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Five related N'-(2,2,2-trichloroethanimidoyl)benzeno-1-carboximidamides

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

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In the solid state, 4-methoxy-\( N'-(2,2,2\text{-trichloroethanimidoyl})\text{benzene-1-carboximidamide}, \quad \text{C}_{10}\text{H}_{10}\text{Cl}_{3}\text{N}_{3}\text{O}, \quad \text{(I)}, \quad \text{N'-(2,2,2\text{-trichloroethanimidoyl})benzene-1-carboximidamide}, \quad \text{C}_{9}\text{H}_{8}\text{Cl}_{3}\text{N}_{3}, \quad \text{(II)}, \quad 4\text{-chloro-} \quad \text{N'-(2,2,2\text{-trichloroethanimidoyl})benzene-1-carboximidamide}, \quad \text{C}_{9}\text{H}_{7}\text{Cl}_{3}\text{N}_{3}, \quad \text{(III)}, \quad 4\text{-bromo-} \quad \text{N'-(2,2,2\text{-trichloroethanimidoyl})benzene-1-carboximidamide}, \quad \text{C}_{9}\text{H}_{7}\text{BrCl}_{3}\text{N}_{3}, \quad \text{(IV)}, \quad \text{and} \quad 4\text{-trifluoromethyl-} \quad \text{N'-(2,2,2\text{-trichloroethanimidoyl})benzene-1-carboximidamide}, \quad \text{C}_{9}\text{H}_{7}\text{Cl}_{4}\text{N}_{3}, \quad \text{(V)}, \quad \text{are nearly identical, within their s.u. values, to the recently reported trifluoromethyl series (Boéré et al., 2011). Crystal structure reports of neutral primary N-imidoylamidines are rare. We recently reported the synthesis and crystal structures of a number of aryltrifluoromethyl N-imidoylamidines (Boéré et al., 2011). We report here the crystal structures of five new trichloromethyl analogues, (I)–(V), bearing electron-releasing and electron-withdrawing substituents on the aryl rings.}

Scheme 1

The molecular structures of (I)–(V) are remarkably similar and displacement ellipsoid plots are shown in Figs. 1, 3, 5, 7 and 8, respectively. The same atom-numbering scheme is used for all five structures [modified in the case of (II) by suffixes ‘A’, ‘B’ and ‘C’ to identify the three crystallographically independent molecules in the asymmetric unit]. Average bond lengths and angles for the \( \text{N}^1=\text{C}^2=\text{N}^3=\text{C}^2=\text{N}^3 \) cores have been compiled, along with s.u. values, and are listed in Table 6.

The average bond lengths show that \( \text{C}^1=\text{N}^1 \) and \( \text{C}^1=\text{N}^2 \) are of intermediate length between single and double bonds, as is characteristic of delocalized amidines, and are identical within their s.u. values. The \( \text{C}^2=\text{N}^3 \) bonds are short and more characteristic of imines, while the \( \text{N}^2=\text{C}^2 \) bonds are longer and approximate to single bonds. By contrast, the two \( \text{C}—\text{N} \) bonds to which the \(-\text{CCl}_3 \) group is attached in (Z)-2,2,2-trichloro-\( N^2 \)-cyanacetamide differ in length by only 0.008 A˚ (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.

Comment

N-Imidoylamidines (i.e. \( N^1 \)-imidoylcarboximidamides) are trinitrogen analogues of pentadienes containing unsaturated \( \text{N}^1=\text{C}^2=\text{N}^3=\text{C}^2=\text{N}^3 \) chains which may have different degrees of substitution at nitrogen. If the substituents at carbon are further N-containing groups, the familiar biguanides are obtained: imidoylamidines have carbon substituents on the backbone C atoms. Primary N-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 \( \pi \)-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 (Koplovich & Pombeiro, 2011).
The pentaazadiene cores of (I)–(V) are close to being planar and form six-membered rings through N1—H2⋯N3 hydrogen bonding [labelled Δ in Scheme 2, which shows a summary of the intra- (labelled Δ and Φ) and intermolecular (labelled Γ, Δ and Π) hydrogen bonds present in compounds (I)–(V)]. Donor–acceptor N⋯N distances for the Δ 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 (Φ 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 (Π in Scheme 2) serves to link the chains thus formed into two-
The intermolecular N1—H1···N2 hydrogen bonds in (III) (dotted lines) form threefold helices along the [010] direction, defining a noncrystallographic threefold screw axis through N1—H1···N2 contacts (see Fig. 4 and Table 2 for symmetry codes). This helix is associated to a second related by inversion by the noncrystallographic threefold screw axis through N1—H1 and Cl2···Cl4 in Scheme 2). In molecule (II), there is an additional intermolecular hydrogen bond between the N1—H1···Cl2 group and atom Cl1B of a neighbouring CCl3 group (A in Scheme 2).

