Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Diethylmethyleniminium chloride

René T. Boeré

Department of Chemistry and Biochemistry, University of Lethbridge, AB, Canada T1K 3M4
Correspondence e-mail: boere@uleth.ca

Received 13 July 2007; accepted 17 July 2007

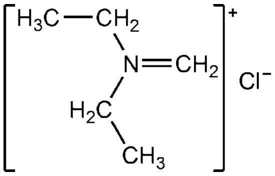
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.002 Å; R factor = 0.021; wR factor = 0.058; data-to-parameter ratio = 15.3.

The title compound, $C_5H_{12}N^+\cdot Cl^-$, contains $[Et_2N{=}CH_2]^+$ and Cl^- ions. The C=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 C—H H atoms and the Cl^- ion, of which the shortest is 2.623 (11) Å.

Related literature

Structures of $[Me_2N{=}CH_2]^+$ ions with Cl^- (Burg, 1989), Br^- and I^- (Clark *et al.*, 1994), and $[NiBr_4]^-$ (Hitchcock *et al.*, 2003) counter-ions have been published. Strong evidence has been obtained for intermolecular C—H···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

$C_5H_{12}N^+\cdot Cl^-$
M_r = 121.61
Monoclinic, $P2_1/n$
a = 6.6023 (4) Å
b = 15.7426 (10) Å
c = 7.0057 (4) Å
β = 106.021 (1)°
V = 699.87 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.44 mm^{-1}
T = 173 (2) K
0.46 × 0.28 × 0.25 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: none
7666 measured reflections
1544 independent reflections
1500 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 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
$\Delta\rho_{\rm max}$ = 0.29 e Å^{-3}
$\Delta\rho_{\rm min}$ = −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)	H2*B*···Cl1^{iv}	2.772 (12)
H6*B*···Cl1	2.623 (11)	H4*A*···Cl1	2.817 (11)
H6*A*···Cl1^{iii}	2.664 (11)	H5*A*···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).

The Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged for a Discovery Grant. The diffractometer 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: PV2019).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bruker (2006). *APEX2* and *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
Burg, A. B. (1989). *Inorg. Chem.* **28**, 1295–1300.
Clark, G. R., Shaw, G. L., Surman, P. W. J., Taylor, M. J. & Steele, D. (1994). *J. Chem. Soc. Faraday Trans.* **90**, 3139–3144.
Hitchcock, P. B., Lee, T. H. & Leigh, J. (2003). *Inorg. Chim. Acta*, **355**, 168–174.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Mayr, H., Ofial, A. R., Würthwein, E.-U. & Aust, N. C. (1997). *J. Am. Chem. Soc.* **119**, 12727–12733.
Ramakrishna, T. V. V., Elias, A. J. & Vij, A. (1999). *Inorg. Chem.* **38**, 3022–3026.
Sheldrick, G. M. (2003). *SHELXTL*. Version 6.14. Bruker AXS Inc., Madison, Wisconsin, USA.
Westrip, S. J. (2007). *publCIF*. In preparation.

doi:10.1107/S160053680703499X

supplementary materials

Acta Cryst. (2007). E**63**, o3581 [**doi:10.1107/S160053680703499X**]

Diethylmethyleniminium chloride

R. T. Boeré

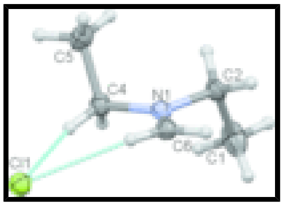
Comment

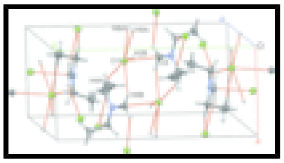
There is considerable interest in the structural chemistry of iminium ions, in large part because they can be the cationic components of ionic liquids. The structure presented here may be compared to that of the [$Me_2N=CH_2$]Cl (Burg, 1989) and [$Me_2N=CH_2$]Br (Clark *et al.*, 1994) structures which 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···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···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···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 × the attached methyl and 1.2 × CH_2 carbons. A similar approach was taken by (Clark *et al.*, 1994).

