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# Five related N'-(2,2,2-trichloroethanimidoyl)benzen

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Five related *N'*-(2,2,2-trichloroethanimidoyl)benzene-1-carboximidamidesRené T. Boéré,<sup>a\*</sup> Tracey L. Roemmele,<sup>a</sup> Savini Suduweli Kondage,<sup>a</sup> Jiamin Zhou<sup>a</sup> and Masood Parvez<sup>b</sup><sup>a</sup>Department of Chemistry and Biochemistry, University of Lethbridge, Lethbridge, Alberta, Canada T1K 3M4, and <sup>b</sup>Department of Chemistry, University of Calgary, Calgary, Alberta, Canada

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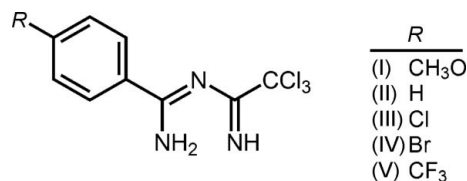
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In the solid state, 4-methoxy-*N'*-(2,2,2-trichloroethanimidoyl)benzene-1-carboximidamide, C<sub>10</sub>H<sub>10</sub>Cl<sub>3</sub>N<sub>3</sub>O, (I), *N'*-(2,2,2-trichloroethanimidoyl)benzene-1-carboximidamide, C<sub>9</sub>H<sub>8</sub>Cl<sub>3</sub>N<sub>3</sub>, (II), 4-chloro-*N'*-(2,2,2-trichloroethanimidoyl)benzene-1-carboximidamide, C<sub>9</sub>H<sub>7</sub>Cl<sub>4</sub>N<sub>3</sub>, (III), 4-bromo-*N'*-(2,2,2-trichloroethanimidoyl)benzene-1-carboximidamide, C<sub>9</sub>H<sub>7</sub>BrCl<sub>3</sub>N<sub>3</sub>, (IV), and 4-trifluoromethyl-*N'*-(2,2,2-trichloroethanimidoyl)benzene-1-carboximidamide, C<sub>10</sub>H<sub>7</sub>Cl<sub>3</sub>F<sub>3</sub>N<sub>3</sub>, (V), display strong intramolecular N—H···N hydrogen bonding across the chelate ring and also intramolecular N—H···Cl contacts. Additional intermolecular hydrogen bonds link the molecules into chains, double chains or sheets in all cases except for compound (V). For compound (II), there are three independent molecules per asymmetric unit.

## Comment

*N*-Imidoylamidines (*i.e.* *N'*-imidoylcarboximidamides) are tri-nitrogen analogues of pentadienes containing unsaturated N=C=N=C=N 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 (Kop-

vlovich & Pombeiro, 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 N=C=N=C=N cores have been compiled, along with s.u. values, and are listed in Table 6.

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 short and more characteristic of imines, while the N2—C2 bonds are longer and approximate to single bonds. By contrast, the two C—N bonds to which the —CCl<sub>3</sub> group is attached in (*Z*)-2,2,2-trichloro-*N'*-cyanoacetamide 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

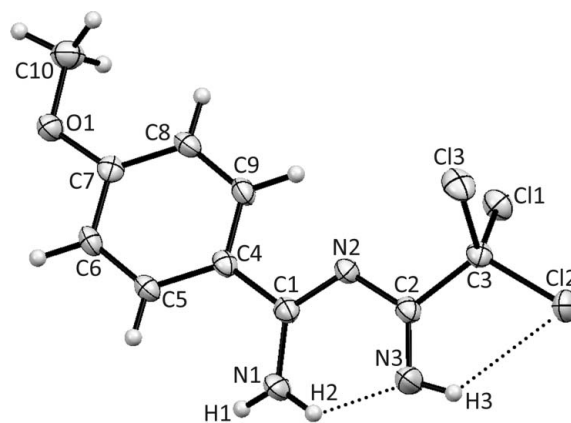
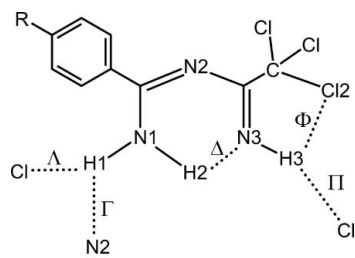


Figure 1

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 suffixes A, B and C. All seven independent molecules display intramolecular N1···N3 and N3···Cl2 hydrogen bonding within the crystal structure, indicated by dotted lines.

