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Diethylmethyleniminium chloride

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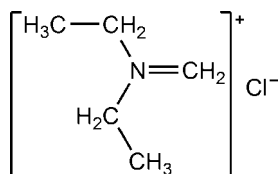
Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.021; wR factor = 0.058; data-to-parameter ratio = 15.3.

The title compound, $\text{C}_5\text{H}_{12}\text{N}^+\cdot\text{Cl}^-$, contains $[\text{Et}_2\text{N}=\text{CH}_2]^+$ and Cl^- ions. The $\text{C}=\text{N}$ double-bond distance is 1.2729 (13) Å and the sum of the angles around the central N atom is 359.92°. There are short contacts [2.973 (1) Å] between the iminium C atom and the Cl^- ion and between five of the $\text{C}-\text{H}$ H atoms and the Cl^- ion, of which the shortest is 2.623 (11) Å.

Related literature

Structures of $[\text{Me}_2\text{N}=\text{CH}_2]^+$ ions with Cl^- (Burg, 1989), Br^- and I^- (Clark *et al.*, 1994), and $[\text{NiBr}_4]^-$ (Hitchcock *et al.*, 2003) counter-ions have been published. Strong evidence has been obtained for intermolecular $\text{C}-\text{H}\cdots\text{Cl}^-$ interactions in the title compound from a detailed NMR investigation (Mayr *et al.*, 1997).

For related literature, see: Allen (2002); Ramakrishna *et al.* (1999).



Experimental

Crystal data

$\text{C}_5\text{H}_{12}\text{N}^+\cdot\text{Cl}^-$
 $M_r = 121.61$
 Monoclinic, $P2_1/n$
 $a = 6.6023$ (4) Å
 $b = 15.7426$ (10) Å
 $c = 7.0057$ (4) Å
 $\beta = 106.021$ (1)°

$V = 699.87$ (7) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.44$ mm⁻¹
 $T = 173$ (2) K
 $0.46 \times 0.28 \times 0.25$ mm

Data collection

Bruker APEXII CCD area-detector
 diffractometer
 Absorption correction: none
 7666 measured reflections

1544 independent reflections
 1500 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.013$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.058$
 $S = 1.06$
 1544 reflections
 101 parameters

12 restraints
 Only H-atom coordinates refined
 $\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.16$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C4—N1	1.4826 (12)	C6—N1	1.2729 (13)
C2—N1	1.4808 (12)		
C6···Cl1 ⁱ	2.973 (1)	H2B···Cl1 ^{iv}	2.772 (12)
H6B···Cl1	2.623 (11)	H4A···Cl1	2.817 (11)
H6A···Cl1 ⁱⁱⁱ	2.664 (11)	H5A···Cl1 ^{iv}	2.925 (14)
C6—N1—C2	121.29 (8)	C2—N1—C4	117.79 (8)
C6—N1—C4	120.84 (8)		

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT-Plus* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2019).

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supplementary materials

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Diethylmethyleniminium chloride

R. T. Boéré

Comment

There is considerable interest in the structural chemistry of iminium ions, in large part because they can be the cationic components of ionic liquids. The structure presented here may be compared to that of the $[\text{Me}_2\text{N}=\text{CH}_2]\text{Cl}$ (Burg, 1989) and $[\text{Me}_2\text{N}=\text{CH}_2]\text{Br}$ (Clark *et al.*, 1994) structures which are reported in the literature (Refcodes VAPREJ and LILLOH, respectively; Allen, 2002). There is a short contact between the iminium carbon atom and the Cl^- anion of 2.973 (1) Å. Interestingly, a similar interaction is seen in the dimethylmethyleniminium bromide, but not in the dimethyleneiminium chloride salt. Mayr, *et al.* have shown that specific cation-anion interactions in iminium halides (C—H \cdots Hal $^-$ hydrogen bonds) may be responsible for the different products that iminium ions with different counterions give in reactions with alkynes and allylsilanes (Mayr *et al.*, 1997). C—H \cdots Hal $^-$ bonds rather than equilibria between ionic and covalent moieties are responsible for the anion dependence of the NMR chemical shifts of iminium ions (Mayr *et al.*, 1997).

Experimental

The title compound was obtained from the reaction of Me_2NH with 1,3,5-trichloro-1-thia-2,4,6-triazine, a reaction which was previously reported to be very susceptible to hydrolysis (Ramakrishna *et al.*, 1999), as the only tractable product. Colourless blocks were obtained and a crystal was mounted on a glass fibre in Paratone oil and diffraction data was collected at 173 (2) K. Refinement proceeded normally, but in view of the interest in intermolecular C—H \cdots Cl $^-$ contacts, it was decided to freely refine all the H atom positions, after they were located using the HFIX command in *SHELXTL*, with the temperature factors set at $1.5 \times$ the attached methyl and $1.2 \times$ CH_2 carbons. A similar approach was taken by (Clark *et al.*, 1994).