Figures





diethylmethyleniminium chloride

Crystal data

$C_5H_{12}N^+\cdot Cl^-$

$M_r = 121.61$

Monoclinic, $P2_1/n$

Hall symbol: -P2yn

$a = 6.6023 (4)$ Å

$b = 15.7426 (10)$ Å

$c = 7.0057 (4)$ Å

$\beta = 106.0210 (10)^\circ$

$V = 699.87 (7)$ Å^3

$Z = 4$

$F_{000} = 264$

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

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

Cell parameters from 7168 reflections

$\theta = 2.6\text{–}28.6^\circ$

$\mu = 0.44$ mm^{-1}

$T = 173 (2)$ K

Block, colourless

0.46 × 0.28 × 0.25 mm

Data collection

Bruker APEX II CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 173(2)$ K

φ and ω scans

Absorption correction: none

7666 measured reflections

1544 independent reflections

1500 reflections with $I > 2\sigma(I)$

$R_{int} = 0.013$

$\theta_{max} = 27.1^\circ$

$\theta_{min} = 2.6^\circ$

$h = -8 \rightarrow 8$

$k = -20 \rightarrow 20$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.058$

$S = 1.06$

1544 reflections

101 parameters

12 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

Only H-atom coordinates refined

$w = 1/[\sigma^2(F_o^2) + (0.0289P)^2 + 0.1779P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.29$ e Å^{-3}

$\Delta\rho_{min} = -0.16$ e Å^{-3}

Extinction correction: SHELXTL,
$Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

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 $F^2 > 2\text{sigma}(F^2)$ 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 ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	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 ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	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 (Å, °)

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···Cl1^{i}	2.973 (1)	H2B^{ii}···Cl1^{iv}	2.772 (12)
H6B···Cl1	2.623 (11)	H4A···Cl1	2.817 (11)
H6A^{ii}···Cl1^{iii}	2.664 (11)	H5A^{ii}···Cl1^{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)
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

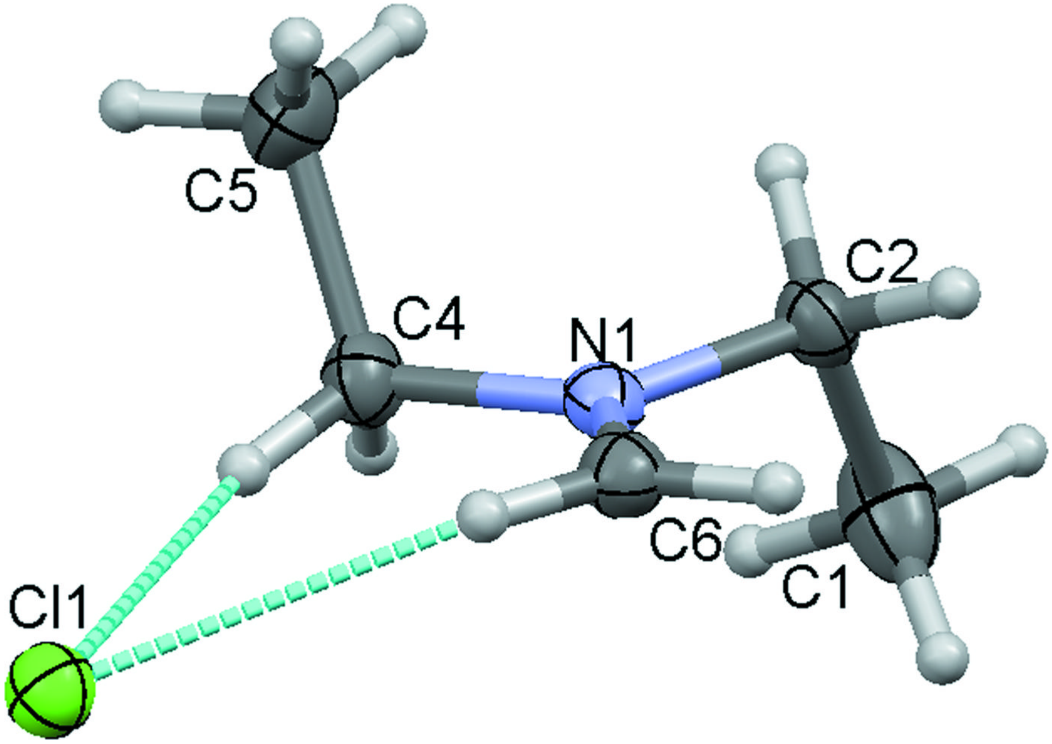


Fig. 2