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## Structure Reports

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4-Methyl-*N'*-(2,2,2-trichloroethanimidoyl)benzene-1-carboximidamide

Tracey L. Roemmele and René T. Boéré\*

Department of Chemistry and Biochemistry, University of Lethbridge, Lethbridge, AB, Canada T1K 3M4

Correspondence e-mail: boere@uleth.ca

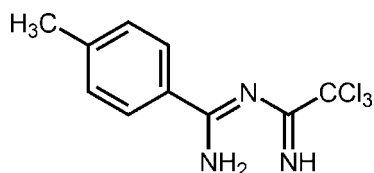
Received 20 October 2011; accepted 26 October 2011

Key indicators: single-crystal X-ray study;  $T = 173$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.029;  $wR$  factor = 0.077; data-to-parameter ratio = 17.5.

The title compound,  $\text{C}_{10}\text{H}_{10}\text{Cl}_3\text{N}_3$ , features a delocalized unsaturated  $\text{N}=\text{C}=\text{N}=\text{C}=\text{N}$  chain and strong intramolecular  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonding across the chelate ring and also intramolecular  $\text{N}-\text{H}\cdots\text{Cl}$  contacts to a  $\text{CCl}_3$ -group Cl atom. The only intermolecular contacts in the lattice are non-classical hydrogen bonds between methyl and  $\text{CCl}_3$  groups. The pseudo-six-membered ring is distinctly non-planar by virtue of rotation about the  $\text{N}-\text{C}$  bond between the carboximidamide and imine components [ $\text{C}-\text{N}-\text{C}-\text{N}$  torsion angle =  $-23.6(2)^\circ$ ].

## Related literature

For crystal structures of closely related *N'*-(trichloro/trifluoroethanimidoyl)aryl-1-carboximidamides, see: Boéré, Roemmele, Suduweli Kondage *et al.* (2011); Boéré, Roemmele & Yu (2011). For a review of this less-common class of chelating ligands, see: Kopylovich & Pombeiro (2011).



## Experimental

## Crystal data

$\text{C}_{10}\text{H}_{10}\text{Cl}_3\text{N}_3$   
 $M_r = 278.56$   
 Monoclinic,  $P2_1/c$   
 $a = 12.2952(7)$  Å

$b = 9.0696(6)$  Å  
 $c = 11.5407(7)$  Å  
 $\beta = 109.661(1)^\circ$   
 $V = 1211.90(13)$  Å<sup>3</sup>

$Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.73$  mm<sup>-1</sup>

$T = 173$  K  
 $0.43 \times 0.34 \times 0.25$  mm

## Data collection

Bruker APEXII CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 2008)  
 $T_{\min} = 0.747$ ,  $T_{\max} = 0.838$

16754 measured reflections  
 2762 independent reflections  
 2594 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.014$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.077$   
 $S = 1.08$   
 2762 reflections  
 158 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.40$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.41$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H2}\cdots\text{N3}$	0.83 (2)	2.07 (2)	2.683 (2)	130.8 (18)
$\text{N3}-\text{H3}\cdots\text{Cl1}$	0.81 (2)	2.49 (2)	2.9993 (15)	122.2 (19)
$\text{C10}-\text{H10A}\cdots\text{Cl2}^i$	0.98	2.93	3.871 (2)	162 (1)
$\text{C10}-\text{H10C}\cdots\text{Cl3}^{ii}$	0.98	2.93	3.581 (2)	125 (1)

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

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT-Plus (Bruker, 2008); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: publCIF (Westrip, 2010).

This research was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada. The diffractometer at the University of Lethbridge X-ray Diffraction Facility was purchased with the help of the NSERC and the University of Lethbridge.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2466).

