ethanol/dry ice bath), the mixture was allowed to react 0.5 hour with stirring followed by warming up to release excess chlorine under N_2 flush. The resulting pale yellow powder of selenium tetrachloride was used *in situ* for further reaction.

7.7 Synthesis of the 1-chloro-1,2,4,6-selenatriazines

All the reactions were started by adding two reactants ($SeCl_4$ and imidoylamidine) cooled in an ice bath, then allowed to warm up to room temperature and heated at reflux. If a white precipitate came out after the mixture was cooled down, it meant reaction was not yet completed. Longer reaction time under reflux was required.

7.7.1 Imidoylamidine HCl reacting with $SeCl_4$ and Cl_2

The suspension of 0.82 g (3.74 mmol) $SeCl_4$ in 40 ml dried acetonitrile was purged with Cl_2, while **A2**·HCl salt (in solid state) was added to the suspension at room temperature. The mixture turned into a clear yellow solution immediately. After removing solvent, the light yellow oil product was treated with chloroform and resulted in lots of white precipitate, which was identified as starting material **A2**·HCl, mp = 211 – 215 °C. ^{1}H NMR (δ, DMSO-d_6) ppm: 2.42 (s, 3H, CH_3), 7.45 (d, 8.4Hz, phenyl), 7.86 (d, 8.4Hz, phenyl), 9.0 (s, NH), 10.9 (s, NH), 11.3 (s, NH). 13C NMR (δ, DMSO-d_6) ppm: 21.0 (s), 92.4 (s), 125.1 (s), 129.1 (s), 129.5 (s), 145.5 (s), 157.4 (s), 171.0 (s).

7.7.2 Imidoylamidine·HCl reacting with $SeCl_4$

To the suspension of 2.74 g (12.4 mmol) selenium tetrachloride in 150 ml dried acetonitrile was added solid **A2**·HCl salt (3.73g, 12.4 mmol) at room temerature. The suspension became a clear yellow solution immediately. The mixture was allowed to heat up to reflux for 5 hours, while a white precipitate came out. The mixture was filtered after cooling down to room temperature, giving a white precipitate which was identified as starting material **A2**·HCl, 1.07g (3.40mmol). ^{1}H NMR (δ, DMSO-d_6) ppm: 2.41 (s, 3H,

CH_3), 3.45 (s, br, NH_2^+), 7.45 (d, 2H, 8.1 Hz, phenyl), 7.84 (d, 2H, 8.2 Hz, phenyl), 9.1 (s, br,NH), 10.9 (s, br, NH). IR 3290 (m), 3111 (s, br), 2996 (s,br), 1684 (s), 1626 (m), 1609 (s), 1559 (w), 1540 (w), 1507 (w), 1437 (s), 1263 (w), 1188 (w), 1153 (w), 1031 (w), 934 (w), 853 (w), 827 (w), 794 (m), 749 (w), 726 (w), 683 (w), 644 (w), 590 (w), 551 (w), 535 (w), 457 (w) cm^{-1}. Raman 3070 (w), 2920 (w), 1611 (s), 1528 (m), 1441 (w), 1385 (w), 1379 (w), 1311 (w), 1213 9w), 1187 (w), 1160 (m), 1027 (w), 1019 (w), 852 (w), 827 (m), 812 (w), 798 (w), 726 (w), 683 (w), 644 (w), 632 (m), 554 (w), 536 (w), 457 (w), 431 (m), 410 (w), 385 (w), 336 (w), 293 (w), 281 (w), 238 (w), 205 (m), 151 (w), 116 (m) cm^{-1}. The filtrate, clear yellow solution, was pumped to remove solvent yielding yellow powder, which was sublimed at 100 °C to give 0.41 g (9%) yellow crystals of 1-chloro-selenatriazine **D2** (see section 7.7.4(2)).

6.7.3 Monitoring reaction of *N*-imidoylamidine with $SeCl_4$

(1) **Reaction of trichloromethyl-*p*-tolyl-imidoylamidine with $SeCl_4$:**

Imidoylamidine **A2** (3.56 g, 12.79 mmol) in 50 ml acetonitrile was added dropwise to the ice bath cooled selenium tetrachloride (2.82 g, 12.79 mmol) suspension in 50 ml acetonitrile. The suspension became clear green-yellow solution, a 20 ml aliquot of which was evaporated to remove solvent to get a yellow powder of complex **B2.** 1H NMR (δ, DMSO-d_6) ppm: 2.39 (s, 3H), 7.35 (d, 2H, 8.1 Hz), 8.20 (d, 2H, 7.9 Hz), 8.9 (s, NH), 9.2 (s, NH).

The remaining solution was warmed up to room temperature and produced white precipitate, part of which was filtered off and dried to identified as complex byproduct **A2**·HCl.

The remaining mixture was refluxed 2 hours till the white solid disappeared. 20 ml clear yellow solution was taken out of the mixture and placed in a freezer for crystallization. Filtering off solution left colorless crystals of 1-chloro-selenatriazine·HCl (**C2**) after drying, mp = 140 – 144 °C. ^{1}H NMR (δ, $CDCl_3$) ppm: 2.50 (s, 3H, CH_3), 7.42 (d, 8.1 Hz, phenyl), 7.79 (d, 8.1Hz, phenyl), 9.24 (s, NH). ^{77}Se NMR (δ, $CDCl_3$) 831.3 ppm, using SeO_2 in H_2O at 1302.6 ppm as external reference.

The remaining mixture was further refluxed 20 hours before cooling down to room temperature and was then placed in a freezer for crystallization. The yellow crystals were identified as 1-chloro-selenatriazine **D2**.

(2) **Reaction of trichloromethyl-*p*-chlorophenyl-imidoylamidine with $SeCl_4$:**

Imidoylamidine **A4** (3.83 g, 12.81 mmol) in 70 ml acetonitrile was added dropwise to the ice bath cooled selenium tetrachloride (2.83 g, 12.81 mmol) suspension in 40 ml acetonitrile. The suspension turned into clear yellow solution, then precipitated white solid. 40 ml of the mixture was taken out and filtered. The filtrate was pumped dry to get a yellow powder of complex **B4**. 1H NMR (δ, DMSO-d_6) ppm: 7.60 (d, 2H, 8.4 Hz), 8.26 (d, 2H, 8.4 Hz), 8.9 (s, NH), 9.3 (s, NH).

The white solid was dried and identified **A4**·HCl, mp = 204 – 207 °C. ^{1}H NMR (δ, DMSO-d_6) ppm: 7.75 (d, 8.6Hz, phenyl), 7.96 (d, 8.6Hz, phenyl), 9.2 (s, NH), 11.1 (s, NH), 11.4 (s, NH). ^{13}C NMR (δ, DMSO-d_6) ppm: 92.2 (s), 127.1 (s), 129.1 (s), 130.9 (s), 139.5 (s), 158.1 (s), 169.9 (s).

The remaining mixture was refluxed 3 days before cooled down to room temperature, with some white solid still present. After filtering, the filtrate was placed in

a freezer for crystallization. The yellow crystals were identified as final product 1-chloro-selenatriazine **D4**.

7.7.4 Synthesis of mono-1-chloro-1,2,4,6-selenatriazines

(1) **1-Chloro-3-trichloromethyl-5-*p*-methoxyphenyl-1,2,4,6-selenatriazine (D1)**: Imidoylamidine **A1** (2.94g,10.00 mmol) in 30 ml dried acetonitrile was added dropwise to the ice bath cooled suspension of selenium tetrachloride (2.21g, 10.00 mmol) in 30 ml acetonitrile. The suspension became a clear green-yellow solution. Warming the solution produced some white precipitate. The mixture was heated at reflux 18 hours to eliminate hydrogen chloride. The orange solution was cooled down to room temperature, a trace amount solid filtered off, and placed in a freezer for crystallization. It did not crystallize. The solution was pumped dry to leave 3.71 g of bright yellow powder, which was sublimed at 100 °C to give **D1** as bright yellow fine crystals 1.86 g (46%), mp 126 – 128 °C.

Mass spectrum (m/e) 405 ($C_{10}H_7N_3OCl_4Se^+$, 5.91%), 370 ($C_{10}H_7N_3OCl_3Se^+$, 40.77%), 133 (C8H7NO+, 100%), 94 (SeN^+, 25.0%).

^{1}H NMR (δ, ppm, $CDCl_3$): 3.91 (s, 3H, -CH_3), 7.01 (d, 2H, 9.2Hz, phenyl), 8.47 (d, 2H, 9.0Hz, phenyl).

^{13}C NMR (δ, ppm, $CDCl_3$): 55.8 (s, -CH_3), 97.0 (s, -CCl_3), 114.6 (s, CH-phenyl), 128.0 (s, C-phenyl), 132.4 (s, CH-phenyl), 165.3 (s, C-phenyl), 169.8 (s, -CN_2), 170.9 (s, -CN_2).

Raman 3084 (w), 3055 (w), 3007 (w), 2852 (w), 1605 (s), 1581 (w), 1511 (m), 1377 (w), 1342 (s), 1316 (w), 1301 (w), 1257 (m), 1227 (w), 1188 (w), 1174 (m), 1116 (w),

1007 (w), 979 (w), 900 (m), 850(w), 805 (w), 764 (w), 746 (w), 701 (w), 661 (w), 646 (w), 632 (w), 576 (w), 459 (w), 418 (w), 400 (w), 361 (w), 324 (w), 304 (s), 292 (s), 271 (s), 223 (w), 205 (m), 173 (w), 159 (w), 139 (w), 117 (w), 101 (s), 84 (s) cm^{-1}.

