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Five related N'-(2,2,2-trichloroethanimidoyl)benzenes

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Five related \( N'-(2,2,2\text{-trichloro}-\text{ethanimidoyl})\text{benzene-1-carboximidamide} \)

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In the solid state, 4-methoxy-\( N'-(2,2,2\text{-trichloroethanimidoyl})\text{benzene-1-carboximidamide, C}_{16}\text{H}_{10}\text{Cl}_{1}\text{N}_{3}\text{O}, (I)} \), \( N'-(2,2,2\text{-trichloroethanimidoyl})\text{benzene-1-carboximidamide, C}_{6}\text{H}_{3}\text{Cl}_{1}\text{N}_{3}, (II) \), 4-chloro-\( N'-(2,2,2\text{-trichloroethanimidoyl})\text{benzene-1-carboximidamide, C}_{6}\text{H}_{3}\text{Cl}_{1}\text{N}_{3}, (III) \), 4-bromo-\( N'-(2,2,2\text{-trichloroethanimidoyl})\text{benzene-1-carboximidamide, C}_{6}\text{H}_{3}\text{Br}_{1}\text{Cl}_{1}\text{N}_{3}, (IV) \), and 4-trifluoromethyl-\( N'-(2,2,2\text{-trichloroethanimidoyl})\text{benzene-1-carboximidamide, C}_{10}\text{H}_{7}\text{Cl}_{1}\text{F}_{3}\text{N}_{3}, (V) \), display strong intra-

Comment

\( N\text{-Imidoylamidines (i.e. } N\text{-imidoylcarboximidamides) are tri-nitrogen analogues of pentadienes containing unsaturated } N\text{-}-(\overline{\text{C}}\text{-}N)^{2}\text{N} \) chains which may have different degrees of substitution at nitrogen. If the substituents at carbon are further \( N\text{-containing groups, the familiar biguanides are obtained; imidoylamidines have carbon substituents on the backbone C atoms. Primary } N\text{-imidoylamidines have three ionizable H atoms on N atoms with the possibility of several tautomeric structures. Tertiary exemplars retain a single ionizable H atom. Both primary and, more commonly, tertiary imidoylamidines are potent chelating ligands as deprotonated monoanions. Applications of metal complexes of this ligand type include the development of molecular magnets (Zheng et al., 2007) and switches (Atkinson et al., 2002), and \( \pi\text{-activation agents for alkynes (Dias et al., 2009), as well as applications in catalysis (Flores et al., 2009). Both the chemistry of the neutral molecules and the coordination chemistry of the deprotonated anions have recently been comprehensively reviewed (Kop-

Figure 1

Displacement ellipsoid plot (drawn at the 30% probability level) of (I) at 173 (2) K. The same atom-numbering scheme is used for (I)–(V), except that in (II) the three independent molecules in the asymmetric unit have \( A', B' \) and \( C' \) to identify the three crystallographically independent molecules in the asymmetric unit. Average bond lengths and angles for the \( N\text{-}-(\overline{\text{C}}\text{-}N)^{2}\text{N} \) cores have been compiled, along with s.u. values, and are listed in Table 6. The average bond lengths show that \( C1\text{--N1} \) and \( C1\text{--N2} \) are of intermediate length between single and double bonds, as is characteristic of delocalized amidines, and are identical within their s.u. values. The \( C2\text{--N} \) bonds are short and more characteristic of imines, while the \( N2\text{--C2} \) bonds are longer and approximate to single bonds. By contrast, the two \( C\text{--N} \) bonds to which the \( -\text{CCl}_{3} \) group is attached in (\( Z\)-2,2,2-trichloro-\( N^{2}\text{-cyanamidamide differ in length by only } 0.008 \) Å (Baker & Boéré, 2009). The averaged bond lengths are nearly identical, within their s.u. values, to the recently reported trifluoromethyl series (Boéré et al., 2011). Other known structures of primary imidoylamidines include an unusual chloroimidoylamidinium salt and two biguanides...
The pentaazadiene cores of (I)–(V) are close to being planar and form six-membered rings through N1—H2...N3 hydrogen bonding [labelled \( \Delta \) in Scheme 2, which shows a summary of the intra- (labelled \( \Delta \) and \( \Phi \)) and intermolecular (labelled \( \Gamma \), \( \Lambda \) and \( \Pi \)) hydrogen bonds present in compounds (I)–(V)]. Donor–acceptor N...N distances for the \( \Delta \) interaction are in the range 2.616 (2)–2.657 (4) Å. The average distance in all seven independent molecules is 2.638 (14) Å. The related trifluoromethyl series displays a very similar N...N distance of 2.66 (2) Å (Boere et al., 2011). Each example also shows short N3—H3...Cl2 contacts (\( \Phi \) in Scheme 2), with an average donor–acceptor distance of 2.984 (18) Å. This weak contact is sufficient to orient atom Cl2 so that it is close to being coplanar with the pentaazadiene core in all seven independent molecules.