![Figure 6](image)

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

![Figure 7](image)

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

![Figure 8](image)

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 [010] direction, defining a noncrystallographic threefold screw axis through N1—H1···N2 contacts (see Fig. 4 and Table 2 for symmetry codes). This helix is associated to a second related by inversion by the N3B···H3B···Cl1A hydrogen bond (II in Scheme 2), which occurs only once in the asymmetric unit. In both (III) and isomorphous (IV), there are twofold helices in the [010] direction, also through N1—H1···N2 contacts (see Fig. 6 for symmetry codes). This helical chain is expanded into a layer along the (010) plane through the N3···H3···Cl4 hydrogen bond in (III) or N3···H3···Br1 in (IV) (II 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···N2 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 (Boeré 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 (G 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 CCl3 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**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C10H11Cl3N3O</td>
<td>V = 1217.23 (17) Å³</td>
</tr>
<tr>
<td>Mr = 294.56</td>
<td>Z = 4</td>
</tr>
<tr>
<td>Monoclinic, P21/c</td>
<td>Mo Kα radiation</td>
</tr>
<tr>
<td>a = 12.0988 (10) Å</td>
<td>μ = 0.74 mm⁻¹</td>
</tr>
<tr>
<td>b = 8.6425 (7) Å</td>
<td>T = 173 K</td>
</tr>
<tr>
<td>c = 12.2023 (10) Å</td>
<td>0.21 × 0.19 × 0.07 mm</td>
</tr>
<tr>
<td>β = 107.445 (1)°</td>
<td></td>
</tr>
</tbody>
</table>

**Data collection**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bruker APEX2 CCD area-detector diffractometer</td>
<td>17246 measured reflections</td>
</tr>
<tr>
<td>Absorption correction: multi-scan (SADABS: Bruker, 2006)</td>
<td>2812 independent reflections</td>
</tr>
<tr>
<td></td>
<td>2448 reflections with I &gt; 2σ(I)</td>
</tr>
<tr>
<td>Truncation limits: 0.697, T max = 0.746</td>
<td>Rint = 0.026</td>
</tr>
</tbody>
</table>

**Table 1**

<table>
<thead>
<tr>
<th>Bond geometry (Å, °) for (I).</th>
</tr>
</thead>
<tbody>
<tr>
<td>D—H···A</td>
</tr>
<tr>
<td>N1—H2···N3</td>
</tr>
<tr>
<td>N3—H3···Cl2</td>
</tr>
<tr>
<td>N1—H1···Cl1</td>
</tr>
<tr>
<td>N3—H3···Cl3</td>
</tr>
</tbody>
</table>

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

Table 2
Hydrogen-bond geometry (Å, °) for (II).