IR 3070 (br), 2997 (w), 2936 (w), 2847 (w), 1684 (w), 1653 (w), 1603 (s), 1579 (m), 1557 (w), 1540(w), 1490 (s), 1466 (w), 1424 (w), 1379 (s), 1335 (s), 1312 (w), 1260 (s), 1184 (w), 1166 (s), 1107 (w), 1029 (m), 975 (m), 899 (w), 846 (m), 804 (m), 766 (m), 747 (w), 715 (w), 701 (m), 659 9w), 577 (m), 515 (w), 414 (m) cm^{-1}.

(2) **1-Chloro-3-trichloromethyl-5-*p*-tolyl-1,2,4,6-selenatriazine (D2)**:

Imidoylamidine **A2** (2.99g,10.7 mmol) in 40 ml acetonitrile was added dropwise to the ice bath cooled selenium tetrachloride (2.36g, 10.7 mmol) suspension in 40 ml acetonitrile. The suspension became a clear green-yellow solution. When the solution was warmed to room temperature, lots of white precipitate came out. The mixture was heated at reflux for 24 hours to become a clear orange solution after all the hydrogen chloride was released. The solution was then allowed to cool down to room temperature and placed in the freezer overnight to crystallize. The crystals were filtered off, dried to yield bright yellow **D2** (3.48g, 83%), mp 136 – 138 °C. The product was sublimed at 100 °C to get thin parallelpiped dark yellow crystals for crystallographic analysis.

Mass spectrum (m/e) 389 ($C_{10}H_7N_3Cl_4Se^+$, 7.9%), 354 ($C_{10}H_7N_3Cl_3Se^+$, 73.1%), 319 ($C_{10}H_7N_3Cl_2Se^+$, 4.0%), 237 ($C_2N_2Cl_3Se^+$, 4.8%), 211 ($C_8H_7N_2Se^+$, 20.5%), 150 ($SeCl_2^+$, 9.5%), 117 ($C_8H_7N^+$, 100%), 94 (SeN^+, 86.0%).

^1H NMR (δ, $CDCl_3$) ppm: 2.47 (s, 3H, $-CH_3$), 7.33 (d, 2H, 7.9Hz, phenyl), 8.39 (d, 2H, 8.2Hz, phenyl).

^{13}C NMR (δ, $CDCl_3$) ppm: 22.1 (s, $-CH_3$), 96.9 (s, $-CCl_3$), 129.9 (s, CH, phenyl), 130.1 (s, CH, phenyl), 133.0 (s, C, phenyl), 145.8 (s, C, phenyl), 170.1 (s, triazine), 171.6 (s, triazine).

^{77}Se NMR (δ, $CDCl_3$) 1217.4 ppm, using SeO_2 in H_2O at 1302.6 ppm as external reference.

Raman 3066 (w), 2921 (w), 1608 (s), 1560 (w), 1509 (w), 1400 (w), 1379 (w), 1333 (w), 1303 (m), 1291 (m), 1213 (w), 1189 (w), 991 (w), 912 (w), 848 (w), 799 (w), 722 (w), 638 (w), 617 (w), 549 (w), 400 (m), 355 (w), 266 (s), 203 (w), 157 (w), 114 (w), 85 (m) cm^{-1}. 1H NMR (δ, CDCl3, ppm): 2.47 (s, 3H, CH_3), 7.32 – 7.35 (d, 2H, phenyl), 8.37 – 8.41 (d, 2H, phenyl). ^{13}C NMR (δ, $CDCl_3$, ppm): 22.1 (s, CH_3), 96.9 (s, CCl_3), 129.9 (s, CH, phenyl), 130.1 (s, CH, phenyl), 133.0 (s, C, phenyl), 145.8 (s, C, phenyl), 170.1 (s, CN_2), 171.6 (s, CN_2).

IR 3113 (s), 1684 (s), 1631 (s), 1608 (s), 1582 (m), 1560 (m), 1506 (w), 1433 (s), 1296 (w), 1207 (w), 1189 (m), 1154 (w), 1098 (w), 1017 (w), 990 (w), 973 (w), 931 (w), 912 (w), 848 (s), 826 (s), 803 (s), 728 (m), 696 (m), 673 (s), 626 (w), 551 (w), 522 (w), 502 (w), 466 (w), 437 (w), 413 (w) cm^{-1}.

(3) **1-Chloro-3-trichloromethyl-5-phenyl-1,2,4,6-selenatriazine (D3)**:

Imidoylamidine **A3** (2.95g,11.14 mmol) in 20 ml acetonitrile was added dropwise to the ice bath cooled selenium tetrachloride (2.46g, 11.14 mmol) suspension in 30 ml acetonitrile. The suspension became a clear green-yellow solution. When warmed up to room temperature, a white precipitate came out of solution. The mixture was heated at reflux for 52 hours to become a clear orange solution after all the hydrogen chloride was

released. The solution was then allowed to cool down to room temperature. It started to crystallize. After 2 hours the mixture was placed in the freezer overnight to further crystallize. The crystals were filtered off and dried to yield orange yellow **D3** (3.87g, 92%), mp 150 – 154 °C, The product can be purified by subliming at 100 °C.

Mass spectrum (m/e) 375 ($C_9H_5N_3Cl_4Se^+$, 15.1%), 340 ($C_9H_5N_3Cl_3Se^+$, 100%), 305 ($C_9H_5N_3Cl_2Se^+$, 5.0%), 237 ($C_2N_2Cl_3Se^+$, 13.3%), 195 ($C_7H_5N_2Se^+$, 11.0%), 150 ($SeCl_2^+$, 7.61%), 129 ($C_8H_5N_2^+$, 20.3%), 117 ($C_7H_5N_2^+$, 5.08%), 103 ($C_7H_5N^+$, 69.2%), 94 (SeN^+, 75.4%), 76 ($C_6H_4^+$, 29.93%).

^{1}H NMR (δ, $CDCl_3$) ppm: 7.53 (t, 2H, 7.8Hz, phenyl), 7.65 (t, 1H, 7.3Hz, phenyl), 8.50 (d, 2H, 7.2Hz, phenyl).

^{13}C NMR (δ, ppm, $CDCl_3$): 96.8 (s, -CCl_3), 129.1 (s, CH-phenyl), 130.0 (s, CH-phenyl), 134.5 (s, CH-phenyl), 135.6 (s, C-phenyl), 170.2 (s, -CN_2), 171.6 (s, -CN_2).

Raman 3070 (w), 3063 (w), 1608 (w), 1595 (s), 1582 (w), 1501 (w), 1488 (m), 1446 (w), 1388 (w), 1325 (m), 1309 (m), 1235 (w), 1174 (w), 1159 (w), 1112 (w), 1025 (w), 1002 (m), 976 (w), 900 (w), 840 (w), 810 (w), 798 (w), 764 (w), 702 (w), 655 (w), 645 (w), 616 (w), 606 (w), 458 (w), 422 (w), 398 (w), 334 (m), 315 (w), 290 (s), 259 (s), 221 (w), 208 9w), 205 (w), 166 (w), 152 (w), 108 (s), 98 (s), 85 (m), 77 (m) cm^{-1}.

IR 3069 (w), 1675 (w), 1594 (w), 1580 (m), 1499 (s), 1444 (s), 1388 (s), 1327 (m), 1309 (w), 1232 (w), 1174 (m), 1159 (w), 1111 (w), 1075 (w), 1026 (w), 1001 (w), 975 (m), 901 (w), 836 (s), 809 (m), 764 (w), 727 (s), 701 (m), 668 (w), 657 (w), 647 (w), 606 (w), 581 (w), 461 (w), 418 (m) cm^{-1}

(4) **1-Chloro-3-trichloromethyl-5-*p*-chlorophenyl-1,2,4,6-selenatriazine (D4)**:

Imidoylamidine **A4** (3.90g,13.04 mmol) in 35 ml dried acetonitrile was added dropwise to the ice bath cooled selenium tetrachloride (2.88g, 13.04 mmol) suspension in 35 ml acetonitrile. The suspension became a clear yellow solution, then turned to cloudy with lots of white precipitate before the **A4** was all added. The mixture was warmed to room temperature and heated at reflux for 66 hours with grey precipitate still present. After filtering off the precipitate, the filtrate was chilled in a freezer (-40°C) for crystallization. The resulting yellow crystals were filtered off, dried under vacuum to leave pure **D4**. Grey solid was sublimed at 110 °C to give brown crystals of **D4**. Total yield of pure product is 3.28 g (61%), mp 148 – 150 °C.

Mass spectrum (m/e) $C_9H_4N_3Cl_5Se^+$ (411, 6.14%), $C_9H_4N_3Cl_4Se^+$ (376, 70.46%), $C_9H_4N_3Cl_3Se^+$ (339, 6.20%), $C_2N_2Cl_3Se^+$ (237, 7.40%), $C_6H_4N_2ClSe^+$ (231, 14.20%), $C_7H_4NCl^+$ (137, 87.10%), $C_7H_4N^+$ (102, 43.50%), SeN^+ (94, 100%), $C_6H_3^+$ (75, 23.40%).

^{1}H NMR (δ, $CDCl_3$) ppm: 7.51 (d, 2H, 8.8Hz, phenyl), 8.44 (d, 2H, 8.8Hz, phenyl).

^{13}C NMR (δ, $CDCl_3$) ppm: 96.6 (s, CCl_3), 129.5 (s, CH-phenyl), 131.2 (s, CH-phenyl), 134.0 (s, C-phenyl), 141.2 (s, C-phenyl), 170.3 (s, triazine), 170.9 (s, triazine).