[Cambridge Structural Database (Allen, 2002) refcodes HDCADPZ (Privett *et al.*, 1987); BIGUAN (Pinkerton & Schwarzenbach, 1978) and BIGUAN01 (Ernst & Cagle, 1977); NIWCAY (Zheng *et al.*, 2007)]. The molecular structure of the new compounds (I)–(V) is reminiscent of diiminoisindoline (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 diiminoisindoline and 1-amino-3-phenyliminoisindoline (Zhang, Uth *et al.*, 2004).



Scheme 2

The pentaazadiene cores of (I)–(V) are close to being planar and form six-membered rings through N1–H2···N3

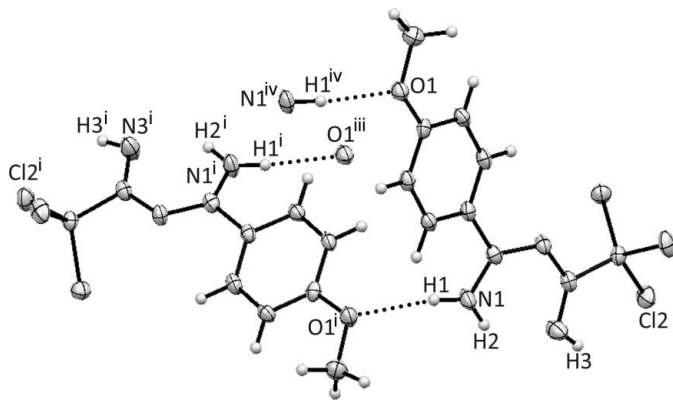


Figure 2

The intermolecular N1–H1···O1 hydrogen bonds in (I) (dotted lines), linking the molecules into a twofold helix in the [010] direction. The two (equivalent) linked molecules are viewed approximately down the *b* axis; extension of the chain to the N1–H1 unit above and to atom O1 below is also shown. Ellipsoids are shown at the 30% probability level. [Symmetry codes: (i)  $-x, y + \frac{1}{2}, -z - \frac{1}{2}$ ; (iii)  $x, y + 1, z$ ; (iv)  $-x, y + \frac{1}{2}, z - \frac{1}{2}$ ]

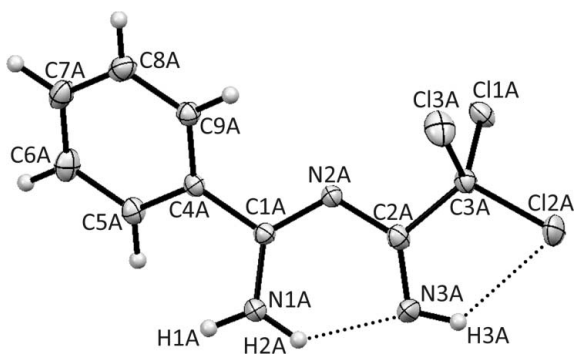


Figure 3

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

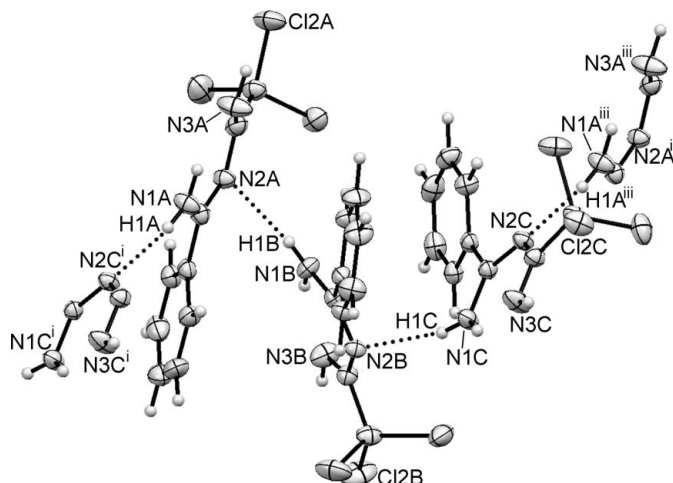


Figure 4

The intermolecular N1–H1···N2 hydrogen bonds in (II) (dotted lines), linking the three unique molecules into a threefold helix in the [100] direction with a noncrystallographic threefold screw axis. The three unique molecules A, B and C are shown, along with the adjacent triazapenta-1,3-diene cores at either end. The view is approximately perpendicular to the *bc* diagonal. Ellipsoids are shown at the 30% probability level. [Symmetry codes: (i)  $x + 1, y, z$ ; (iii)  $x - 1, y, z$ ]