The intermolecular hydrogen bonding is also very noteworthy. Within the crystal structure, molecules of (I) are linked by N1—H1...O1 hydrogen bonds that form a twofold helix along the [010] direction (see Fig. 2 and Table 1 for symmetry codes). N3—H3...Cl2 hydrogen bond (\( \Pi \) in Scheme 2) serves to link the chains thus formed into two-
The intermolecular N1—H1···N2 hydrogen bonds in (III) (dotted lines), forming chains of equivalent molecules aligned exactly with the ac diagonal of the unit cell, resulting in a twofold helix along the [100] direction. Compound (IV) is isomorphous with (III). Ellipsoids are shown at the 30% probability level. [Symmetry codes: (i) x − 1/2, −y + 1/2, z − 1/2; (ii) x + 1, y, z + 1; (iii) x, −y + 1, z + 1/2; (iv) x + 1, y, z + 1.]

**Figure 6**

Displacement ellipsoid plot (drawn at the 30% probability level) of (IV) at 173 (2) K.

**Figure 7**

Displacement ellipsoid plot (drawn at the 30% probability level) of (IV) at 173 (2) K.

**Figure 8**

Displacement ellipsoid plot (drawn at the 30% probability level) of (V) at 173 (2) K.

dimensional sheets that run parallel to (101) planes. More significantly, the three independent molecules of (II) form threefold helices along the [100] direction, defining a noncrystallographic threefold screw axis through N1—H1···N2iii contacts (see Fig. 4 and Table 2 for symmetry codes). This helix is associated to a second related by inversion by the N3B—H3B···Cl1Ai hydrogen bond (Π in Scheme 2), which occurs only once in the asymmetric unit. In both (III) and (IV), there are twofold helices in the [100] direction, also through N1—H1···N2iii contacts (see Fig. 6 for symmetry codes). This helical chain is expanded into a layer along the (040) plane through the N3—H3···Cl4h hydrogen bond in (III) or N3—H3···Br1ii in (IV) (Π in Scheme 2). Only (V) does not display intermolecular hydrogen bonding, presumably a consequence of the rather bulky CF3 group on the aryl ring. In (II), (III) and (IV), hydrogen bonds of the type N1—H1···N2ii link a terminal NH2 group on one molecule with the central (backbone) N atom of a neighbouring molecule (A in Scheme 2). The average donor–acceptor distance for this interaction is 3.12 (3) Å, which is also, within the s.u. values, equal to such bonds in the trifluoromethyl series at 3.09 (9) Å. While complete atom transfer would generate a diimine tautomer, all seven examples here and from the trifluoromethyl series (Boere et al., 2011) show the single tautomeric form in the solid-state structure. The terminal NH2 group is typically involved in ring-forming (H2) and chain-forming (H1) interactions, while the terminal —NH group has contacts to atom Cl2 and, except in (V), displays additional intermolecular interactions with other Cl or Br atoms (Γ in Scheme 2). In molecule C of (II), there is an additional intermolecular hydrogen bond between the N1C—H1C group and atom Cl1B of a neighbouring CC1i group (A in Scheme 2).