Raman 3078 (w), 3059 (w), 1609 (w), 1590 (s), 1574 (w), 1500 (w), 1486 (w), 1404 (w), 1377 (w), 1334 (s), 1285 (w), 1229 (w), 1172 (w), 1115 (w), 1085 (m), 1015 (w), 980 (w), 900 (m), 851 (w), 846 (w), 807 (w), 774 (w), 756 (w), 711 (w), 696 (w), 654 (w), 641 (w), 628 (w), 456 (w), 414 (w), 399 (w), 352 (w), 334 (w), 290 (s), 266 (m), 238 (w), 220 (w), 201 (w), 168 (w), 157 (w), 124 (w), 96 (s), 70 (w) cm^{-1},

IR 3121 (br), 3031 (s), 1675 (s), 1617 (m), 1592 (s), 1557 (w), 1539 (w), 1521 (w), 1506 (w), 1490 (w), 1472 (w), 1457 (w), 1436 (s), 1387 (w), 1182 (w), 1150 (w), 1088

(s), 1024 (w), 1013 (m), 933 (w), 850 (s), 798 (s), 736 (w), 678 (m), 627 (w), 615 (m), 531 (w),494 (w), 463 (w), 418 (w) cm^{-1}.

(5) **1-Chloro-3-trichloromethyl-5-*p*-bromophenyl-1,2,4,6-selenatriazine (D5)**: Imidoylamidine **A5** (2.18g, 6.35 mmol) in 30 ml dried acetonitrile was added dropwise to the ice bath cooled selenium tetrachloride (1.40g, 6.35 mmol) suspension in 50 ml acetonitrile. The suspension became a clear yellow solution in the ice bath, then turned into cloudy with lots of white precipitate when warmed up to room temperature. With heating at reflux for 3 hours, the precipitate disappeared. The solution was then allowed to slowly cool down to room temperature. It started to crystallize. After chilling the mixture to –10 °C overnight for further crystallization, the resulting yellow crystals were filtered off and dried under vacuum to give 1.90 g (66%) **D5**, mp 163 – 165 °C.

Mass spectrum (m/e) $C_9H_4N_3BrCl_4Se^+$ (455, 14.87%), $C_9H_4N_3BrCl_3Se^+$ (420, 100.00%), $C_9H_4N_3BrCl_2Se^+$ (385, 3.60%), $C_9H_4N_3BrCl_3^+$ (342, 20.66%), $C_7H_4N_2BrSe^+$ (275, 9.17%), $C_2N_2Cl_3Se^+$ (237, 5.01%), $SeCl_2^+$ (150, 8.59%), $SeCl^+$ (115, 14.65%), $C_7H_4N^+$ (102, 83.23%), $C_6H_3^+$ (75, 36.47%).

^1H NMR (δ, $CDCl_3$) ppm: 7.68 (d, 2H, 8.7Hz, phenyl), 8.36 (d, 2H, 8.8Hz, phenyl).

^{13}C NMR (δ, $CDCl_3$) ppm: 96.7 (s, CCl_3), 130.0 (s, C-phenyl), 131.3 (s, CH-phenyl), 132.5 (s, CH-phenyl), 134.5 (s, C-phenyl), 170.4 (s, triazine), 170.9 (s, triazine).

Raman 3074 (w), 3056 (w), 1584 (s), 1501 (w), 1493 (w), 1376 (w), 1335 (s), 1229 (w), 1174 (w), 1113 (w), 1069 (m), 899 (m), 850 (w), 806 (w), 754 (w), 684 9w), 626 (w), 406 (w), 348 (w), 324 (w), 289 (s), 262 (m), 228 (w), 208 (w), 186 (w), 159 (w), 120 (w), 95 (s) cm^{-1}.

IR 3091 (br), 1684 (m), 1585 (s), 1570 (w), 1537 (w), 1490 (s), 1432 (w), 1401 (s), 1377 (s), 1329 (s), 1282 (w), 1224 (w), 1173 (m), 1110 (w), 1071 (m), 1010 (s), 976 (m), 898 (w), 845 (s), 806 (m), 768 (w), 754 (s), 705 (m), 650 (w), 602 (w), 530 (w), 482 (w), 467 (w), 430 (m), 405 (w) cm^{-1}.

(6) **1-Chloro-3-trichloromethyl-5-*p*-trifluoromethylphenyl-1,2,4,6-selenatriazine (D6)**: Imidoylamidine **A6** (2.99g, 9.00 mmol) in 40 ml dried acetonitrile was added dropwise to the ice bath cooled selenium tetrachloride (1.99 g, 9.00 mmol) suspension in 40 ml dried acetonitrile. The suspension became a clear yellow solution. When the solution was warmed up to room temperature, no precipitate came out. The mixture was heated at reflux 22 hours before pumping off solvent and drying to yield a brown powder of **D6** 3.76 g (8.46 mmol, 94%), which was sublimed at 100 °C to give dark yellow crystals, mp 123–125 °C.

Mass spectrum (m/e) 443 ($C_{10}H_4N_3Cl_4F_3Se^+$, 7.85%), 426 ($C_{10}H_4N_3Cl_4F_2Se^+$, 3.90%), 408 ($C_{10}H_4N_3Cl_3F_3Se^+$, 100%), 373 ($C_{10}H_4N_3Cl_2F_3Se^+$, 5.28%), 258 ($C_{10}H_4N_3ClF_3^+$, 3.53 %), 237($C_2N_2Cl_3Se^+$, 5.41%), 214 ($C_3N_2Cl_2Se^+$, 18.19%), 197 ($C_9H_4N_2F_3^+$, 23.36%), 171 ($C_8H_4F_3N^+$, 21.11%), 152 ($C_8H_4F_2N^+$, 45.30%), 145 ($C_7H_4F_3^+$, 37.58%), 115 ($SeCl^+$, 23.51%), 102 ($C_7H_4N^+$, 15.84%), 75 ($C_6H_3^+$, 15.70%).

^1H NMR (δ, $CDCl_3$) ppm: 7.80 (d, 2H, 8.2Hz, phenyl), 8.61 (d, 2H, 8.1Hz, phenyl).

^{13}C NMR (δ, $CDCl_3$) ppm: 96.5 (s, $-CCl_3$), 123.9 (q, 273 Hz, $-CF_3$), 126.1 (q, 3.9 Hz, CH-phenyl), 130.2 (s, CH-phenyl), 135.2 (q, 33 Hz, C-phenyl), 138.8 (s, C-phenyl), 170.5 (s, $-CN_2$).

Raman 3084 (w), 1618 (s), 1514 (w), 1506 (w), 1414 (w), 1390 (w), 1333 (m), 1232 (w), 1186 (w), 1113 (w), 1068 (w), 1017 (w), 979 (w), 902 (m), 884 (w), 850 (w), 810 (w), 788 (w), 770 (w), 749 (m), 675 (w), 654 (w), 633 (w), 594 (w), 472 (w), 439 (w), 408 (w), 378 (w), 328 (m), 314 (w), 297 (s), 272 (s), 209 (w), 190 (w), 159 (w), 113 (m), 84 (s) cm^{-1}.

IR 3122 (br), 1695 (s), 1627 (w), 1500 (w), 1437 (m), 1387 (w), 1324 (s), 1260 (w), 1183 (s), 1124 (s), 1161 (w), 1068 (s), 1017 (s), 930 (w), 857 (s), 802 (m), 758 (w), 739 (w), 667 (s), 603 (m), 589 (w), 522 (w), 461 (w), 414 (w) cm^{-1}.

(7) **1-Chloro-3-trichloromethyl-5-*p*-cyanophenyl-1,2,4,6-selenatriazine (D7)**: Imidoylamidine **A7** (1.35g, 5.16 mmol) in 40 ml acetonitrile was added dropwise to the ice bath cooled suspension of selenium tetrachloride (1.14g, 5.16 mmol) in 40 ml acetonitrile. The suspension turned into a clear yellow solution without precipitate even when warmed to room temperature, and heated reflux for 21 hours. The yellow solution was cooled down to room temperature and placed in a freezer overnight. It did not crystallize. Evaporation of solvent left 1.46 g yellow powder, which was sublimed at 110 °C to give 1.20 g (58%) yellow block crystals **D7** suitable for crystallography analysis, mp 135 – 138 °C.

Mass spectrum (m/e) 400 ($C_{10}H_4N_4Cl_4Se^+$, 2.21%), 365 ($C_{10}H_4N_4Cl_3Se^+$, 90.81%), 330 ($C_{10}H_4N_4Cl_2Se^+$, 8.82%), 237 ($C_2N_2Cl_3Se^+$, 8.20%), 128 ($C_8H_4N_2^+$, 49.4%), 94 (SeN^+, 100%), 76 ($C_6H_4^+$, 14.8%).

^1H NMR (δ, $CDCl_3$) ppm: 7.83 (d, 2H, 8.8Hz, phenyl), 8.60 (d, 2H, 8.7Hz, phenyl).

^{13}C NMR (δ, $CDCl_3$) ppm: 96.4 (s, CCl_3), 117.5 (s, C-phenyl), 118.2 (s, CN), 130.2 (s, CH-phenyl), 132.8 (s, CH-phenyl), 139.4 (s, C-phenyl), 170.1 (s, triazine), 170.6 (s, triazine).

IR 3095 (s), 2231 (m), 1684 (s), 1620 (w), 1576 (w), 1500 (m), 1436 (m), 1408 (w), 1382 (s), 1303 (w), 1291 (w), 1197 (w), 1174 (w), 1147 (w), 1106 (w), 1017 (m), 980 (w), 975 (w), 928 (w), 910 (w), 854 (s), 841 (w), 803 (s), 764 (m), 722 (w), 714 (w), 668 (m), 653 (w), 641 (w), 626 (w), 558 (w), 544 (m), 525 (w), 517 (w), 504 (w), 457 (w), 414 (s) cm^{-1}.

