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

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In the solid state, 4-methoxy-$N'-(2,2,2$-trichloroethanimidoyl)-benzene-1-carboximidamide, $C_{10}H_{10}Cl_{3}N_{3}O$, (I), $N'-(2,2,2$-trichloroethanimidoyl)benzene-1-carboximidamide, $C_{9}H_{8}Cl_{3}N_{3}$, (II), 4-chloro-$N'-(2,2,2$-trichloroethanimidoyl)benzene-1-carboximidamide, $C_{9}H_{7}Cl_{3}N_{3}$, (III), 4-bromo-$N'-(2,2,2$-trichloroethanimidoyl)benzene-1-carboximidamide, $C_{9}H_{7}BrCl_{3}N_{3}$, (IV), and 4-trifluoromethyl-$N'-(2,2,2$-trichloroethanimidoyl)benzene-1-carboximidamide, $C_{10}H_{7}Cl_{3}F_{3}N_{3}$, (V), display strong intramolecular N—H · · · Cl contacts. Additional intermolecular hydrogen bonding between the molecules is observed in some cases. The average bond lengths show that C1—N1 and C1—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—N3 bonds 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 (Zheng & Pombeiro, 2011). Crystal structure reports of neutral primary N-imidoylamidines are rare. We recently reported the synthesis and crystal structures of a number of aryltrifluoro-methyl 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.
The molecular structure of the new compounds (I)–(V) is reminiscent of diiminoisoindoline (Zhang, Njus et al., 2004), including the observation of the amino tautomer in the solid state. Furthermore, the hydrogen-bonding pattern in the new compounds is similar to that in diiminoisoindoline and 1-amino-3-phenyliminoisoindoline (Zhang, Uth et al., 2004).

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] (Boereè 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 in 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), forming chains of equivalent molecules aligned exactly with the ac diagonal of the unit cell, resulting in a two-fold helix along the [101] direction. Compound (IV) is isomorphous with (III). Ellipsoids are shown at the 30% probability level. [Symmetry codes: (i) x, −y + 1/2, z − 1/2; (ii) x, y, z; (iii) x, −y + 1/2, z; (iv) x + 1, y, z + 1.]

Figure 6
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 two-fold helix along the [101] direction. Compound (IV) is isomorphous with (III). Ellipsoids are shown at the 30% probability level. [Symmetry codes: (i) x, −y + 1/2, z − 1/2; (ii) x, y, z; (iii) x, −y + 1/2, z; (iv) x + 1, y, z + 1.]

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···Cl1Aiv hydrogen bond (Π in Scheme 2), which occurs only once in the asymmetric unit. In both (III) and isomorphous (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···Cl4iv 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···N2iiii 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 (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 CC1 group (A in Scheme 2).

Experimental
Compounds (I)–(V) were prepared using a modification of a literature procedure (Peters & Schaefer, 1964) by addition of trichloroacetamide 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.

Table 1
Hydrogen-bond geometry (Å, °) for (I).

<table>
<thead>
<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>D···A</th>
<th>D···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>
<td>132 (2)</td>
</tr>
<tr>
<td>N3—H3···Cl2</td>
<td>0.86 (2)</td>
<td>2.43 (2)</td>
<td>2.9791 (15)</td>
<td>123 (2)</td>
</tr>
<tr>
<td>N1—H1···Cl1</td>
<td>0.85 (1)</td>
<td>2.20 (2)</td>
<td>3.0315 (17)</td>
<td>166 (2)</td>
</tr>
<tr>
<td>N3—H3···Cl3</td>
<td>0.86 (2)</td>
<td>2.76 (2)</td>
<td>3.4077 (15)</td>
<td>134 (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

Table 2
Hydrogen-bond geometry (Å, º) 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 · · · N3</td>
<td>0.89 (2)</td>
<td>1.99 (3)</td>
<td>2.657 (4)</td>
<td>130 (3)</td>
</tr>
<tr>
<td>N3—H3 · · · Cl1</td>
<td>0.88 (2)</td>
<td>2.38 (3)</td>
<td>2.969 (3)</td>
<td>125 (3)</td>
</tr>
<tr>
<td>N1—H1 · · · N21</td>
<td>0.88 (2)</td>
<td>2.26 (2)</td>
<td>3.126 (4)</td>
<td>172 (3)</td>
</tr>
<tr>
<td>N1—H1 · · · N2</td>
<td>0.87 (2)</td>
<td>2.28 (2)</td>
<td>3.136 (4)</td>
<td>171 (3)</td>
</tr>
<tr>
<td>N3—H3 · · · Cl2B</td>
<td>0.88 (2)</td>
<td>2.41 (3)</td>
<td>2.978 (3)</td>
<td>122 (3)</td>
</tr>
<tr>
<td>N1—H2 · · · N3B</td>
<td>0.89 (2)</td>
<td>1.94 (3)</td>
<td>2.646 (4)</td>
<td>135 (3)</td>
</tr>
<tr>
<td>N3—H3 · · · Cl3A</td>
<td>0.88 (2)</td>
<td>2.91 (3)</td>
<td>3.383 (3)</td>
<td>115 (3)</td>
</tr>
<tr>
<td>N1—H2 · · · N3C</td>
<td>0.89 (2)</td>
<td>1.91 (3)</td>
<td>2.644 (4)</td>
<td>138 (3)</td>
</tr>
<tr>
<td>N5C—H5C · · · Cl2C</td>
<td>0.87 (2)</td>
<td>2.47 (3)</td>
<td>3.023 (3)</td>
<td>122 (3)</td>
</tr>
<tr>
<td>N1—H2 · · · N2B</td>
<td>0.87 (2)</td>
<td>2.24 (2)</td>
<td>3.072 (3)</td>
<td>160 (3)</td>
</tr>
<tr>
<td>N1—H2 · · · 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, º) 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 · · · N2</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 · · · C1</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 · · · C4</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; (ii) x −1/2, −y + 1/2, z −1/2.