**Experimental**

Compounds (I)–(V) were prepared using a modification of a literature procedure (Peters & Schaefer, 1964) by addition of trichloroacetonitrile to the corresponding para-substituted benzamidines in acetonitrile. Crystals suitable for X-ray diffraction were grown by vacuum sublimation in a three-zone tube furnace, or by slow cooling of acetonitrile solutions [m.p. 377–379 K for (I), 341–342 K for (II), 384–386 K for (III), 371–372 K for (IV) and 369–370 K for (V)]. A full hemisphere of data was collected for all five structures at low temperature (173 K) using molybdenum radiation.

**Compound (I)**

**Crystal data**

C6H7Cl3N3O

Mr = 294.56

Z = 4

Monoclinic, P21/c

Mo Kα radiation

a = 12.0988 (10) Å

b = 8.6425 (7) Å

c = 12.2023 (10) Å

β = 107.445 (1)°

**Data collection**

Bruker APEX2 CCD area-detector diffractometer

Absorption correction: multi-scan (SADABS: Bruker, 2006)

2448 reflections with I > 2σ(I)

R(int) = 0.026

Tmin = 0.697, Tmax = 0.746

**Table 1**

Hydrogen-bond geometry (Å, °) for (I).

<table>
<thead>
<tr>
<th>D—H···A</th>
<th>D—H···A</th>
<th>D—H···A</th>
<th>D—H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1—H2···N3</td>
<td>0.86 (1)</td>
<td>2.00 (2)</td>
<td>2.647 (2)</td>
</tr>
<tr>
<td>N3—H3···Cl2</td>
<td>0.86 (2)</td>
<td>2.43 (2)</td>
<td>2.9791 (15)</td>
</tr>
<tr>
<td>N1—H1···O1i</td>
<td>0.85 (1)</td>
<td>2.20 (2)</td>
<td>3.0315 (17)</td>
</tr>
<tr>
<td>N3—H3···Cl3ii</td>
<td>0.86 (2)</td>
<td>2.76 (2)</td>
<td>3.4077 (15)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) −x, y + 1/2, −z + 1/2; (ii) −x + 1, y + 1/2, −z + 1/2.


Bowen et al., C6H7Cl3N3O and four analogues
Table 2
Hydrogen-bond geometry (Å, °) for (II).

<table>
<thead>
<tr>
<th>D—H—A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1—H2···N3A</td>
<td>0.89 (2)</td>
<td>1.99 (3)</td>
<td>2.657 (4)</td>
<td>130 (3)</td>
</tr>
<tr>
<td>N3A—H3A···Cl2A</td>
<td>0.88 (2)</td>
<td>2.38 (3)</td>
<td>2.969 (3)</td>
<td>125 (3)</td>
</tr>
<tr>
<td>N1A—H1A···N2C</td>
<td>0.86 (2)</td>
<td>2.26 (2)</td>
<td>3.126 (4)</td>
<td>172 (3)</td>
</tr>
<tr>
<td>N1B—H1B···N2A</td>
<td>0.87 (2)</td>
<td>2.28 (2)</td>
<td>3.136 (4)</td>
<td>171 (3)</td>
</tr>
<tr>
<td>N3B—H3B···Cl2B</td>
<td>0.88 (2)</td>
<td>2.41 (3)</td>
<td>2.978 (3)</td>
<td>123 (3)</td>
</tr>
<tr>
<td>N1B—H2B···N3B</td>
<td>0.89 (2)</td>
<td>1.94 (3)</td>
<td>2.646 (4)</td>
<td>135 (3)</td>
</tr>
<tr>
<td>N3B—H3B···Cl1B</td>
<td>0.88 (2)</td>
<td>2.91 (3)</td>
<td>3.383 (3)</td>
<td>115 (3)</td>
</tr>
<tr>
<td>N1C—H2C···N3C</td>
<td>0.89 (2)</td>
<td>1.91 (3)</td>
<td>2.644 (4)</td>
<td>138 (3)</td>
</tr>
<tr>
<td>N3C—H3C···Cl2C</td>
<td>0.87 (2)</td>
<td>2.47 (3)</td>
<td>3.023 (3)</td>
<td>122 (3)</td>
</tr>
<tr>
<td>N1C—H1C···N2B</td>
<td>0.87 (2)</td>
<td>2.24 (2)</td>
<td>3.072 (3)</td>
<td>160 (3)</td>
</tr>
<tr>
<td>N1C—H1C···Cl1B</td>
<td>0.87 (2)</td>
<td>2.90 (3)</td>
<td>3.511 (3)</td>
<td>128 (3)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x + 1, y, z; (ii) −x + 1, −y + 2, −z.