(8) **1-Chloro-3-trichloromethyl-5-(2,6-diisopropyl)phenyl-1,2,4,6-selenatriazine (D8):** Imidoylamidine **A8** (2.80g, 8.03 mmol) in 30 ml acetonitrile was added dropwise to the ice bath cooled selenium tetrachloride (1.77g, 8.03 mmol) suspension in 30 ml acetonitrile. The suspension turned into a clear yellow solution and did not precipitate after warming to room temperature, then refluxed for 24 hours. The solution was evaporated to remove solvent and dried yielding 3.66 g grey powder, which was purified by subliming at 90 °C to give 1.55 g (41%) yellow needles of **D8** suitable for crystallographic analysis, mp 131 – 135 °C,

Mass spectrum (m/e) 424 ($C_{15}H_{17}N_3Cl_3Se^+$, 48.57%), 388 ($C_{15}H_{16}N_3Cl_2Se^+$, 9.84%), 344 ($C_{15}H_{17}N_3Cl_3^+$, 6.08%), 308 ($C_{15}H_{17}N_3Cl_2^+$, 8.14%), 281 ($C_{13}H_{17}N_2Se^+$, 32.06%), 274 ($C_{15}H_{17}N_3Cl^+$, 23.53%), 265 ($C_{15}H_6N_3Cl^+$, 8.55%), $C_{13}H_{17}N_2^+$ (201, 100%), (186, 63.04%), $C_{12}H_{14}N^+$ (172, 44.05%), $C_{11}H_{11}N^+$ (157, 28.79%), $C_{11}H_{10}N^+$ (156, 26.71%), $C_{10}H_{10}N^+$ (144, 17.00%), $C_{10}H_7^+$ (127, 10.22%), $C_9H_7^+$ (115, 24.15%), SeN^+ (94, 11.41%), $C_6H_5^+$ (77, 11.43%).

^{1}H NMR (δ, $CDCl_3$) ppm: 1.21 (d, 12H, 6.7Hz, CH_3), 2.68 (m, CH), 7.24 (d, 2H, 7.9Hz, phenyl), 7.42 (t, 1H, 7.6Hz, phenyl).

^{13}C NMR (δ, $CDCl_3$) ppm: 19.6 (s, CH_3), 26.5 (s, CH), 91.7 (s, CCl_3), 118.7 (s, CH-phenyl), 125.8 (s, C-phenyl), 131.3 (s, CH-phenyl), 141.3 (s, C-phenyl), 164.9 (s, triazine), 173.3 (s, triazine).

Raman: 3068 (w), 3030 (w), 2970 (m), 2932 (m), 2904 (m), 2965 (m), 1591 (m), 1460 (w), 1443 (w), 1301 (w), 1287 (w), 1235 (w), 1106 (w), 1040 (w), 908 (w), 884 (w), 841 (w), 818 (w), 776 (w), 766 (m), 679 (m), 668 (w), 638 (w), 586 (w), 411 (m), 404 (w), 360 (m), 335 (m), 303 (s), 280 (m), 199 (w), 158 (w), 142 (w), 127 (s), 98 (s) cm^{-1}.

IR 1963 (s), 2926 (w), 2867 (w), 1645 (w), 1590 (w), 1559 (w), 1496 (s), 1458 (m), 1386 (m), 1375 (s), 1329 (m), 1286 (m), 1237 (w), 1182 (w), 1125 (w), 1104 (w), 1083 (m), 1056 (w), 1039 (w), 974 (m), 907 (w), 840 (s), 809 (s), 745 (w), 766 (w), 752 (s), 694 (w), 680 (w), 666 (s), 586 (m), 456 (w), 404 (m) cm^{-1}.

(9) **1-Chloro-3-trifluoromethyl-5-*p*-methoxyphenyl-1,2,4,6-selenatriazine (D9)**: Imidoylamidine **A9** (4.59g, 18.70 mmol) in 40 ml dried acetonitrile was added dropwise to the ice bath cooled suspension of selenium tetrachloride (4.13g, 18.70 mmol) in 20 ml acetonitrile. The suspension turned into a clear yellow solution in the ice bath, then precipitated white solid after warming up to room temperature. The mixture was heated to reflux for 48 hours with a small amount of precipitate still present. The solution was cooled down to room temperature, filtered to remove precipitate, put in freezer (-40°C) for crystallization. The resulting green-yellow needles were filtered off, dried under vacuum to give 3.20 g (48%) **D9**, mp 100 – 103 °C,

Mass spectrum (m/e) 357 ($C_{10}H_7N_3OF_3ClSe^+$, 20.95%), 322 ($C_{10}H_7N_3OF_3Se^+$, 84.82%), 227 ($C_8H_7N_2OSe^+$, 12.10%), 147 ($C_8H_7N_2O^+$, 35.63%), 133 ($C_8H_7NO^+$, 100%), 118 ($C_7H_4NO^+$, 6.16%), 103 ($C_7H_5N^+$, 17.18%), 94 (SeN^+, 38.67%), 76 ($C_6H_4^+$, 5.39%).

^{1}H NMR (δ, $CDCl_3$) ppm: 3.91 (s, 3H, $-CH_3$), 7.00 (d, 2H, 9.2Hz, phenyl), 8.42 (d, 2H, 9.2Hz, phenyl).

^{13}C NMR (δ, $CDCl_3$) ppm: 55.9 (s, $-CH_3$), 114.6 (s, CH-phenyl), 118.0 (q, 281Hz, CF_3), 127.7 (s, C-phenyl), 132.4 (s, CH-phenyl), 162.2 (q, 37Hz, triazine), 165.5 (s, C-phenyl), 169.9 (s, triazine).

Raman 3079 (w), 3066 (w), 2936 (w), 2844 (w), 1599 (s), 1514 (m), 1427 (w), 1421 (w), 1352 (s), 1316 (w), 1304 (w), 1260 (s), 1183 (w), 1170 (s), 1144 (w), 1082 (w), 1007 (w), 943 (m), 842 (w), 785 (w), 746 (w), 715 (w), 673 (w), 633 (w), 580 (w), 336 (w), 306 (s), 285 (w), 264 (w), 236 (w), 219 (w), 187 (w), 150 (w), 94 (s), 84 (s) cm^{-1}.

IR 3081 (br), 1700 (s), 1603 (s), 1506 (m), 1457 (w), 1430 (s), 1407 (s), 1351 (w), 1317 (m), 1266 (s), 1210 (s), 1186 (w), 1157 (s), 1028 (m), 850 (m), 785 (w), 757 (w), 687 (m), 655 (m), 631 (w), 573 (m), 515 (w), 503 (w), 415 (w) cm^{-1}.

(10) **1-Chloro-3-trifluoromethyl-5-*p*-tolyl-1,2,4,6-selenatriazine (D10)**:

Imidoylamidine **A10** (2.20g, 9.60 mmol) in 35 ml acetonitrile was added dropwise to the ice bath cooled selenium tetrachloride (2.12g, 9.60 mmol) suspension in 25 ml acetonitrile. The suspension became a clear green-yellow solution. When the solution was warmed to room temperature, white precipitate came out. After heating at reflux for one hour, the white precipitate disappeared. The mixture was refluxed a total of 20 hours to make sure all the hydrogen chloride was released. The solution was concentrated to

about 20 ml and placed in the freezer at -10 °C for 4 hours then to –40 °C overnight to crystallize. The crystals were filtered and dried to yield bright green-yellow coarse needles of **D10** (2.38g, 73%), mp 105 – 107 °C.

Mass spectrum (m/e) 341 ($C_{10}H_7N_3ClF_3Se^+$, 31.03%), 306 ($C_{10}H_7N_3F_3Se^+$, 117.35%), 211 ($C_8H_7N_2Se^+$, 15.99%), 131 ($C_8H_7N_2^+$, 27.0%), 117 ($C_8H_7N^+$, 62.9%), 94 (SeN^+, 100%), 77 ($C_6H_5^+$, 12.0%), 69 (CF_3^+, 146.2%).

^{1}H NMR (δ, $CDCl_3$, ppm): 2.39 (s, 3H, CH_3), 7.24 – 7.28 (d, 2H, phenyl), 8.26 – 8.29 (d, 2H, phenyl).

^{13}C NMR (δ, $CDCl_3$, ppm): 22.1 (s, CH_3), 118 (q, 281 Hz, CF_3), 129.9 (s, CH, phenyl), 130.1 (s, CH, phenyl), 132.6 (s, C, phenyl), 146.0 (s, C, phenyl), 162.4 (q, 37 Hz, triazine), 170.6 (s, triazine).

Raman 3078 (w), 3037 (w), 2923 (w), 1606 (s), 1506 (m), 1385 (w), 1346 (s), 1297 (s), 1281 (w), 1211 (w), 1187 (w), 1177 (m), 1148 (w), 1082 (w), 942 (m), 840 (w), 788 (w), 777 (w), 750 (m), 731 (w), 710 (w), 679 (w), 638 (w), 356 (w), 295 (s), 268 (w), 237 (m), 183 (w), 145 (w), 98 (m), 72 (w) cm^{-1}.