## References

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**supplementary materials**

*Acta Cryst.* (2011). E67, o3137 [ doi:10.1107/S1600536811044710 ]

## 4-Methyl-*N'*-(2,2,2-trichloroethanimidoyl)benzene-1-carboximidamide

T. L. Roemmele and R. T. Boéré

### Comment

The title compound (Figure 1), commonly known as an imidoylamidine, was prepared as part of our continuing interest in *C,N,S* based heterocycles (Boéré, Roemmele & Yu, 2011). The molecular structure is very similar to seven independent molecules from our previous study (Boéré, Roemmele, Suduweli Kondage *et al.*, 2011), with only a single tautomeric form being evidenced in the crystal lattice. The bond lengths and angles for the  $N\cdots C\cdots N\cdots C\cdots N$  core are nearly identical within the s.u. values to the comparison group. Intramolecular hydrogen bonding occurs between  $N1-H2\cdots N3$  at 2.683 (2) Å to form a *pseudo* six membered ring. This hydrogen bond is slightly longer (just outside the s.u. values) than the previously reported average of 2.638 (14) Å, which is likely due to a slight rotation of the core ( $C1-N2-C2-N3$  torsion angle = 23.6 (2) °) which causes  $N3$  to be twisted out of the plane of the other four atoms ( $N1,C1,N2,C2$ ) compared to a range of 4.2 (5) to 16.0 (2) ° for this torsion angle in the comparison group. Also noteworthy is a short intramolecular  $N3-H3\cdots C11$  contact at 2.9993 (15) Å, which is within s.u. values of the other known trichloromethyl imidoylamidines. The most surprising feature is the complete lack of intermolecular hydrogen bonding involving the NH or  $NH_2$  groups, which was previously observed only in the structure of 4-trifluoromethyl-*N'*-(2,2,2-trichloroethanimidoyl)benzene-1-carboximidamide. In fact, the only short contacts are non-classical hydrogen bonds between the methyl and  $CCl_3$  groups, specifically from  $H10A$  to  $Cl2^i$  and  $H10C$  to  $Cl3^{ii}$  at 2.9272 (5) and 2.9245 (5) Å (Figure 2).

### Experimental

The title compound was prepared as were those described in Boéré, Roemmele, Suduweli Kondage *et al.* (2011) by addition of trichloroacetonitrile to *N,N,N'*-4-methylbenzamidine in acetonitrile. Crystals suitable for X-ray diffraction were grown by vacuum sublimation (m.p. 315–317 K).

### Refinement

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

### Figures

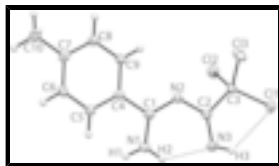


Fig. 1. Displacement ellipsoid plot (drawn at the 30% probability level) of the title compound. Intramolecular  $N1\cdots N3$  and  $N3\cdots C11$  hydrogen bonds (dotted lines) occur in the molecular structure within the crystal lattice.

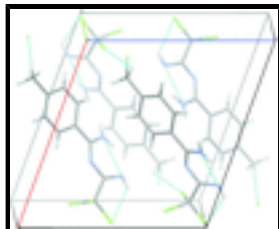


Fig. 2. Crystal packing diagram showing the short intermolecular contacts as well as the intramolecular hydrogen bonds.

## 4-methyl-N'-(2,2,2-trichloroethanimidoyl)benzene-1-carboximidamide

### Crystal data

$C_{10}H_{10}Cl_3N_3$

$M_r = 278.56$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 12.2952$  (7) Å

$b = 9.0696$  (6) Å

$c = 11.5407$  (7) Å

$\beta = 109.661$  (1)°

$V = 1211.90$  (13) Å<sup>3</sup>

$Z = 4$

$F(000) = 568$

$D_x = 1.527$  Mg m<sup>-3</sup>

Melting point: 315 K

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 9876 reflections

$\theta = 2.9$ – $27.5$ °

$\mu = 0.73$  mm<sup>-1</sup>

$T = 173$  K

Prism, colourless

$0.43 \times 0.34 \times 0.25$  mm

### Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: X-ray, Bruker D8 graphite