<table>
<thead>
<tr>
<th></th>
<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</td>
<td>0.87 (2)</td>
<td>1.92 (3)</td>
<td>2.626</td>
<td>84.3 (3)</td>
<td>N1—H2</td>
</tr>
<tr>
<td>N2—H3</td>
<td>0.88 (2)</td>
<td>2.42 (4)</td>
<td>3.041</td>
<td>107.7 (3)</td>
<td>N2—H3</td>
</tr>
<tr>
<td>N3—H2</td>
<td>0.88 (2)</td>
<td>2.966 (3)</td>
<td>125 (3)</td>
<td>N3—H2</td>
<td></td>
</tr>
<tr>
<td>N3—H3</td>
<td>0.85 (2)</td>
<td>3.383 (3)</td>
<td>115 (3)</td>
<td>N3—H3</td>
<td></td>
</tr>
<tr>
<td>Symmetry codes: (i) x − 1, y, z − 3, (ii) −x + 1, −y + 2, −z.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th></th>
<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</td>
<td>0.87 (2)</td>
<td>1.92 (3)</td>
<td>2.626</td>
<td>84.3 (3)</td>
<td>N1—H2</td>
</tr>
<tr>
<td>N1—H3</td>
<td>0.88 (2)</td>
<td>2.42 (4)</td>
<td>3.041</td>
<td>107.7 (3)</td>
<td>N1—H3</td>
</tr>
<tr>
<td>N1—H1</td>
<td>0.87 (2)</td>
<td>2.56 (2)</td>
<td>3.116</td>
<td>124 (2)</td>
<td>N1—H1</td>
</tr>
<tr>
<td>N3—H1</td>
<td>0.85 (2)</td>
<td>2.90 (3)</td>
<td>3.511 (2)</td>
<td>N3—H1</td>
<td></td>
</tr>
<tr>
<td>Symmetry codes: (i) x − 1, y + z, z + 1, (ii) −x + z, −y + 1, z + 1.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th></th>
<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</td>
<td>0.88 (2)</td>
<td>1.93 (2)</td>
<td>2.616</td>
<td>85.5 (3)</td>
<td>N1—H2</td>
</tr>
<tr>
<td>N3—H3</td>
<td>0.85 (2)</td>
<td>2.42 (2)</td>
<td>2.989 (9)</td>
<td>N3—H3</td>
<td></td>
</tr>
<tr>
<td>N1—H1</td>
<td>0.85 (2)</td>
<td>2.56 (2)</td>
<td>3.116 (2)</td>
<td>N1—H1</td>
<td></td>
</tr>
<tr>
<td>N3—H1</td>
<td>0.85 (2)</td>
<td>2.95 (2)</td>
<td>3.652 (18)</td>
<td>N3—H1</td>
<td></td>
</tr>
<tr>
<td>Symmetry codes: (i) x + 1, y + z, z + 1, (ii) −x + z, −y + 1, z + 1.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th></th>
<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</td>
<td>0.87 (2)</td>
<td>1.96 (2)</td>
<td>2.628</td>
<td>81.5 (3)</td>
<td>N1—H2</td>
</tr>
<tr>
<td>N3—H3</td>
<td>0.97 (2)</td>
<td>2.45 (2)</td>
<td>2.977</td>
<td>115.2 (3)</td>
<td>N3—H3</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 refcodes BIGU011 (Ernst & Cagle, 1977) and NIWCAY (Zheng et al., 2007)].

<table>
<thead>
<tr>
<th>Bond</th>
<th>Average in (I)</th>
<th>Average in biguanides</th>
<th>Angle</th>
<th>Average in (I)</th>
<th>Average in biguanides</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1—C1</td>
<td>1.32 (5)</td>
<td>1.325 (2)</td>
<td>127.3 (3)</td>
<td>126.5 (2)</td>
<td>128.6 (2)</td>
</tr>
<tr>
<td>C1—N2</td>
<td>1.323 (2)</td>
<td>1.329 (2)</td>
<td>124 (3)</td>
<td>117.8 (4)</td>
<td></td>
</tr>
<tr>
<td>C2—N3</td>
<td>1.370 (3)</td>
<td>1.382 (2)</td>
<td>120.1 (2)</td>
<td>118.1 (2)</td>
<td></td>
</tr>
<tr>
<td>C2—C3</td>
<td>1.552 (7)</td>
<td>1.23 (2)</td>
<td>127 (3)</td>
<td>128.1 (2)</td>
<td></td>
</tr>
<tr>
<td>C1—C4</td>
<td>1.488 (5)</td>
<td>1.100 (4)</td>
<td>122.7 (4)</td>
<td>122.7 (4)</td>
<td></td>
</tr>
</tbody>
</table>

Refractive

\[ R[F^2 > 2\sigma(F^2)] = 0.055 \]

H atoms treated by a mixture of independent and constrained refinement

9708 reflections

434 parameters

9 restraints

Compound (III)