IR 3064 (s), 1696 (s), 1652 (w), 1635 (w), 1606 (s), 1576 (w), 1558 (w), 1517 (w), 1503 (s), 1465 (w), 1430 (s), 1399 (w), 1350 (s), 1310 (w), 1299 (w), 1282 (s), 1207 (s), 1185 (w), 1150 (s), 1081 (w), 1019 (m), 942 (m), 849 (w), 839 (m), 778 (s), 753 (w), 733 (m), 708 (m), 685 (w), 668 (w), 656 (w), 567 (w), 483 (w), 464 (w), 422 (s) cm^{-1}

(11) **1-Chloro-3-trifluoromethyl-5-phenyl-1,2,4,6-selenatriazine (D11)**: Imidoylamidine **A11** (3.52g,16.36 mmol) in 20 ml acetonitrile was added dropwise to the ice bath cooled selenium tetrachloride (3.61g, 16.36 mmol) suspension in 20 ml

acetonitrile. The suspension became a clear green-yellow solution. When the solution was warmed to room temperature, white precipitate came out. The mixture was heated at reflux for 24 hours to become a clear yellow solution after all the hydrogen chloride was released. The solution was pumped to concentrate to 15 ml, placed in the freezer at –10 °C for four hours then overnight at –40 °C to crystallize. The crystals were filtered off and dried. The filtrate was pumped to remove solvent then crystallized in 10 ml CH_2Cl_2. Total yield of **D11** is 3.38g (63%), mp 113 – 117 °C. Further purification can be achieved by subliming at 80 °C.

Mass spectrum (m/e) 327 ($C_9H_5N_3F_3ClSe^+$, 10.6%), 292 ($C_9H_5N_3F_3Se^+$, 100%), 214 ($C_9H_7N_3F_3^+$, 20.6%), 103 ($C_7H_5N^+$, 32.5%), 94 (SeN^+, 74.2%), 77 ($C_6H_5^+$, 19.4%).

^{1}H NMR (δ, $CDCl_3$) ppm: 7.53 (t, 2H, 7.5Hz), 7.66 (t, 1H, 7.3Hz), 8.46 (d, 2H, 7.2Hz).

^{13}C NMR (δ, $CDCl_3$) ppm: 118.0 (q, 280Hz, CF_3), 129.1 (s, 2CH, phenyl), 130.0 (s, 2CH, phenyl), 134.7 (s, CH, phenyl), 135.3 (s, C, phenyl), 162.6 (q, 38Hz, triazine), 170.7 (s, triazine).

IR 3196 (s), 3087 (s), 1665 (s), 1635 (w), 1601 (w), 1576 (w), 1558 (w), 1539 (w), 1521 (w), 1499 (w), 1450 (m), 1415 (s), 1305 (w), 1210 (s), 1155 (s), 1091 (w), 1028 (w), 1002 (w), 844 (s), 784 (w), 694 (s), 667 (s), 604 (w), 591 (m), 516 (w), 415 (m) cm^{-1}

(12) **1-Chloro-3-trifluoromethyl-5-*p*-chlorophenyl-1,2,4,6-selenatriazine (D12)**: Imidoylamidine **A12** (4.12g,16.50 mmol) in 50 ml dried acetonitrile was added dropwise to the ice bath cooled selenium tetrachloride (3.64g, 16.50 mmol) suspension in 50 ml acetonitrile. The suspension turned into a clear yellow solution, then cloudy with lots of

white precipitate before **A12** was all added. The mixture was warmed to room temperature and heated at reflux for 3 hours until precipitate disappeared. The solution was cooled down to room temperature then to -40°C for crystallization, but resulted in white crystals. The mixture was further refluxed overnight with total refluxing time of 29 hours before being chilled in the freezer again for crystallization. The resulting yellow crystals were filtered off, dried under vacuum to give 4.51 g (76%) **D12**, mp 111 – 114 °C, which can be further purified by sublimation at 80 °C.

Mass spectrum (m/e) 361 ($C_9H_4N_3F_3Cl_2Se^+$, 6.83%), 326 ($C_9H_4N_3F_3ClSe^+$, 77.32%), 231 ($C_6H_4N_2ClSe^+$, 5.20%), 137 ($C_7H_4NCl^+$, 63.76%), 102 ($C_7H_4N^+$, 39.28%), 94 (SeN^+, 100%), 75 ($C_6H_3^+$, 26.82%).

^{1}H NMR (δ, $CDCl_3$) ppm: 7.50 (d, 2H, 8.7Hz, phenyl), 8.39 (d, 2H, 8.5Hz, phenyl).

^{13}C NMR (δ, $CDCl_3$) ppm: 117.9 (q, 281Hz, CF_3), 129.5 (s, CH-phenyl), 131.2 (s, CH-phenyl), 133.7 (s, C-phenyl), 141.4 (s, C-phenyl), 162.6 (q, 38Hz, triazine), 169.8 (s, triazine).

Raman 3087 (w), 3062 (w), 1592 (s), 1511 (w), 1486 (m), 1383 (w), 1360 (w), 1340 (s), 1287 (w), 1222 (w), 1192 (w), 1172 (m), 1092 (m), 1078 (w), 1014 (w), 947 (m), 854 (w), 832 (w), 786 (w), 765 (w), 703 (m), 680 (w), 667 (w), 629 (w), 421 (w), 363 (w), 342 (w), 312 (s), 301 (w), 276 (w), 258 (w), 228 (w), 187 (w), 136 (w), 102 (m), 93 (m), 77 (w), 69 (w) cm^{-1}.

IR 3089 (br), 1696 (s), 1592 (s), 1506 (s), 1420 (s), 1392 (w), 1341 (s), 1304 (w), 1286 (m), 1208 (s), 1188 (w), 1170 (s), 1092 (s), 1077 (w), 1013 (m), 945 (w), 852 (m), 832 (w), 783 (m), 763 (w), 739 (w), 703 (m), 663 (w), 637 (w), 594 (w), 519 (w), 489 (w), 416 (m) cm^{-1}.

(13) **1-Chloro-3-trifluoromethyl-5-*p*-bromophenyl-1,2,4,6-selenatriazine (D13)**: Imidoylamidine (5.79g, 19.70 mmol) in 40 ml dried acetonitrile was added dropwise to the ice bath cooled selenium tetrachloride (4.35g, 19.70 mmol) suspension in 30 ml acetonitrile. The suspension turned into a clear yellow solution in the ice bath, then cloudy with lots of precipitate when warmed to room temperature. After heating at reflux for 25 hours, the precipitate disappeared. The solution was placed in a freezer at –10 °C for crystallization, but some black solid appeared. The mixture was filtered, pumped to remove solvent and dried yielding a yellow powder (7.34 g) which was purified by sublimation at 90 °C to give 5.03 g (63%) yellow crystals of **D13**, mp 120 – 124 °C.

Mass spectrum (m/e) 405 ($C_9H_4N_3BrClF_3Se^+$, 6.93%), 370 ($C_9H_4N_3BrF_3Se^+$, 57.64%), 294 ($C_9H_4N_3BrF_3^+$, 4.50%), 275 ($C_7H_4N_2BrSe^+$, 4.50%), 181 ($C_7H_4NBr^+$, 12.77%), 102 ($C_7H_4N^+$, 55.81%), 75 ($C_6H_3^+$, 25.61%).

^{1}H NMR (δ, $CDCl_3$) ppm: 7.66 (d, 2H, 8.7Hz, phenyl), 8.30 (d, 2H, 8.6Hz, phenyl).

^{13}C NMR (δ, $CDCl_3$) ppm: 117.9 (q, 281Hz, CF_3), 130.2 (s, C-phenyl), 131.2 (s, CH-phenyl), 132.5 (s, CH-phenyl), 134.1 (s, C-phenyl), 162.6 (q, 38Hz, triazine), 169.9 (s, triazine).

IR: 3091 (s, br), 1684 (m), 1585 (s), 1570 (w), 1537 (w), 1490 (s), 1432 (w), 1401 (s), 1377 (s), 1329 (s), 1282 (w), 1224 (w), 1173 (m), 1110 (w), 1071 (m), 1010 (s), 976 (m), 898 (w), 845 (s), 806 (m), 768 (w), 754 (s), 705 (m), 650 (w), 602 (w), 530 (w), 482 (w), 467 (w), 430 (w) cm^{-1}.

Raman: 3074 (w), 3056 (w), 1584 (s), 1501 (w), 1483 (w), 1401 (w), 1376 (w), 1335 (m), 1229 (w), 1174 (w), 1113 (w), 1069 (m), 1011 (w), 899 (m), 850 (w), 806 (w), 754

(w), 684 (w), 626 (w), 406 (w), 348 (w), 324 (w), 289 (s), 281 (w), 262 (m), 208 (w), 186 (w), 159 (w), 120 (w), 95 (s) cm^{-1}.

(14) **1-Chloro-3-trifluoromethyl-5-*p*-trifluoromethylphenyl-1,2,4,6-selenatriazine (D14)**: Imidoylamidine **A14** (4.01g,14.16 mmol) in 40 ml dried acetonitrile was added dropwise to the ice bath cooled selenium tetrachloride (3.12g, 14.16 mmol) suspension in 40 ml acetonitrile. The suspension became a clear green-yellow solution. Warming up the solution resulted in a white solid precipitating. The mixture was heated at reflux 57 hours to become cloudy brown solution with small amount of precipitate. The solution was cooled down to room temperature, filtered, then evaporated to remove solvent to leave a brown powder 4.64 g when dried, which was sublimed at 70 °C yielding brown yellow crystals of **D14** (3.21g, 57%), mp 124 – 126 °C.

Mass spectrum (m/e) 395 ($C_{10}H_4N_3F_6ClSe^+$, 3.75%), 360 ($C_{10}H_4N_3F_6Se^+$, 67.75%), 341 ($C_{10}H_4N_3F_5Se^+$, 4.41%), 171 ($C_8H_4F_3N^+$, 36.86%), 152 ($C_8H_4F_2N^+$, 25.95%), 145 ($C_7H_4F_3^+$, 23.22%), 94 (SeN^+, 100%).