Table 3
Hydrogen-bond geometry (Å, °) for (III).

<table>
<thead>
<tr>
<th>D—H—A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1—H2···N3</td>
<td>0.87 (2)</td>
<td>1.92 (3)</td>
<td>2.628 (4)</td>
<td>137 (3)</td>
</tr>
<tr>
<td>N3—H3···C2</td>
<td>0.88 (2)</td>
<td>2.42 (4)</td>
<td>2.982 (3)</td>
<td>122 (3)</td>
</tr>
<tr>
<td>N1—H1···N2i</td>
<td>0.87 (2)</td>
<td>2.68 (4)</td>
<td>3.125 (4)</td>
<td>113 (3)</td>
</tr>
<tr>
<td>N1—H1···C1i</td>
<td>0.87 (2)</td>
<td>2.95 (3)</td>
<td>3.507 (3)</td>
<td>124 (3)</td>
</tr>
<tr>
<td>N3—H3···C4i</td>
<td>0.88 (2)</td>
<td>2.85 (3)</td>
<td>3.585 (3)</td>
<td>143 (3)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x − 1/2, −y + 1/2, z − 1/2; (ii) x − 1/2, −y + 1/2, z + 1/2.

Table 4
Hydrogen-bond geometry (Å, °) for (IV).

<table>
<thead>
<tr>
<th>D—H—A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1—H2···N3</td>
<td>0.88 (2)</td>
<td>1.93 (2)</td>
<td>2.616 (2)</td>
<td>135 (2)</td>
</tr>
<tr>
<td>N3—H3···C2</td>
<td>0.85 (2)</td>
<td>2.42 (2)</td>
<td>2.9809 (3)</td>
<td>124 (2)</td>
</tr>
<tr>
<td>N1—H1···N2i</td>
<td>0.85 (2)</td>
<td>2.56 (2)</td>
<td>3.1162 (3)</td>
<td>124 (2)</td>
</tr>
<tr>
<td>N1—H1···C1ii</td>
<td>0.85 (2)</td>
<td>2.95 (2)</td>
<td>3.6523 (18)</td>
<td>141 (2)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x + 1/2, y + 1/2, z + 1/2; (ii) x − 1/2, −y + 1/2, z + 1/2.

Table 5
Hydrogen-bond geometry (Å, °) for (V).

<table>
<thead>
<tr>
<th>D—H—A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1—H2···N3</td>
<td>0.87 (2)</td>
<td>1.96 (2)</td>
<td>2.628 (2)</td>
<td>133 (2)</td>
</tr>
<tr>
<td>N3—H3···C2</td>
<td>0.87 (2)</td>
<td>2.45 (2)</td>
<td>2.9779 (17)</td>
<td>119 (2)</td>
</tr>
</tbody>
</table>

Table 6
Average bond lengths (Å) and angles (°) for compounds (I)–(V), and comparison with the averages in two biguanides [CSD recordes BIGUAN01 (Ernst & Cagle, 1977) and NIWCAY (Zheng et al., 2007)].

