Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

4-Chloro-*N*-(trimethylammonio)benzamide chloride monohydrate

Kenneth W. Muir,* David G. Morris and Cindy Ong Woei Chii

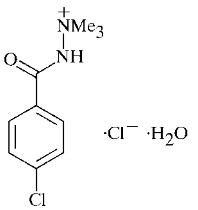
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland
Correspondence e-mail: ken@chem.gla.ac.uk

Received 5 December 2003
Accepted 19 December 2003
Online 17 January 2004

The structure of the cation in the ylide hydrochloride [$Me_3NNHC(O)C_6H_4$-Cl-*p*]Cl·H_2O, or $C_{10}H_{14}ClN_2O^+ \cdot Cl^- \cdot H_2O$, is compared with that of the free ylide. Protonation lengthens the N—C(O) bond but shortens the C=O and N—N bonds by ~0.03 Å and increases the dihedral angle between the phenyl and ylide planes.

Comment

The structures of trimethylammonio–nitrogen ylides, $Me_3N(+)$-$N(-)X$, (I), are known for many of the common electron-withdrawing stabilizing groups *X*, such as $C(O)C_6H_4$-Cl-*p* [(I*a*); Morris *et al.*, 2003], $P(O)Ph_2$ [(I*b*); Muir *et al.*, 1999], SO_2Tol [(I*c*); Cameron *et al.*, 1976], $C_6Cl_3N_2$ [(I*d*); Kartsev *et al.*, 1994], C(O)Ph [(I*e*); Cameron *et al.*, 1972] and NO_2 [(I*f*); Smith *et al.*, 1997; Cameron *et al.*, 1972]. These compounds are bases and form hydrochlorides $[Me_3N\text{–}NH\text{–}X]^+ \cdot Cl^-$, (II). In the course of studying the ability of nitrogen ylides, (I), to act as ligands (Morris *et al.*, 2003), we were surprised to find that there is no structural example of a corresponding hydrochloride, (II) [*QUEST* and *CONQUEST* search programs were used with Version 5.24 of the Cambridge Structural Database (Allen, 2002; 272 066 entries, November 2002) to obtain results not otherwise accessible]. Accordingly, we report here the structure of (II*a*) [$X = C(O)C_6H_4$-Cl-*p*] and compare it with that of its parent ylide, (I*a*).



(II*a*)

Crystals of (II*a*) contain equal numbers of [Me_3NNH-$C(O)C_6H_4$-Cl-*p*]$^+$ cations, Cl^- anions and water molecules. Conventional hydrogen bonds link the Cl^- anions and water molecules into infinite chains (Fig. 1 and Table 2) running along *b*; each water molecule bridges Cl^- ions related by the operation of a 2_1 screw axis. An N—H···O hydrogen bond links each cation to a chain. The structure also contains C—H···Cl hydrogen bonds [C1···Cl1^{ii} = 3.611 (2) Å and C3···Cl1^{iii} = 3.703 (2) Å; symmetry codes: (ii) $1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$; (iii) $1 + x$, *y*, *z*] and π–π interactions between interleaved phenyl rings (see Fig. 2), which lead to several short C···C contacts, the shortest being C6···C8^{iv} [3.308 (2) Å; symmetry code: (iv) $2 - x$, $1 - y$, *z*] and C8···C10^{v} [3.346 (2) Å; symmetry code: (v) $1 - x$, $1 - y$, $-z$]. Except for the C1—H···Cl1^{ii} hydrogen bond, these interactions link different chains together.

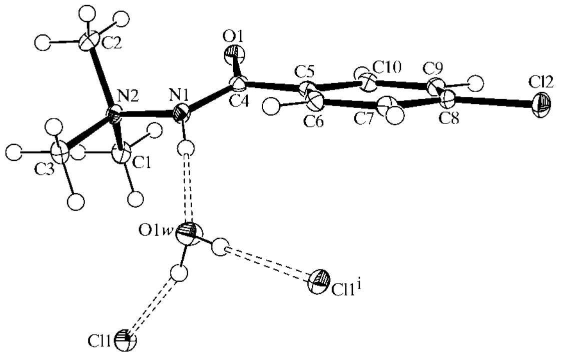


Figure 1
A view of (II*a*), with displacement ellipsoids shown at the 50% probability level. Hydrogen bonds are shown as broken lines.