^1H NMR (δ, $CDCl_3$) ppm: 7.79 (d, 2H, 8.4Hz, phenyl), 8.57 (d, 2H, 8.2Hz, phenyl).

^{13}C NMR (δ, $CDCl_3$) ppm: 117.9 (q, 281Hz, $-CF_3$), 126.1 (q, 3.9 Hz, phenyl), 130.1 (s, CH, phenyl), 135.9 (q, 33Hz, phenyl), 138.5 (s, phenyl), 162.8 (q, 38Hz, trizaine), 169.6 (s, triazine).

Raman: 3084 (w), 1618 (s), 1514 (m), 1506 (m), 1414 (w), 1390 (w), 1338 (m), 1232 (w), 1186 (w), 1113 (w), 1068 (w), 979 (w), 902 (m), 850 (w), 810 (w), 788 (w), 770 (w), 749 (m), 675 (w), 654 (w), 633 (w), 472 (w), 439 (w), 408 (m), 328 (m), 315 (w), 297 (s), 272 (s), 209 (w), 190 (w), 179 (w), 159 (w), 114 (m), 84 (s) cm^{-1}.

IR 3111 (br), 1949 (w), 1821 (w), 1681 (m), 1626 (w), 1586 (w), 1501 (s), 1414 (s), 1390 (s), 1430 (s), 1246 (w), 1228 (w), 1178 (s), 1163 (s), 1122 (s), 1109 (s), 1068 (s), 1016 (s), 976 (m), 901 (w), 860 (s), 848 (m), 809 (m), 788 (w), 771 (s), 749 (w), 723 (s), 702 (m), 675 (w), 654 (w), 629 (w), 590 (w), 524 (w), 492 (w), 472 (w), 436 (m), 403 (m) cm^{-1}.

(15) **1-Chloro-3-trifluoromethyl-5-*p*-cyanophenyl-1,2,4,6-selenatriazine (D15)**: Imidoylamidine **A15** (1.50g, 7.07 mmol) in 50 ml acetonitrile was added dropwise to the ice bath cooled suspension of selenium tetrachloride (1.56g, 7.07 mmol) in 30 ml acetonitrile. The suspension turned into a clear yellow solution without precipitate even if warmed to room temperature and refluxed for 28 hours. The solution was evaporated to remove solvent and dried yielding a sticky yellow product, which was sublimed at 110 °C to give brown non-crystal solid of **D15** (1.2 g, 48%), mp 135 – 138 °C.

^{1}H NMR (δ, $CDCl_3$) ppm: 7.83 (d, 2H, 8.5Hz), 8.56 (d, 2H, 8.6Hz).

^{13}C NMR (δ, $CDCl_3$) ppm: 117.6 (s, C-phenyl), 117.8 (q, 281Hz, CF_3), 118.1 (s, CN), 130.1 (s, CH-phenyl), 132.7 (s, CH-phenyl), 139.0 (s, C-phenyl), 162.8 (q, 38Hz, triazine), 169.0 (s, triazine).

IR 3095 (s), 2231 (m), 1684 (s), 1620 (w), 1576 (w), 1500 (m), 1436 (m), 1408 (w), 1382 (s), 1303 (w), 1291 (w), 1197 (w), 1174 (w), 1147 (w), 1106 (w), 1017 (m), 980 (w), 975 (w), 928 (w), 910 (w), 854 (s), 841 (w), 803 (s), 764 (m), 722 (w), 714 (w), 668 (m), 653 (w), 641 (w), 626 (w), 558 (w), 544 (m), 525 (w), 517 (w), 504 (w), 457 (w), 414 (s) cm^{-1}.

(16) **1-Chloro-3-trifluoromethyl-5-(2,6-diisopropyl)phenyl-1,2,4,6-selenatriazine (D16)**: Imidoylamidine **A16** (2.55g, 8.52 mmol) in 40 ml acetonitrile was added dropwise to the ice bath cooled selenium tetrachloride (1.88g, 8.52 mmol) suspension in 40 ml acetonitrile. The suspension turned into a clear yellow solution without precipitate even if warmed to room temperature, and refluxed for 20 hours. The final brown solution was evaporated to remove solvent, dried and sublimed at 90 °C to get yellow needles of **D16** suitable for crystallographic analysis (1.94 g, 55%), mp 102 – 105 °C.

Mass spectrum (m/e) 376 ($C_{15}H_{17}N_3F_3Se^+$, 49.72%), 296 ($C_{15}H_{17}N_3F_3^+$, 94.79%), 281 ($C_{13}H_{17}N_2Se^+$, 14.52%), 264 ($C_{13}H_{14}NSe^+$, 17.54%), 201 ($C_{13}H_{17}N_2^+$, 100%), 186 ($C_{13}H_{16}N^+$, 68.96%), 172 ($C_{12}H_{14}N^+$, 73.42%), 77 ($C_6H_5^+$, 13.36%).

^{1}H NMR (δ, $CDCl_3$) ppm: 1.21 (d, 12H, 6.7Hz, CH_3), 2.59 (m, CH), 7.24 (d, 2H, 7.6Hz, phenyl), 7.42 (t, 1H, 7.8Hz, phenyl).

^{13}C NMR (δ, $CDCl_3$) ppm: 24.3 (s, CH_3), 31.3 (s, CH), 117.8 (q, 281Hz, CF_3), 123.5 (s, CH-phenyl), 130.7 (s, C-phenyl), 135.5 (s, CH-phenyl), 146.1 (s, C-phenyl), 162.0 (s, br, triazine), 177.1 (s, br, triazine).

IR 3076 (br), 2968 (s), 2926 (w), 2872 (w), 1753 (w), 1671 (s), 1606 (w), 1511 (w), 1458 (m), 1409 (m), 1368 (w), 1308 (w), 1207 (s), 1187 (s), 1142 (m), 1057 (w), 917 (w), 840 (w), 808 (w), 762 (w), 723 (w), 677 (w), 599 (w), 467 (w), 418 (w) cm^{-1}.

Raman 3072 (w), 2973 (m), 2937 (w), 2907 (w), 2867 (w), 1592 (m), 1506 (w), 1462 (w), 1445 (w), 1356 (w), 1239 (w), 1106 (w), 1038 (m), 947 (w), 886 (w), 818 (w), 764 (w), 754 (w), 683 (s), 655 (w), 591 (w), 494 (w), 443 (w), 411 (w), 368 (w), 343 (w), 315 (s), 298 (s), 266 (w), 234 (w), 207 (w), 179 (w), 141 (s), 85 (s) cm-1.

7.7.4 Synthesis of the bis(selenatriazine chloride)benzenes

(1) **1,3-bis(1-Chloro-3-trichloromethyl-1,2,4,6-selenatriazinyl)benzene (D17)**: Diimidoylamidine **A17** (1.52g, 3.37 mmol) in 50 ml acetonitrile was added dropwise to the ice bath cooled suspension of selenium tetrachloride (1.49g, 6.74 mmol) in 30 ml acetonitrile. The suspension turned into a clear yellow solution. The mixture was warmed to room temperature and then heated at reflux for 60 hours. The solution was evaporated to remove solvent and dried yielding 1.93 g dark yellow powder, which was sublimed at 190 °C to give fine yellow crystals (0.12g, 5%) of **D17**, mp 255 – 260 °C.

Mass spectrum (m/e) 674 ($C_{12}H_4N_6Cl_8Se_2^+$, 1.45%), 639 ($C_{12}H_4N_6Cl_7Se_2^+$, 65.8%), 604 ($C_{12}H_4N_6Cl_6Se_2^+$, 31.5%), 365 ($C_{10}H_4N_4Cl_3Se^+$, 65.0%), 150 ($SeCl_2^+$, 53.3%), 115 ($C_8H_4N^+$, 100%), 94 (SeN^+, 90.5%).

^{1}H NMR (δ, $CDCl_3$) ppm: 7.73 (t, 1H, 8.1Hz), 8.76 (d, 2H, 7.9Hz), 9.64 (s, 1H). (δ, DMSO-d_6) ppm: 7.75 (t, 1H, 5.0Hz), 8.53 (d, 2H, 6.4Hz), 9.33 (s, 1H).

^{13}C NMR (δ, DMSO-d_6) ppm: 97.3 (s, CCl_3), 128.3 (s), 129.0 (s), 132.0 (s), 136.7 (s), 166.2 (s, br).

(2) **1,3-bis(1-Chloro-3-trifluoromethyl-1,2,4,6-selenatriazinyl)benzene (D18)**: Diimidoylamidine **A18** (2.08g, 5.90 mmol) in 50 ml acetonitrile was added dropwise to the ice bath cooled suspension of selenium tetrachloride (2.60g, 11.80 mmol) in 30 ml acetonitrile. The suspension became a clear yellow solution once all of the diimidoylamidine was added. The mixture was warmed to room temperature, and then heated at reflux for 50 hours. The solution was evaporated to remove solvent and dried yielding 2.93 g dark yellow powder, which was sublimed at 110 °C to give fine yellow

crystals of **D18** (0.20g, 6%), mp 132 – 134 °C. ^{1}H NMR (δ, DMSO-d_6) ppm: 7.87 (t, 7.8 Hz), 8.67 (d, 14 Hz), 9.36 (s)

(3) **1,4-Bis(1-Chloro-3-trifluoromethyl-1,2,4,6-selenatriazinyl)benzene (D19)**: Diimidoylamidine **A19** (1.47 g (4.17 mmol) in 50 ml dried CH_3CN was added dropwise to the suspension of 1.84 g (8.34 mmol) $SeCl_4$ in 25 ml dried CH_3CN cooled in ice bath. The suspension instantly turned to a clear yellow solution, which was warmed up and heated at reflux for 2 days. The final solution was chilled at –10 °C to crystallize, yielding 0.62 g (26%) fine yellow crystals of **D19**, mp 238 – 242 °C. 1H NMR (δ, DMSO-d_6) ppm: 8.40 (s). ^{13}C NMR (δ, DMSO-d_6) ppm: 117.9 (q, 281 Hz), 157.7 (q, 38 Hz), 164.9 (s), 139.6 (s), 128.3 (s).