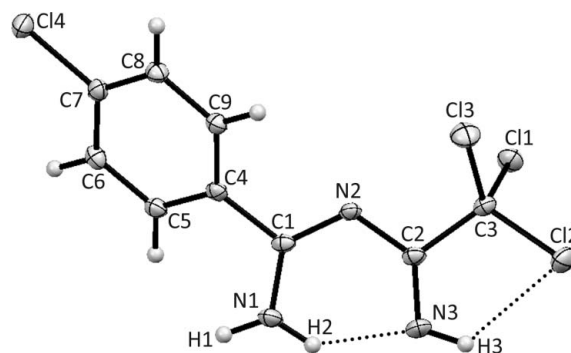
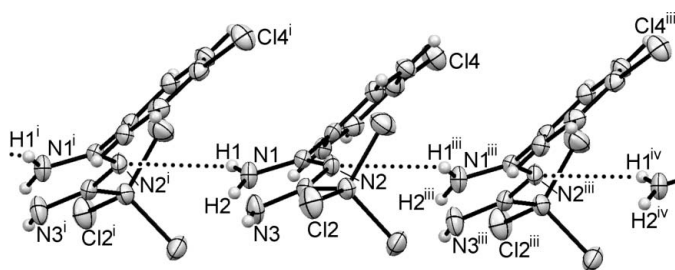


Figure 5

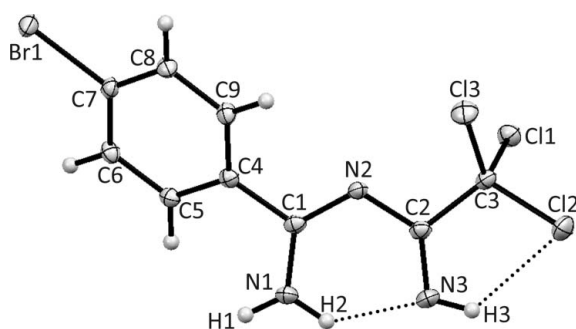
Displacement ellipsoid plot (drawn at the 30% probability level) of (III) at 173 (2) K.

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] (Boéré *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.

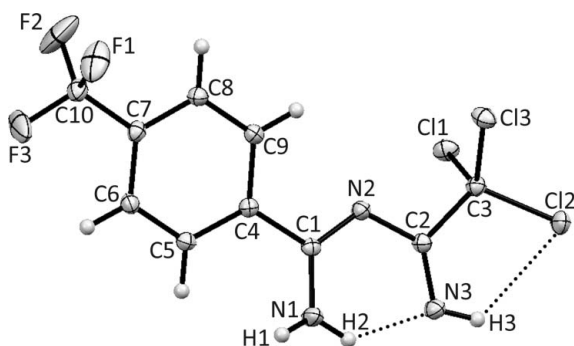
The intermolecular hydrogen bonding is also very noteworthy. Within the crystal structure, molecules of (I) are linked by N1–H1···O1<sup>i,iii</sup> hydrogen bonds that form a twofold helix along the [010] direction (see Fig. 2 and Table 1 for symmetry codes). N3–H3···Cl3<sup>ii</sup> hydrogen bond ( $\Pi$  in Scheme 2) serves to link the chains thus formed into two-

**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 twofold helix along the [101] direction. Compound (IV) is isomorphous with (III). Ellipsoids are shown at the 30% probability level. [Symmetry codes: (i)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (iii)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (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...N2<sup>i,iii</sup> 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<sup>ii</sup> hydrogen bond ( $\Pi$  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...N2<sup>i,iii</sup> contacts (see Fig. 6 for symmetry codes). This helical chain is expanded into a layer along the (040) plane through the N3—H3...Cl4<sup>ii</sup> hydrogen bond in (III) or N3—H3...Br1<sup>ii</sup> in (IV) ( $\Pi$  in Scheme 2). Only

(V) does not display intermolecular hydrogen bonding, presumably a consequence of the rather bulky CF<sub>3</sub> group on the aryl ring. In (II), (III) and (IV), hydrogen bonds of the type N1—H1...N2<sup>i,iii</sup> link a terminal NH<sub>2</sub> group on one molecule with the central (backbone) N atom of a neighbouring molecule ( $\Lambda$  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 (Boéré *et al.*, 2011) show the single tautomeric form in the solid-state structure. The terminal NH<sub>2</sub> 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 ( $\Gamma$  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 CCl<sub>3</sub> group ( $\Lambda$  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 benzimidines 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

C <sub>10</sub> H <sub>10</sub> Cl <sub>3</sub> N <sub>3</sub> O	$V = 1217.23 (17) \text{ \AA}^3$
$M_r = 294.56$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 12.0988 (10) \text{ \AA}$	$\mu = 0.74 \text{ mm}^{-1}$
$b = 8.6425 (7) \text{ \AA}$	$T = 173 \text{ K}$
$c = 12.2023 (10) \text{ \AA}$	$0.21 \times 0.19 \times 0.07 \text{ mm}$
$\beta = 107.445 (1)^\circ$	