Crystal data

\[ C_4H_8ClN_3 \]

\[ M_r = 298.98 \]

Triclinic, \( \text{P} \)

\( a = 5.762 \) Å

\( b = 22.707 \) Å

\( c = 9.713 \) Å

\( \beta = 106.031 \) °

Data collection

Bruker APEXII CCD area-detector

16666 measured reflections

2803 independent reflections

154 parameters

3 restraints

Compound (II)

Crystal data

\[ C_6H_10Cl_3N_4 \]

\[ M_r = 264.53 \]

Monoclinic, \( \text{P}2_1/n \)

\( a = 10.2999 (3) \) Å

\( b = 10.9423 (3) \) Å

\( c = 15.6902 (4) \) Å

\( \alpha = 90.0 (2) \)

\( \beta = 85.5092 (12) \)

Data collection

Nonius KappaCCD area-detector diffractometer

14588 measured reflections

9708 independent reflections

Absorption correction: multi-scans

\( T_{	ext{min}} = 0.876, T_{	ext{max}} = 0.928 \)

Compound (IV)

Crystal data

\[ C_6H_12BrClN_4 \]

\[ M_r = 343.44 \]

Monoclinic, \( \text{P}2_1/n \)

\( a = 5.8124 (17) \) Å

\( b = 23.379 (7) \) Å

\( c = 9.715 (3) \) Å

\( \beta = 107.407 (3) \)

Refractive

\[ R[F^2 > 2\sigma(F^2)] = 0.050 \]

H atoms treated by a mixture of independent and constrained refinement

2248 reflections with \( I > 2\sigma(I) \)

\( R_{	ext{int}} = 0.041 \)

Compound (V)

Crystal data

\[ C_6H_10ClN_3 \]

\[ M_r = 259.79 \]

Monoclinic, \( \text{P}2_1/n \)

\( a = 5.8124 (17) \) Å

\( b = 23.379 (7) \) Å

\( c = 9.715 (3) \) Å

\( \beta = 107.407 (3) \)

Refractive

\[ R[F^2 > 2\sigma(F^2)] = 0.055 \]

H atoms treated by a mixture of independent and constrained refinement

2248 reflections with \( I > 2\sigma(I) \)

\( R_{	ext{int}} = 0.041 \)

3 restraints

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

\( \Delta \rho_{\text{max}} = 0.61 e \AA^{-3} \)

\( \Delta \rho_{\text{min}} = -0.36 e \AA^{-3} \)

\begin{align*}
\text{Compound data} & \\
C_{10}H_{7}Cl_{3}F_{3}N_{3} & \\
V = 1274.0 (3) \AA^3 & \\
Z = 4 & \\
\mu = 0.74 \text{ mm}^{-1} & \\
T = 173 \text{ K} & \\
\omega = 0.25 \times 0.25 \times 0.12 \text{ mm} & \\
\text{Data collection} & \\
Bruker APEXII CCD area-detector diffractometer & \\
Absorption correction: multi-scan & \\
(SADABS; Bruker, 2006) & \\
\( T_{\text{min}} = 0.699, T_{\text{max}} = 0.746 \) & \\
\text{Refinement} & \\
\( R[F^2 > 2\sigma(F^2)] = 0.036 \) & \\
w\( R(F^2) = 0.098 \) & \\
\( S = 1.06 \) & \\
3191 reflections & \\
181 parameters & \\
3 restraints & \\
\text{C-bound H atoms were treated as riding, with C—H = 0.98 \AA} & \\
and U_{eq}(H) = 1.5U_{eq}(C) for methyl and C—H = 0.95—0.96 \AA & \\
and U_{eq}(H) = 1.2U_{eq}(C) for all other H atoms. The three N-bound H-atom positions \text{ were refined using a distance restraint of 0.88 \AA} & \\
and with U_{eq}(H) = 1.2U_{eq}(N). \)

For all five compounds, data collection: APEX2 (Bruker, 2006); cell refinement: SAINT-Plus (Bruker, 2006); data reduction: SAINT-Plus (program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXTL (Sheldrick, 2008); molecular graphics: Mercury (Macrae et al., 2008); software used to prepare material for publication: pubCIF (Westrip, 2010).

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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