7.8 Synthesis of 1,2,4,6-Selenatriazinyl Radicals

(1) **3-Trichloromethyl-5-*p*-methoxyphenyl-selenatriazine (E1)**: 0.78 g (1.92 mmol) 1-chloro-selenatriazine **D1** in 30 ml dried CH_3CN (well dissolved, trace amount of solid was filtered) was added to the hot solution (80 °C) of 0.37 g (0.96 mmol) Ph_3Sb in 5 ml CH_3CN in 5 minutes without stirring. The solution turned into dark red instantly, which started crystallization at about 70 °C when slowly cooled down. After filtering and drying, black crystals of **E1** were collected, 0.39g (55%) mp = 140 – 142 °C.

(2) **3-Trichloromethyl-5-*p*-tolylselenatriazine (E2)**: 0.56g (1.44 mmol) 1-Chloro-selenatriazine **D2** was well dissolved in 50 ml dried CH_3CN and a trace amount of solid was filtered off. The filtrate was heated up & stabilized at about 55 °C. 0.28g (0.79 mmol) Ph_3Sb in 5 ml dried CH_3CN was added to the filtrate dropwise in a period of 2

hours without stirring. Black spots appeared at the end of dropwise addition. The mixture was then allowed to cool down slowly to room temperature, then to ice bath 5 hours for further crystallization. After filtering, the solid was dried under vacuum to yield shiny black needles of free radical **E2**, 0.28g (55%) mp 136 –139 °C. Mass spectrum (m/e) 354 ($C_{10}H_7N_3Cl_3Se^+$, 50.38%), 319 ($C_{10}H_7N_3Cl_2Se^+$, 5.09%), 237 ($C_2N_2Cl_3Se^+$, 5.2%), 211 ($C_8H_7N_2Se^+$, 23.1%), 117 ($C_8H_7N^+$, 88.3%), 94 (SeN^+, 100%). IR 3061 (w), 1661 (w), 1608 (m), 1576 (w), 1559 (w), 1465 (s), 1436 (w), 1407 (w), 1355 (s), 1307 (m), 1298 (w), 1279 (m), 1246 (w), 1213 (w), 1176 (s), 1117 (w), 1064 (w), 1038 (w), 1020 (m), 996 (w), 964 (m), 898 (m), 837 (m), 828 (s), 798 (m), 776 (w), 740 (s), 734 (m), 690 (s), 696 (m), 647 (w), 635 (m), 556 (m), 481 (m), 460 (w), 411 (m) cm^{-1}.

(3) **3-Trichloromethyl-5-phenyl-selenatriazine (E3)**: 0.90g (2.39 mmol) 1-Chloro-selenatriazine **D3** was well dissolved in 60 ml dried CH_3CN. No solid impurity was found in solution. The yellow solution was heated up & stabilized at about 55 °C. 0.47g (1.32 mmol) Ph_3Sb in 5 ml dried CH_3CN was added to the filtrate dropwise in a period of 2 hours without stirring. A few black spots appeared at the end of addition of Ph_3Sb. The mixture was then allowed to cool slowly to room temperature, then to ice bath 5 hours for further crystallization. After filtering, the solid was dried under vacuum to yield thin black plates of free radical **E3**, 0.52g (64%) mp 130 – 133 °C. Mass spectrum (m/e) 340 ($C_9H_5N_3Cl_3Se^+$, 57.52%), 305 ($C_9H_5N_3Cl_2Se^+$, 8.10%), 237 ($C_2N_2Cl_3Se^+$, 9.90%), 195 ($C_7H_5N_2Se^+$, 13.80%), 103 ($C_7H_5N^+$, 84.8%), 94 (SeN^+, 100%), 76 ($C_6H_4^+$, 36.40%. IR 3056 (w), 1695 (w), 1653 (w), 1593 (w), 1559 (w), 1522 (w), 1506 (w), 1471 (s), 1439 (s), 1350 (s), 1311 (m), 1276 (m), 1245 (m), 1173 (s), 1103 (w), 1072 (m), 1025 (m),

1001 (w), 962 (m), 938 (w), 894 (m), 831 (s), 799 (s), 757 (s), 708 (s), 693 (s), 645 (s), 606 (s), 463 (w), 446 (w), 414 (s) cm^{-1}.

(4) **3-Trifluoromethyl-5-*p*-methoxyphenyl-selenatriazine (E9)**: 0.74 g (2.08 mmol) 1-chloro-selenatriazine **D9** in 20 ml dried CH_3CN (well dissolved, trace amount of solid was filtered) was added to the hot solution (80 °C) of Ph_3Sb in 5 ml CH_3CN in 5 minutes without stirring. The solution turned into dark red instantly, which started crystallization at about 70 °C when slowly cooled down. After filtering and drying, black crystals of **E9** were collected suitable for crystallographic analysis, 0.22g (33%) mp = 149 – 152 °C.

(5) **3-Trifluoromethyl-5-*p*-tolyl-selenatriazine (E10)**: 0.78g (2.29 mmol) Selenatriazine **D10** was well dissolved in 25 ml dried CH_3CN. Some solid impurity in solution was filtered off. The yellow filtrate was heated up and stabilized at about 55 °C. 0.445g (1.26 mmol) Ph_3Sb in 5 ml dried CH_3CN was added to the filtrate dropwise in a period of 2.5 hours without stirring. Black spots appeared during the addition of Ph_3Sb. The mixture was then allowed to cool down slowly to room temperature, then to ice bath 5 hours for further crystallization. After filtering, the solid was dried under vacuum to yield shiny black bricks of **E10** suitable for crystallographic analysis, 0.34g (49%) mp 155 – 157 °C. Mass spectrum (m/e) 306 ($C_{10}H_7N_3F_3Se^+$, 88.27%), 117 ($C_8H_7N^+$, 46.76%), 94 (SeN^+, 100%). IR 3038 (, br, m), 1734 (w), 1675 (m), 1653 (w), 1610 (m), 1576 (w), 1559 (w), 1539 (w), 1501 (s), 1402 (m), 1346 (s), 1298 (w), 1263 (m), 1220 (s), 1175 (s), 1142 (s), 1074 (m), 1020 (w), 933 (m), 877 (w), 829 (s), 785 (w), 766 (m), 729 (m), 704 (m), 668 (w), 634 (w), 577 (w), 533 (w), 476 (w), 458 (w), 413 (m) cm^{-1}.

(6) **3-Trifluoromethyl-5-*p*-bromophenyl-selenatriazine (E13)**: 0.75g (1.85 mmol) Selenatriazine **D13** in 7 ml dried CH_3CN was charged in one end of the H-vessel flask, and 0.36 g (1.02 mmol) Ph_3Sb in 7 ml dried CH_3CN in the other end. Both sides were frozen and evacuated to degas three times. Combining two solutions by diffusion formed red fine crystals of **E13** 0.52g (64%) after drying, mp 130 – 133 °C. Mass spectrum (m/e) 370 ($C_9H_4N_3BrF_3Se^+$, 50.80%), 274 ($C_7H_4N_2BrSe^+$, 3.59%), 181 ($C_7H_4NBr^+$, 18.25%), 102 ($C_7H_4N^+$, 64.73%), 94 (SeN^+, 100%), 75 ($C_6H_3^+$, 28.66%). IR 3083 (w), 1684 (w), 1586 (m), 1574 (m), 1510 (s), 1487 (m), 1399 (s), 1340 (s), 1282 (w), 1263 (s), 1225 (s), 1192 (w), 1174 (w), 1145 (w), 1107 (w), 1069 (s), 1013 (s), 937 (w), 830 (m), 768 (s), 759 (w), 748 (m), 730 (w), 700 (m), 676 (m), 650 (w), 629 (w), 569 (w), 473 (w), 458 (w), 421 (m) cm^{-1}.

(7) **3-trifluoromethyl-5-*p*-trifluoromethylphenyl-selenatriazine (E14)**: 0.70 g (1.78 mmol) 1-Chloro-selenatriazine **D14** well dissolved in 20 ml dried CH_3CN (trace amount of solid was filtered) was added dropwise to the hot solution (80 °C) of Ph_3Sb in 10 ml CH_3CN in 5 minutes without stirring. The solution turned into dark red instantly, which was then slowly cooled down to room temperature for crystallization. After filtering and drying, fine red crystals of **E14** were collected, 0.17g (26%) mp = 135 – 138 °C.

Table 7.1. Crystal data and structure refinement for **C8**.