### Data collection

Bruker APEXII CCD area-detector diffractometer	17246 measured reflections
Absorption correction: multi-scan ( <i>SADABS</i> ; Bruker, 2006)	2812 independent reflections
$T_{\min} = 0.697, T_{\max} = 0.746$	2448 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.026$

**Table 1**

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H2...N3	0.86 (1)	2.00 (2)	2.647 (2)	132 (2)
N3—H3...Cl2	0.86 (2)	2.43 (2)	2.9791 (15)	123 (2)
N1—H1...O1 <sup>i</sup>	0.85 (1)	2.20 (2)	3.0315 (17)	166 (2)
N3—H3...Cl3 <sup>ii</sup>	0.86 (2)	2.76 (2)	3.4077 (15)	134 (2)

Symmetry codes: (i)  $-x, y + \frac{1}{2}, -z - \frac{1}{2}$ ; (ii)  $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$ .

**Table 2**

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1A—H2A...N3A	0.89 (2)	1.99 (3)	2.657 (4)	130 (3)
N3A—H3A...Cl2A	0.88 (2)	2.38 (3)	2.969 (3)	125 (3)
N1A—H1A...N2C <sup>i</sup>	0.88 (2)	2.26 (2)	3.126 (4)	172 (3)
N1B—H1B...N2A	0.87 (2)	2.28 (2)	3.136 (4)	171 (3)
N3B—H3B...Cl2B	0.88 (2)	2.41 (3)	2.978 (3)	122 (3)
N1B—H2B...N3B	0.89 (2)	1.94 (3)	2.646 (4)	135 (3)
N3B—H3B...Cl1A <sup>ii</sup>	0.88 (2)	2.91 (3)	3.383 (3)	115 (3)
N1C—H2C...N3C	0.89 (2)	1.91 (3)	2.644 (4)	138 (3)
N3C—H3C...Cl2C	0.87 (2)	2.47 (3)	3.023 (3)	122 (3)
N1C—H1C...N2B	0.87 (2)	2.24 (2)	3.072 (3)	160 (3)
N1C—H1C...Cl1B	0.87 (2)	2.90 (3)	3.511 (3)	128 (3)

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

**Table 3**

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H2...N3	0.87 (2)	1.92 (3)	2.628 (4)	137 (3)
N3—H3...Cl2	0.88 (2)	2.42 (4)	2.982 (3)	122 (3)
N1—H1...N2 <sup>i</sup>	0.87 (2)	2.68 (4)	3.125 (4)	113 (3)
N1—H1...Cl1 <sup>i</sup>	0.87 (2)	2.95 (3)	3.507 (3)	124 (3)
N3—H3...Cl4 <sup>ii</sup>	0.88 (2)	2.85 (3)	3.585 (3)	143 (3)

Symmetry codes: (i)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (ii)  $x - \frac{3}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ .

**Table 4**

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H2...N3	0.88 (2)	1.93 (2)	2.616 (2)	135 (2)
N3—H3...Cl2	0.85 (2)	2.42 (2)	2.9809 (19)	124 (2)
N1—H1...N2 <sup>i</sup>	0.85 (2)	2.56 (2)	3.116 (2)	124 (2)
N3—H3...Br1 <sup>ii</sup>	0.85 (2)	2.95 (2)	3.6523 (18)	141 (2)

Symmetry codes: (i)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (ii)  $x + \frac{3}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ .

**Refinement**

$R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.064$   
 $S = 1.05$   
 2812 reflections  
 164 parameters  
 3 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.25 \text{ e } \text{Å}^{-3}$

**Compound (II)**

**Crystal data**

$\text{C}_9\text{H}_8\text{Cl}_3\text{N}_3$   
 $M_r = 264.53$   
 Triclinic,  $P\bar{1}$   
 $a = 10.2999 (3) \text{ Å}$   
 $b = 10.9423 (3) \text{ Å}$   
 $c = 15.6902 (4) \text{ Å}$   
 $\alpha = 85.5518 (12)^\circ$   
 $\beta = 86.5092 (12)^\circ$

$\gamma = 81.5436 (11)^\circ$   
 $V = 1741.67 (8) \text{ Å}^3$   
 $Z = 6$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.76 \text{ mm}^{-1}$   
 $T = 173 \text{ K}$   
 $0.18 \times 0.15 \times 0.10 \text{ mm}$

**Data collection**

Nonius KappaCCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 2006)  
 $T_{\min} = 0.876, T_{\max} = 0.928$