Figures



diethylmethyleniminium chloride

Crystal data

$\text{C}_5\text{H}_{12}\text{N}^+\text{Cl}^-$

$M_r = 121.61$

Monoclinic, $P2_1/n$

Hall symbol: -P2yn

$a = 6.6023$ (4) Å

$F_{000} = 264$

$D_x = 1.154$ Mg m $^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 7168 reflections

$\theta = 2.6\text{--}28.6^\circ$

supplementary materials

$b = 15.7426 (10) \text{ \AA}$	$\mu = 0.44 \text{ mm}^{-1}$
$c = 7.0057 (4) \text{ \AA}$	$T = 173 (2) \text{ K}$
$\beta = 106.0210 (10)^\circ$	Block, colourless
$V = 699.87 (7) \text{ \AA}^3$	$0.46 \times 0.28 \times 0.25 \text{ mm}$
$Z = 4$	

Data collection

Bruker APEX II CCD area-detector diffractometer	1500 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{\text{int}} = 0.013$
Monochromator: graphite	$\theta_{\text{max}} = 27.1^\circ$
$T = 173(2) \text{ K}$	$\theta_{\text{min}} = 2.6^\circ$
φ and ω scans	$h = -8 \rightarrow 8$
Absorption correction: none	$k = -20 \rightarrow 20$
7666 measured reflections	$l = -8 \rightarrow 8$
1544 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.021$	Only H-atom coordinates refined
$wR(F^2) = 0.058$	$w = 1/[\sigma^2(F_o^2) + (0.0289P)^2 + 0.1779P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
1544 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
101 parameters	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
12 restraints	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXTL, $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.036 (3)

Special details

Geometry. All e.s.d.'s 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.

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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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supplementary materials

C11	0.22927 (3)	0.601617 (15)	0.36447 (3)	0.02793 (10)
C1	1.12954 (18)	0.72306 (8)	0.8063 (2)	0.0445 (3)
H1A	1.041 (2)	0.7606 (10)	0.846 (3)	0.067*
H1B	1.123 (3)	0.7328 (11)	0.661 (2)	0.067*
H1C	1.274 (2)	0.7299 (10)	0.890 (2)	0.067*
C5	0.67421 (19)	0.59059 (8)	0.98303 (18)	0.0368 (3)
H5A	0.806 (2)	0.5944 (9)	1.090 (2)	0.055*
H5B	0.649 (2)	0.5315 (9)	0.937 (2)	0.055*
H5C	0.555 (2)	0.6072 (9)	1.038 (2)	0.055*
C4	0.67811 (15)	0.64901 (6)	0.81260 (15)	0.0272 (2)
H4A	0.5433 (18)	0.6488 (8)	0.7100 (17)	0.033*
H4B	0.7143 (19)	0.7068 (7)	0.8580 (18)	0.033*
C2	1.06293 (14)	0.63213 (7)	0.82196 (15)	0.0270 (2)
H2A	1.142 (2)	0.5943 (7)	0.7609 (19)	0.032*
H2B	1.080 (2)	0.6142 (8)	0.9549 (17)	0.032*
C6	0.78309 (16)	0.58266 (6)	0.54673 (15)	0.0262 (2)
H6A	0.8909 (18)	0.5658 (8)	0.4865 (18)	0.031*
H6B	0.6375 (18)	0.5758 (8)	0.4823 (18)	0.031*
N1	0.83797 (12)	0.62006 (5)	0.71424 (12)	0.02214 (17)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.02520 (14)	0.03059 (15)	0.02709 (15)	-0.00273 (8)	0.00568 (9)	-0.00059 (8)
C1	0.0278 (5)	0.0331 (6)	0.0677 (8)	-0.0042 (4)	0.0050 (5)	-0.0157 (6)
C5	0.0366 (6)	0.0413 (6)	0.0376 (6)	-0.0005 (5)	0.0184 (5)	0.0048 (5)
C4	0.0254 (5)	0.0267 (5)	0.0308 (5)	0.0027 (4)	0.0101 (4)	-0.0018 (4)
C2	0.0210 (4)	0.0325 (5)	0.0252 (5)	0.0032 (4)	0.0027 (3)	0.0013 (4)
C6	0.0271 (5)	0.0243 (4)	0.0267 (5)	0.0001 (4)	0.0068 (4)	0.0016 (4)
N1	0.0216 (4)	0.0194 (3)	0.0251 (4)	0.0017 (3)	0.0058 (3)	0.0027 (3)

Geometric parameters (\AA , $^\circ$)