Detector resolution: 0.015 pixels mm<sup>-1</sup>  
phi and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Bruker, 2008)

$T_{\min} = 0.747$ ,  $T_{\max} = 0.838$

16754 measured reflections

2762 independent reflections

2594 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.014$

$\theta_{\max} = 27.5$ °,  $\theta_{\min} = 1.8$ °

$h = -15 \rightarrow 15$

$k = -11 \rightarrow 11$

$l = -14 \rightarrow 14$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.077$

$S = 1.08$

2762 reflections

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0354P)^2 + 0.6197P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

158 parameters

$$\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$$

0 restraints

$$\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$$

### Special details

**Experimental.** A crystal coated in Paratone oil was mounted on the end of a thin glass capillary and cooled in the gas stream of the diffractometer Kryoflex device.

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -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.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.60366 (11)	0.08801 (14)	0.75586 (12)	0.0251 (3)
C2	0.78479 (12)	0.15175 (16)	0.89254 (13)	0.0296 (3)
C3	0.89517 (12)	0.22286 (16)	0.88006 (12)	0.0282 (3)
C4	0.50862 (11)	0.12222 (14)	0.63920 (12)	0.0247 (3)
C5	0.39803 (12)	0.06308 (16)	0.61262 (13)	0.0308 (3)
H5	0.3829	-0.0045	0.6682	0.037*
C6	0.31014 (12)	0.10232 (17)	0.50565 (14)	0.0330 (3)
H6	0.2354	0.0609	0.4888	0.040*
C7	0.32937 (12)	0.20122 (16)	0.42266 (13)	0.0299 (3)
C8	0.44024 (12)	0.25899 (17)	0.44926 (13)	0.0313 (3)
H8	0.4552	0.3263	0.3934	0.038*
C9	0.52899 (12)	0.22015 (16)	0.55551 (13)	0.0283 (3)
H9	0.6040	0.2603	0.5715	0.034*
C10	0.23320 (14)	0.2455 (2)	0.30785 (15)	0.0413 (4)
H10A	0.1764	0.1656	0.2828	0.062*
H10B	0.2648	0.2651	0.2419	0.062*
H10C	0.1957	0.3347	0.3240	0.062*
N1	0.59080 (12)	-0.02814 (15)	0.82081 (13)	0.0339 (3)
N2	0.69301 (10)	0.17656 (14)	0.78685 (11)	0.0298 (3)
N3	0.78334 (13)	0.08069 (19)	0.98683 (13)	0.0434 (3)
Cl1	1.01604 (3)	0.20856 (5)	1.01601 (3)	0.04137 (12)
Cl2	0.92765 (3)	0.12843 (5)	0.76109 (4)	0.04211 (12)
Cl3	0.87281 (4)	0.41134 (4)	0.84076 (5)	0.04654 (12)
H1	0.5360 (18)	-0.087 (2)	0.7925 (18)	0.045 (5)*
H2	0.6389 (17)	-0.041 (2)	0.8902 (18)	0.039 (5)*
H3	0.846 (2)	0.083 (3)	1.041 (2)	0.055 (6)*