14588 measured reflections  
 7908 independent reflections  
 4900 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.076$

**Table 5**

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H2...N3	0.87 (2)	1.96 (2)	2.628 (2)	133 (2)
N3—H3...Cl2	0.87 (2)	2.45 (2)	2.9779 (17)	119 (2)

**Table 6**

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

Bond	Average in (I)–(V)	Average in biguanides	Angle	Average in (I)–(V)	Average in biguanides
N1—C1	1.327 (5)	1.325 (2)	N1—C1—N2	125.6 (2)	128.6 (2)
C1—N2	1.323 (7)	1.329 (2)	N1—C1—C4	117.8 (4)	
N2—C2	1.370 (3)	1.382 (2)	C4—C1—N2	116.7 (3)	
C2—N3	1.278 (3)	1.295 (2)	C1—N2—C2	120.1 (2)	118.1 (2)
C2—C3	1.552 (7)		N2—C2—N3	127.3 (3)	128.1 (2)
C1—C4	1.488 (5)		N2—C2—C3	110.0 (4)	
			N3—C2—C3	122.7 (4)	

**Refinement**

$R[F^2 > 2\sigma(F^2)] = 0.055$   
 $wR(F^2) = 0.151$   
 $S = 0.97$   
 7908 reflections  
 434 parameters  
 9 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.47 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.49 \text{ e } \text{Å}^{-3}$

**Compound (III)**

**Crystal data**

$\text{C}_9\text{H}_7\text{Cl}_4\text{N}_3$   
 $M_r = 298.98$   
 Monoclinic,  $P2_1/n$   
 $a = 5.762 (2) \text{ Å}$   
 $b = 22.711 (8) \text{ Å}$   
 $c = 9.713 (4) \text{ Å}$   
 $\beta = 106.031 (4)^\circ$

$V = 1221.7 (8) \text{ Å}^3$   
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.94 \text{ mm}^{-1}$   
 $T = 173 \text{ K}$   
 $0.32 \times 0.10 \times 0.08 \text{ mm}$

**Data collection**

Bruker APEXII CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 2006)  
 $T_{\min} = 0.613, T_{\max} = 0.746$

16666 measured reflections  
 2803 independent reflections  
 2248 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.041$

**Refinement**

$R[F^2 > 2\sigma(F^2)] = 0.050$   
 $wR(F^2) = 0.122$   
 $S = 1.21$   
 2803 reflections  
 154 parameters  
 3 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.50 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.35 \text{ e } \text{Å}^{-3}$

**Compound (IV)**

**Crystal data**

$\text{C}_9\text{H}_7\text{BrCl}_3\text{N}_3$   
 $M_r = 343.44$   
 Monoclinic,  $P2_1/n$   
 $a = 5.8124 (17) \text{ Å}$   
 $b = 23.379 (7) \text{ Å}$   
 $c = 9.715 (3) \text{ Å}$   
 $\beta = 107.407 (3)^\circ$

$V = 1259.7 (6) \text{ Å}^3$   
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 3.87 \text{ mm}^{-1}$   
 $T = 173 \text{ K}$   
 $0.22 \times 0.20 \times 0.11 \text{ mm}$

**Data collection**

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

17762 measured reflections  
2898 independent reflections  
2563 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.068$

**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  
 $\Delta\rho_{\text{max}} = 0.61 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.36 \text{ e } \text{\AA}^{-3}$

**Compound (V)****Crystal data**

$\text{C}_{10}\text{H}_7\text{Cl}_3\text{F}_3\text{N}_3$   
 $M_r = 332.54$   
Monoclinic,  $P2_1/n$   
 $a = 11.2939 (17) \text{ \AA}$   
 $b = 8.3914 (13) \text{ \AA}$   
 $c = 13.505 (2) \text{ \AA}$   
 $\beta = 95.505 (2)^\circ$

$V = 1274.0 (3) \text{ \AA}^3$   
 $Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 0.74 \text{ mm}^{-1}$   
 $T = 173 \text{ K}$   
 $0.25 \times 0.25 \times 0.12 \text{ mm}$

**Data collection**

Bruker APEXII CCD area-detector diffractometer  
Absorption correction: multi-scan (SADABS; Bruker, 2006)  
 $T_{\min} = 0.699$ ,  $T_{\max} = 0.746$

18460 measured reflections  
3191 independent reflections  
2862 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.018$

**Refinement**

$R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.098$   
 $S = 1.06$   
3191 reflections  
181 parameters  
3 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.90 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.58 \text{ e } \text{\AA}^{-3}$

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

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.

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