Protonation of (I*a*) at atom N1 causes only minor changes in conformation and bonding. The N1—C4—C5—C6 torsion angle opens from −5.1 (2)° in (I*a*) to −21.17 (18)° in (II*a*), thereby relieving the intramolecular H1···H6 contact (2.23 Å). In (II*a*), atoms Cl2 and C4–C10 are coplanar to within 0.008 (1) Å, and the sequence C3—N2—N1—C4—C5 is nearly planar, with torsion angles across N2—N1 and N1—C4 of 179.31 (11) and −176.70 (11)° [Table 1; *cf.* 178.7 (1) and

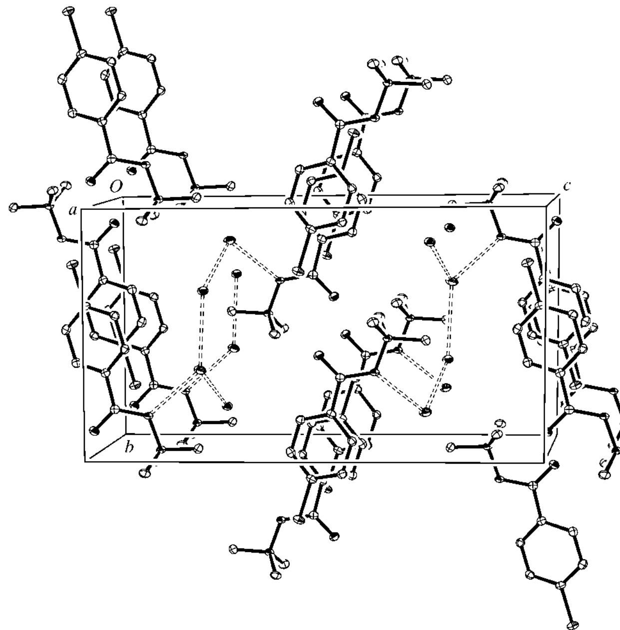


Figure 2
A view of the unit-cell contents (H atoms have been omitted).

DOI: 10.1107/S0108270103029421

−179.7 (1)° in (I*a*)]. The N1—C4 and C4—O1 bond lengths in (II*a*) [1.3739 (18) and 1.2212 (17) Å] are, respectively, longer and shorter than the corresponding values in (I*a*) [1.338 (2) and 1.258 (2) Å] and (I*e*) [1.313 (6) and 1.243 (5) Å], indicating less delocalization across the N—C bond in the hydrochloride, though rehybridization at atom N1 may also be significant (see below). More surprisingly, given the larger coordination number of atom N1 in (II*a*), its N1—N2 bond [1.4469 (16) Å] is shorter than the value in (I*a*) [1.474 (2) Å]. The N—N bonds in (I*a*)–(I*f*) fall in the narrow range 1.470–1.476 Å, except for the value in (I*b*) [1.450 (4) Å]. The N2—N1—C4 angle in (II*a*) [119.73 (11)°] is more obtuse than the angles in (I*a*) [113.5 (1)°] and (I*e*) [114.2 (3)°]. A change in the hybridization at atom N1, so that it contributes more *s* character to the N1—N2 and N1—C4 bonds of (II*a*) than to the corresponding bonds of (I*a*), would explain these trends. Although the $Me_3N(+)NHCH_2CH_2CO_2^-$ zwitterion is formally analogous to (II), its three-coordinate N atom is linked to the unsaturated $-CO_2^-$ group through a fully saturated C atom, resulting in marked differences in coordination (N—N = 1.491 Å, N—C = 1.444 Å and N—N—C = 113.9°; Kemme *et al.*, 1983; Allen, 2002) from (II*a*).