## supplementary materials

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### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0274 (6)	0.0241 (6)	0.0277 (6)	0.0044 (5)	0.0141 (5)	0.0011 (5)
C2	0.0292 (7)	0.0314 (7)	0.0289 (7)	-0.0001 (5)	0.0107 (5)	0.0021 (5)
C3	0.0278 (6)	0.0279 (7)	0.0279 (6)	0.0003 (5)	0.0080 (5)	0.0000 (5)
C4	0.0263 (6)	0.0229 (6)	0.0271 (6)	0.0036 (5)	0.0118 (5)	-0.0007 (5)
C5	0.0304 (7)	0.0297 (7)	0.0338 (7)	-0.0013 (5)	0.0130 (6)	0.0035 (6)
C6	0.0259 (6)	0.0352 (7)	0.0378 (8)	-0.0007 (6)	0.0105 (6)	-0.0002 (6)
C7	0.0291 (7)	0.0315 (7)	0.0292 (6)	0.0074 (5)	0.0100 (5)	-0.0009 (5)
C8	0.0332 (7)	0.0330 (7)	0.0300 (7)	0.0036 (6)	0.0137 (6)	0.0054 (6)
C9	0.0266 (6)	0.0300 (7)	0.0309 (7)	0.0014 (5)	0.0131 (5)	0.0015 (5)
C10	0.0324 (8)	0.0489 (9)	0.0384 (8)	0.0086 (7)	0.0066 (6)	0.0064 (7)
N1	0.0350 (7)	0.0292 (6)	0.0353 (7)	-0.0021 (5)	0.0090 (5)	0.0079 (5)
N2	0.0278 (6)	0.0333 (6)	0.0281 (6)	-0.0013 (5)	0.0091 (5)	0.0061 (5)
N3	0.0373 (7)	0.0599 (9)	0.0306 (6)	-0.0050 (7)	0.0080 (6)	0.0124 (6)
Cl1	0.0336 (2)	0.0485 (2)	0.0339 (2)	-0.00458 (15)	0.00062 (15)	-0.00111 (15)
Cl2	0.0371 (2)	0.0550 (3)	0.0387 (2)	-0.00594 (17)	0.01858 (16)	-0.01338 (17)
Cl3	0.0414 (2)	0.02872 (19)	0.0694 (3)	0.00018 (15)	0.01851 (19)	0.00905 (17)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

C1—N2	1.3098 (18)	C6—C7	1.389 (2)
C1—N1	1.3328 (18)	C6—H6	0.9500
C1—C4	1.4885 (18)	C7—C8	1.395 (2)
C2—N3	1.270 (2)	C7—C10	1.504 (2)
C2—N2	1.3732 (18)	C8—C9	1.3849 (19)
C2—C3	1.5525 (19)	C8—H8	0.9500
C3—Cl1	1.7657 (14)	C9—H9	0.9500
C3—Cl3	1.7662 (15)	C10—H10A	0.9800
C3—Cl2	1.7739 (14)	C10—H10B	0.9800
C4—C9	1.3955 (19)	C10—H10C	0.9800
C4—C5	1.3964 (19)	N1—H1	0.84 (2)
C5—C6	1.386 (2)	N1—H2	0.83 (2)
C5—H5	0.9500	N3—H3	0.81 (2)
N2—C1—N1	125.34 (13)	C6—C7—C8	118.11 (13)
N2—C1—C4	116.76 (12)	C6—C7—C10	120.94 (14)
N1—C1—C4	117.90 (13)	C8—C7—C10	120.94 (14)
N3—C2—N2	126.87 (14)	C9—C8—C7	121.33 (13)
N3—C2—C3	123.71 (13)	C9—C8—H8	119.3
N2—C2—C3	109.41 (11)	C7—C8—H8	119.3
C2—C3—Cl1	112.81 (10)	C8—C9—C4	120.22 (13)
C2—C3—Cl3	111.13 (10)	C8—C9—H9	119.9
Cl1—C3—Cl3	108.12 (8)	C4—C9—H9	119.9
C2—C3—Cl2	107.62 (10)	C7—C10—H10A	109.5
Cl1—C3—Cl2	108.12 (8)	C7—C10—H10B	109.5
Cl3—C3—Cl2	108.94 (8)	H10A—C10—H10B	109.5