Identification code	**C8**	
Empirical formula	$C_{15}H_{18}Cl_5N_3$ Se	
Formula weight	496.53	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P $2_1/n$	
Unit cell dimensions	a = 13.6049(9) Å	α = 90°.
	b = 18.2021(12) Å	β = 100.5342(9)°.
	c = 16.8386(11) Å	γ = 90°.
Volume	4099.6(5) $Å^3$	
Z	8	
Density (calculated)	1.609 Mg/m^3	
Absorption coefficient	2.487 mm^{-1}	
F(000)	1984	
Crystal size	0.44 x 0.21 x 0.17 mm^3	
Theta range for data collection	1.77 to 26.40°.	
Index ranges	-17<=h<=17, -16<=k<=22, -21<=l<=21	
Reflections collected	24187	
Independent reflections	8385 [R(int) = 0.0463]	
Completeness to theta = 26.40°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6772 and 0.4075	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8385 / 0 / 433	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R_1 = 0.0368, wR_2 = 0.0758	
R indices (all data)	R_1 = 0.0637, wR_2 = 0.0845	
Largest diff. peak and hole	0.610 and -0.446 e.$Å^{-3}$	

Table 7.2. Crystal data and structure refinement for **D2.**

Identification code	**D2**	
Empirical formula	$C_{10}H_7Cl_4N_3Se$	
Formula weight	389.95	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P $2_1/n$	
Unit cell dimensions	a = 7.8158(6) Å	α = 90°.
	b = 5.5405(4) Å	β = 95.8977(10)°.
	c = 31.154(2) Å	γ = 90°.
Volume	1341.95(17) $Å^3$	
Z	4	
Density (calculated)	1.930 Mg/m^3	
Absorption coefficient	3.577 mm^{-1}	
F(000)	760	
Crystal size	0.44 x 0.21 x 0.12 mm^3	
Theta range for data collection	1.31 to 26.41°.	
Index ranges	-9<=h<=9, -6<=k<=6, -38<=l<=38	
Reflections collected	8976	
Independent reflections	2724 [R(int) = 0.0293]	
Completeness to theta = 26.41°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6735 and 0.3021	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2724 / 0 / 164	
Goodness-of-fit on F^2	1.265	
Final R indices [I>2sigma(I)]	R_1 = 0.0323, wR_2 = 0.0909	
R indices (all data)	R_1 = 0.0384, wR_2 = 0.0934	
Largest diff. peak and hole	0.717 and -0.767 e.$Å^{-3}$	

Table 7.3 Crystal data and structure refinement for **D7**.

Identification code	**D7**	
Empirical formula	$C_{10}H_4Cl_4N_4Se$	
Formula weight	400.93	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.6279(6) Å	α = 70.0037(10)°.
	b = 8.8939(7) Å	β = 79.4428(9)°.
	c = 11.1769(9) Å	γ = 78.0135(10)°.
Volume	691.80(10) $Å^3$	
Z	2	
Density (calculated)	1.925 Mg/m^3	
Absorption coefficient	3.474 mm^{-1}	
F(000)	388	
Crystal size	0.24 x 0.20 x 0.18 mm^3	
Theta range for data collection	1.95 to 26.37°.	
Index ranges	-9<=h<=9, -11<=k<=11, -13<=l<=13	
Reflections collected	5203	
Independent reflections	2813 [R(int) = 0.0214]	
Completeness to theta = 26.37°	99.2 %	
Absorption correction	Integration	
Max. and min. transmission	0.5736 and 0.4894	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2813 / 0 / 172	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R_1 = 0.0248, wR_2 = 0.0596	
R indices (all data)	R_1 = 0.0288, wR_2 = 0.0613	
Largest diff. peak and hole	0.560 and -0.376 e.$Å^{-3}$	

Table 7.4 Crystal data and structure refinement for **D8**.

Identification code	**D8**	
Empirical formula	$C_{15}H_{17}Cl_4N_3Se$	
Formula weight	460.08	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	F dd2	
Unit cell dimensions	a = 31.960(3) Å	α = 90°.
	b = 37.718(4) Å	β = 90°.
	c = 6.3413(6) Å	γ = 90°.
Volume	7644.2(13) $Å^3$	
Z	16	
Density (calculated)	1.599 Mg/m^3	
Absorption coefficient	2.525 mm^{-1}	
F(000)	3680	
Crystal size	0.59 x 0.10 x 0.08 mm^3	
Theta range for data collection	1.67 to 26.41°.	
Index ranges	-39<=h<=39, -46<=k<=46, -7<=l<=7	
Reflections collected	14973	
Independent reflections	3898 [R(int) = 0.0727]	
Completeness to theta = 26.41°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8235 and 0.3173	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3898 / 1 / 208	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R_1 = 0.0709, wR_2 = 0.1819	
R indices (all data)	R_1 = 0.1131, wR_2 = 0.2070	
Absolute structure parameter	0.00(2)	
Largest diff. peak and hole	1.180 and -0.351 e.$Å^{-3}$	

Table 7.5 Crystal data and structure refinement for **D10**.

Identification code	**D10**	
Empirical formula	$C_{10}H_7Cl\ F_3N_3Se$	
Formula weight	340.60	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P $2_1/c$	
Unit cell dimensions	a = 9.7889(19) Å	α = 90°.
	b = 7.9136(15) Å	β = 113.417(2)°.
	c = 17.093(3) Å	γ = 90°.
Volume	1215.1(4) $Å^3$	
Z	4	
Density (calculated)	1.862 Mg/m^3	
Absorption coefficient	3.332 mm^{-1}	
F(000)	664	
Crystal size	0.36 x 0.28 x 0.27 mm^3	
Theta range for data collection	2.27 to 26.45°.	
Index ranges	-12<=h<=11, 0<=k<=9, 0<=l<=21	
Reflections collected	5749	
Independent reflections	5775 [R(int) = 0.0000]	
Completeness to theta = 26.45°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4665 and 0.3801	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5775 / 0 / 165	
Goodness-of-fit on F^2	0.932	
Final R indices [I>2sigma(I)]	R_1 = 0.0329, wR_2 = 0.0717	
R indices (all data)	R_1 = 0.0495, wR_2 = 0.0753	
Largest diff. peak and hole	0.650 and -0.305 e.$Å^{-3}$	

Table 7.6 Crystal data and structure refinement for **D16.**

Identification code	**D16**	
Empirical formula	$C_{15}\ H_{17}\ Cl\ F_3\ N_3\ Se$	
Formula weight	410.73	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I 2/a	
Unit cell dimensions	a = 28.823(3) Å	α = 90°.
	b = 6.3494(7) Å	β = 102.8357(19)°.
	c = 19.602(2) Å	γ = 90°.
Volume	3497.7(7) $Å^3$	
Z	8	
Density (calculated)	1.560 Mg/m^3	
Absorption coefficient	2.329 mm^{-1}	
F(000)	1648	
Crystal size	0.49 x 0.16 x 0.06 mm^3	
Theta range for data collection	1.45 to 26.41°.	
Index ranges	-36<=h<=36, -7<=k<=7, -22<=l<=24	
Reflections collected	12024	
Independent reflections	3581 [R(int) = 0.0624]	
Completeness to theta = 26.41°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8729 and 0.3948	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3581 / 0 / 236	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R_1 = 0.0446, wR_2 = 0.1012	
R indices (all data)	R_1 = 0.0881, wR_2 = 0.1187	
Largest diff. peak and hole	0.430 and -0.306 $e.Å^{-3}$	

Table 7.7 Crystal data and structure refinement for **E9**.

Identification code	**E9**	
Empirical formula	$C_{20}H_{14}F_6N_6O_2Se_2$	
Formula weight	642.29	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.1776(8) Å	α = 88.2731(17)°.
	b = 11.3941(13) Å	β = 88.5986(17)°.
	c = 13.4985(15) Å	γ = 81.7154(17)°.
Volume	1091.7(2) $Å^3$	
Z	2	
Density (calculated)	1.954 Mg/m^3	
Absorption coefficient	3.472 mm^{-1}	
F(000)	628	
Crystal size	0.33 x 0.15 x 0.07 mm^3	
Theta range for data collection	1.51 to 26.40°.	
Index ranges	-8<=h<=8, -14<=k<=14, -16<=l<=16	
Reflections collected	8126	
Independent reflections	4424 [R(int) = 0.0409]	
Completeness to theta = 26.40°	99.2 %	
Absorption correction	Integration	
Max. and min. transmission	0.7931 and 0.3937	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4424 / 0 / 325	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R_1 = 0.0397, wR_2 = 0.0815	
R indices (all data)	R_1 = 0.0763, wR_2 = 0.1071	
Largest diff. peak and hole	0.609 and -0.461 $e.Å^{-3}$	

Table 7.8 Crystal data and structure refinement for **E10**.

Identification code	**E10**	
Empirical formula	$C_{20}H_{14}F_6N_6Se_2$	
Formula weight	610.29	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.5007(9) Å	α= 110.5312(10)°.
	b = 14.8000(11) Å	β= 101.9075(11)°.
	c = 15.0406(11) Å	γ = 107.1659(10)°.
Volume	2148.9(3) $Å^3$	
Z	4	
Density (calculated)	1.886 Mg/m^3	
Absorption coefficient	3.515 mm^{-1}	
F(000)	1192	
Crystal size	0.39 x 0.27 x 0.18 mm^3	
Theta range for data collection	1.54 to 26.42°.	
Index ranges	-14<=h<=14, -18<=k<=18, -18<=l<=18	
Reflections collected	16096	
Independent reflections	8761 [R(int) = 0.0301]	
Completeness to theta = 26.42°	99.0 %	
Absorption correction	Integration	
Max. and min. transmission	0.5703 and 0.3410	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8761 / 0 / 617	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R_1 = 0.0363, wR_2 = 0.0811	
R indices (all data)	R_1 = 0.0582, wR_2 = 0.0887	
Largest diff. peak and hole	0.715 and -0.550 $e.Å^{-3}$	

7.10 References

1. Felix, O.; Hosseini, M. W.; Cian, A. D.; Fischer, J. *New J. Chem. Commun.* **1997**, *21*, 285

2. Boeré R. T.; Oakley, r. T.; Reed, R. W. *J. Organomet. Chem.* **1987**, *331*, 161.

3. Roemmele, T. L. *M. Sci. Thesis*, University of Lethbridge, **2002**.