Table 4
Hydrogen-bond geometry (Å, º) 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>2.989 (3)</td>
<td>124 (2)</td>
</tr>
<tr>
<td>N1—H1 · · · N2</td>
<td>0.85 (2)</td>
<td>2.56 (2)</td>
<td>3.116 (2)</td>
<td>124 (2)</td>
</tr>
<tr>
<td>N3—H3 · · · Br1</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; (ii) x + 1/2, −y + 1/2, z − 1/2.

Table 5
Hydrogen-bond geometry (Å, º) 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>2.977 (17)</td>
<td>119 (2)</td>
</tr>
</tbody>
</table>

Table 6
Average bond lengths (Å) and angles (º) for compounds (I)–(V), and comparison with the averages in two biguanides [CSD refcodes BIGUANO1 (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>1.327 (5)</td>
<td>1.329 (3)</td>
<td>117.8 (4)</td>
<td></td>
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</tr>
<tr>
<td>C1—C2</td>
<td>1.323 (2)</td>
<td>1.329 (3)</td>
<td>117.8 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N2—C2</td>
<td>1.370 (3)</td>
<td>1.382 (2)</td>
<td>118.1 (2)</td>
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<td></td>
</tr>
<tr>
<td>C2—N3</td>
<td>1.278 (3)</td>
<td>1.295 (2)</td>
<td>118.2 (2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Re refinement

Refinement R[F^2 > 2σ(F^2)] = 0.055

wR(F^2) = 0.064

S = 1.05

2812 reflections

164 parameters

3 restraints

Compound (III)

Crystal data
C_{14}H_{13}Cl_{2}N_{3}

M_w = 298.98

Monoclinic, C2/a

Z = 4

a = 5.762 (2) Å

b = 22.711 (8) Å

c = 9.713 (4) Å

β = 106.031 (4)º

Crystal collection

Bruker APEX2 CCD area-detector diffractometer

16666 measured reflections

2203 independent reflections

2248 reflections with I > 2σ(I)

Refinement

R[F^2 > 2σ(F^2)] = 0.050

wR(F^2) = 0.122

S = 1.21

2803 reflections

154 parameters

3 restraints

Compound (IV)

Crystal data
C_{18}H_{13}Cl_{2}N_{3}

M_w = 343.44

Monoclinic, P2_1/n

Z = 4

a = 5.812 (17) Å

b = 23.379 (7) Å

c = 9.715 (3) Å

β = 107.407 (3)º

Crystal collection

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan
(SADABS; Bruker, 2006)
\( T_{\text{max}} = 0.483, T_{\text{min}} = 0.684 \)

Refinement

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

\( R_w = 0.068 \)

\( R_{\text{factor}} \) and \( wR_{\text{factor}} \) for all reflections

\( \Delta \rho_{\text{max}} = 0.61 \ \text{e} \ \text{Å}^{-3} \)
\( \Delta \rho_{\text{min}} = -0.36 \ \text{e} \ \text{Å}^{-3} \)

H atoms treated by a mixture of independent and constrained refinement

\( \Delta \rho_{\text{max}} = 0.90 \ \text{e} \ \text{Å}^{-3} \)
\( \Delta \rho_{\text{min}} = -0.58 \ \text{e} \ \text{Å}^{-3} \)

C-bound H atoms were treated as riding, with C—H = 0.98 Å and \( U_{\text{iso}}(H) = 1.5U_{\text{eq}}(C) \) for methyl and C—H = 0.95–0.96 Å and \( U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C) \) for all other H atoms. The three N-bound H-atom positions were refined using a distance restraint of 0.88 Å and with \( U_{\text{iso}}(H) = 1.2U_{\text{eq}}(N) \).

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