C9—C4—C5	118.73 (13)	C7—C10—H10C	109.5
C9—C4—C1	119.31 (12)	H10A—C10—H10C	109.5
C5—C4—C1	121.92 (12)	H10B—C10—H10C	109.5
C6—C5—C4	120.46 (13)	C1—N1—H1	121.3 (14)
C6—C5—H5	119.8	C1—N1—H2	118.1 (14)
C4—C5—H5	119.8	H1—N1—H2	121 (2)
C5—C6—C7	121.15 (13)	C1—N2—C2	120.34 (12)
C5—C6—H6	119.4	C2—N3—H3	111.7 (16)
C7—C6—H6	119.4		
N3—C2—C3—C11	-5.2 (2)	C4—C5—C6—C7	-0.2 (2)
N2—C2—C3—C11	175.64 (10)	C5—C6—C7—C8	0.7 (2)
N3—C2—C3—C13	-126.84 (15)	C5—C6—C7—C10	-178.90 (14)
N2—C2—C3—C13	54.02 (14)	C6—C7—C8—C9	-0.4 (2)
N3—C2—C3—C12	113.95 (16)	C10—C7—C8—C9	179.23 (14)
N2—C2—C3—C12	-65.19 (13)	C7—C8—C9—C4	-0.5 (2)
N2—C1—C4—C9	15.26 (18)	C5—C4—C9—C8	1.0 (2)
N1—C1—C4—C9	-165.53 (13)	C1—C4—C9—C8	-176.86 (12)
N2—C1—C4—C5	-162.49 (13)	N1—C1—N2—C2	1.5 (2)
N1—C1—C4—C5	16.73 (19)	C4—C1—N2—C2	-179.38 (12)
C9—C4—C5—C6	-0.6 (2)	N3—C2—N2—C1	-23.6 (2)
C1—C4—C5—C6	177.12 (13)	C3—C2—N2—C1	155.50 (12)

Hydrogen-bond geometry (Å, °)

<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	0.83 (2)	2.07 (2)	2.683 (2)	130.8 (18)
N3—H3...C11	0.81 (2)	2.49 (2)	2.9993 (15)	122.2 (19)
C10—H10A...C12 <sup>i</sup>	0.98	2.93	3.871 (2)	162.(1)
C10—H10C...C13 <sup>ii</sup>	0.98	2.93	3.581 (2)	125.(1)

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

Fig. 1

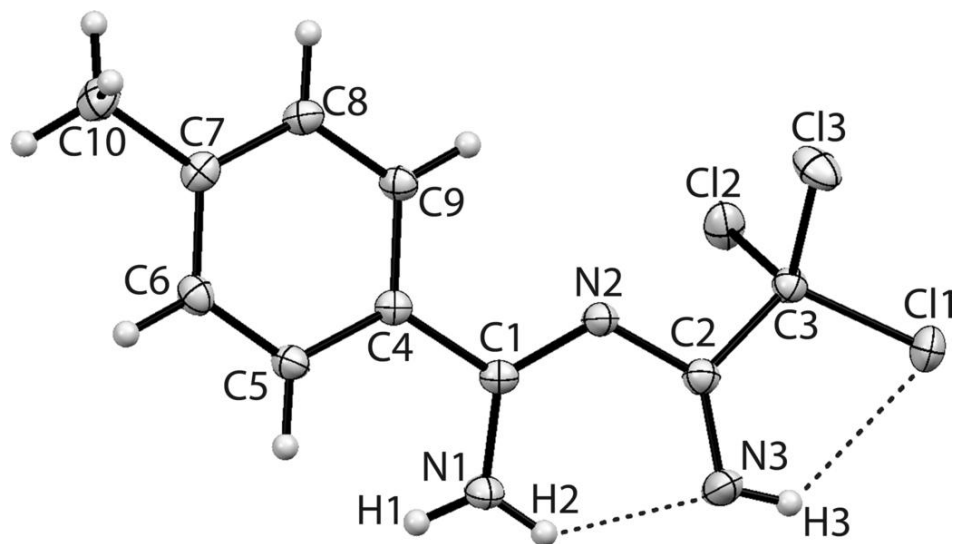




Fig. 2