<table>
<thead>
<tr>
<th>Bond</th>
<th>Average in (I)–(V)</th>
<th>Average in biguanides</th>
<th>Angle</th>
<th>Average in (I)–(V)</th>
<th>Average in biguanides</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1—C1</td>
<td>1.327 (5)</td>
<td>1.325 (2)</td>
<td>151</td>
<td>1.325 (2)</td>
<td>1.328 (3)</td>
</tr>
<tr>
<td>C1—N2</td>
<td>1.323 (2)</td>
<td>1.329 (2)</td>
<td>122</td>
<td>1.329 (2)</td>
<td>1.334 (3)</td>
</tr>
<tr>
<td>C2—N3</td>
<td>1.278 (3)</td>
<td>1.295 (2)</td>
<td>125</td>
<td>1.295 (2)</td>
<td>1.307 (3)</td>
</tr>
<tr>
<td>C1—N2—C2</td>
<td>120.1 (2)</td>
<td>120.1 (2)</td>
<td>117</td>
<td>120.1 (2)</td>
<td>118.1 (2)</td>
</tr>
<tr>
<td>C2—C3</td>
<td>115.7 (3)</td>
<td>115.7 (3)</td>
<td>119</td>
<td>115.7 (3)</td>
<td>118.1 (2)</td>
</tr>
<tr>
<td>C1—C4</td>
<td>110.0 (4)</td>
<td>110.0 (4)</td>
<td>120</td>
<td>110.0 (4)</td>
<td>118.1 (2)</td>
</tr>
</tbody>
</table>

Refinement
R[F^2 > 2σ(F^2)] = 0.055
wR(F^2) = 0.064
S = 1.05
8708 reflections
434 parameters
9 restraints

H atoms treated by a mixture of independent and constrained refinement
Δρ_{max} = 0.47 e Å^{-3}
Δρ_{min} = −0.49 e Å^{-3}

Data collection
Bruker APEXII CCD area-detector diffractometer
16666 measured reflections
2803 independent reflections
2248 reflections with I > 2σ(I)
R_{int} = 0.041

Refinement
R[F^2 > 2σ(F^2)] = 0.050
wR(F^2) = 0.1022
S = 1.21
2803 reflections
154 parameters
3 restraints

H atoms treated by a mixture of independent and constrained refinement
Δρ_{max} = 0.50 e Å^{-3}
Δρ_{min} = −0.35 e Å^{-3}

Compound (III)
Crystal data
C_{14}H_{16}Cl_{14}N_{8},
M_r = 298.98
Monoclinic, P2_1/n
a = 5.762 (2) Å
b = 22.711 (8) Å
T = 173 K

µ = 0.94 mm^{-1}
0.32 × 0.10 × 0.08 mm

Data collection
Nonius KappaCCD area-detector diffractometer
14588 measured reflections
7908 independent reflections
R_{int} = 0.076

Refinement
R[F^2 > 2σ(F^2)] = 0.050
wR(F^2) = 0.1022
S = 1.21
2803 reflections
154 parameters
3 restraints

H atoms treated by a mixture of independent and constrained refinement
Δρ_{max} = 0.50 e Å^{-3}
Δρ_{min} = −0.35 e Å^{-3}

Compound (IV)
Crystal data
C_{14}H_{16}Br_{14}N_{8},
M_r = 343.44
Monoclinic, P2_1/n
a = 5.8124 (17) Å
b = 23.379 (7) Å
µ = 3.87 mm^{-1}
0.22 × 0.20 × 0.11 mm
Data collection
Bruker APEXII CCD area-detector
diffractometer
Absorption correction: multi-scan
(SADABS; Bruker, 2006)
\( T_{\text{min}} = 0.483, \ T_{\text{max}} = 0.684 \)

Refinement

\[ R[F^2 > 2\sigma(F^2)] = 0.024 \]
\[ wR(F^2) = 0.062 \]
\[ S = 1.08 \]
2898 reflections
157 parameters

H atoms treated by a mixture of
independent and constrained refinement
\( \Delta p_{\text{max}} = 0.61 \text{ e} \AA^{-3} \)
\( \Delta p_{\text{min}} = -0.36 \text{ e} \AA^{-3} \)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: YP3005). Services for accessing these data are described at the back of the journal.

References