C1—C2	1.5105 (16)	C4—H4A	0.978 (11)
C1—H1A	0.930 (14)	C4—H4B	0.971 (11)
C1—H1B	1.016 (14)	C2—N1	1.4808 (12)
C1—H1C	0.976 (14)	C2—H2A	0.968 (11)
C5—C4	1.5130 (15)	C2—H2B	0.949 (11)
C5—H5A	0.981 (13)	C6—N1	1.2729 (13)
C5—H5B	0.983 (13)	C6—H6A	0.960 (11)
C5—H5C	1.000 (13)	C6—H6B	0.949 (11)
C4—N1	1.4826 (12)		
C6...C11 ⁱ	2.973 (1)	H2B ⁱⁱ ...C11 ^{iv}	2.772 (12)
H6B...C11	2.623 (11)	H4A...C11	2.817 (11)
H6A ⁱⁱ ...C11 ⁱⁱⁱ	2.664 (11)	H5A ⁱⁱ ...C11 ^{iv}	2.925 (14)
C2—C1—H1A	111.1 (11)	N1—C4—H4B	107.3 (7)
C2—C1—H1B	106.4 (10)	C5—C4—H4B	111.5 (7)
H1A—C1—H1B	110.4 (14)	H4A—C4—H4B	109.6 (10)

supplementary materials

C2—C1—H1C	108.5 (10)	N1—C2—C1	110.84 (8)
H1A—C1—H1C	110.1 (14)	N1—C2—H2A	106.6 (8)
H1B—C1—H1C	110.3 (14)	C1—C2—H2A	110.3 (7)
C4—C5—H5A	111.3 (9)	N1—C2—H2B	107.2 (8)
C4—C5—H5B	110.8 (9)	C1—C2—H2B	113.2 (8)
H5A—C5—H5B	110.0 (13)	H2A—C2—H2B	108.5 (11)
C4—C5—H5C	109.4 (9)	N1—C6—H6A	118.4 (8)
H5A—C5—H5C	108.2 (13)	N1—C6—H6B	119.0 (8)
H5B—C5—H5C	107.1 (13)	H6A—C6—H6B	122.4 (11)
N1—C4—C5	110.45 (8)	C6—N1—C2	121.29 (8)
N1—C4—H4A	106.1 (7)	C6—N1—C4	120.84 (8)
C5—C4—H4A	111.6 (8)	C2—N1—C4	117.79 (8)

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

Fig. 1

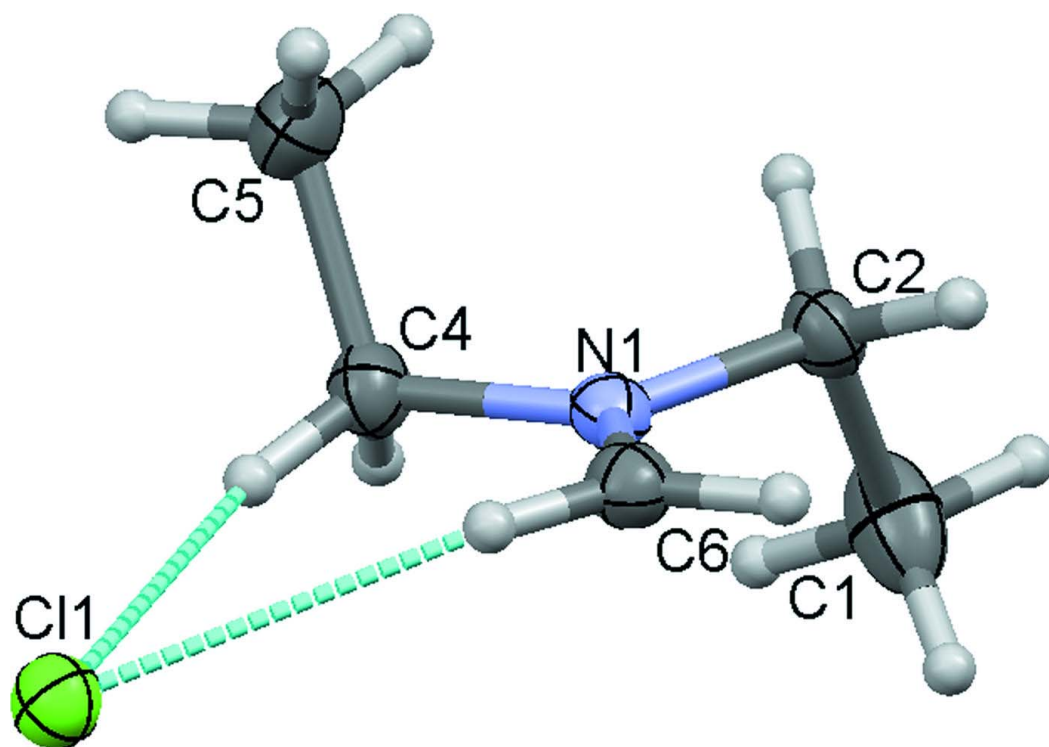


Fig. 2