The atomic U^{ij} values are moderately well reproduced by a **TLS** analysis (Schomacher & Trueblood, 1968) [$R_2 = (\Delta U^2/U^2)^{1/2} = 0.13$]; they also pass the Hirshfeld (1976) rigid-bond test, the worst discrepancy being $\Delta U = 0.0021$ (8) Å^2 for C4—O1.

Experimental

An aqueous solution of the parent ylide was prepared according to the method of Morris *et al.* (2003). It was then added to an equimolar quantity of 0.1 *M* HCl. The resulting solution was concentrated by heating in a rotary evaporator; crystals of the title compound precipitated on cooling.

Crystal data

$C_{10}H_{14}ClN_2O^+\cdot Cl^-\cdot H_2O$
$M_r = 267.15$
Monoclinic, $P2_1/c$
$a = 7.0302$ (2) Å
$b = 9.9377$ (2) Å
$c = 17.8571$ (5) Å
$\beta = 98.279$ (1)°
$V = 1234.57$ (6) Å^3
$Z = 4$

$D_x = 1.437$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2648 reflections
$\theta = 1.0$–27.5°
$\mu = 0.51$ mm^{-1}
$T = 100$ (2) K
Needle, colourless
0.40 × 0.12 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer
Thick-slice ω scans
10 868 measured reflections
2806 independent reflections
2465 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.049$
$\theta_{\rm max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R(F) = 0.030$
$wR(F^2) = 0.073$
$S = 1.05$
2806 reflections
160 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.026P)^2 + 0.67P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.29$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C4—O1	1.2212 (17)	C4—C5	1.4956 (19)
C4—N1	1.3739 (18)	N1—N2	1.4469 (16)
O1—C4—N1	123.85 (13)	C4—N1—N2	119.73 (11)
O1—C4—C5	122.22 (12)	C4—N1—H1	122.0 (12)
N1—C4—C5	113.92 (12)	N2—N1—H1	112.3 (12)
N1—C4—C5—C6	−21.17 (18)	C5—C4—N1—N2	−176.70 (11)
N1—C4—C5—C10	159.46 (12)	C4—N1—N2—C3	179.31 (11)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1*W*	0.86 (2)	1.92 (2)	2.7813 (17)	176 (2)
O1*W*—H1*W*···Cl1	0.89 (2)	2.30 (2)	3.1497 (12)	160 (2)
O1*W*—H2*W*···Cl1$^{\rm i}$	0.78 (3)	2.40 (3)	3.1745 (12)	175 (2)

Symmetry code: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

H atoms bonded to atoms N1 and O1*W* were refined freely. The positions of the other H atoms were finally determined using riding constraints assuming C—H bond lengths of 0.95 and 0.98 Å, respectively, for Csp^2 and Csp^3 atoms. For each methyl group, a single orientation parameter was also refined.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; structure solutoin: *SHELXS*97 (Sheldrick, 1997); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors thank the EPSRC and Glasgow University for support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1295). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Cameron, A. F., Duncanson, F. D. & Morris, D. G. (1976). *Acta Cryst.* B**32**, 1987–1990.
Cameron, A. F., Hair, N. J. & Morris, D. G. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 1071–1076.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Hirshfeld, F. L. (1976). *Acta Cryst.* A**32**, 239–244.
Kartsev, V. G., Gizatullina, E. M., Aliev, Z. G., Talipov, S. A. & Nabatov, A. S. (1994). *Khim. Geterotsikl. Soedin. SSSR* (*Chem. Heterocycl. Compd*), p. 505.
Kemme, A. A., Bleidelis, Ya. Ya., Kalvin'sh, I. Ya. & Eremeev, A. V. (1983). *Latv. PSR Zinat. Akad. Vestis Kim. Ser.* p. 215.
Morris, D. G., Muir, K. W. & Chii, C. O. W. (2003). *Polyhedron*, **22**, 3345–3353.
Muir, K. W., Morris, D. G. & Innes, V. (1999). *Croat. Chem. Acta*, **72**, 511–518.
Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Schomacher, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Smith, G. T., Mallinson, P. R., Frampton, C. S. & Howard, J. A. K. (1997). *J. Chem. Soc. Perkin Trans.* 2, pp. 1329–1338.