Crystal Structure of Acetamidinium Chloride

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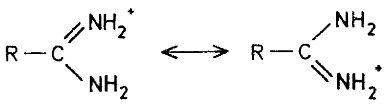
The crystal structure of the title compound has been determined by the heavy atom method from *X*-ray diffractometer data and refined by full-matrix least-squares to *R* 0.037 for 855 observed reflections. Crystals are monoclinic, space group *C*2/*c*, *a* = 11.673(2), *b* = 9.862(2), *c* = 9.601(1) Å, β = 111.71(2), *Z* = 4. The structure comprises a planar CCN_2 skeleton with equal C–N bonds (mean C–N 1.30_7 Å) and a short C–C single bond [1.477(3) Å]. The chloride ion is surrounded by four amino-hydrogen atoms 2.33(2)—2.46(2) Å; two of the hydrogen contacts are to the same cation from independent NH_2 groups in a ' chelate ' arrangement.

THE amidines are typically strong bases which protonate to form amidinium salts. The cation has been represented as the resonance hybrid:



In order to establish accurate geometry for the unsubstituted amidinium grouping, we have determined the crystal structure of acetamidinium chloride. It was prepared as long deliquescent needles, m.p. 176—178 °C [*cf.* lit., 164—166 (ref. 1), 177—178° (ref. 2)] by the method of Dox;[1] a coated needle section 0.35 × 0.45 × 0.52 mm was used for the crystallographic work.

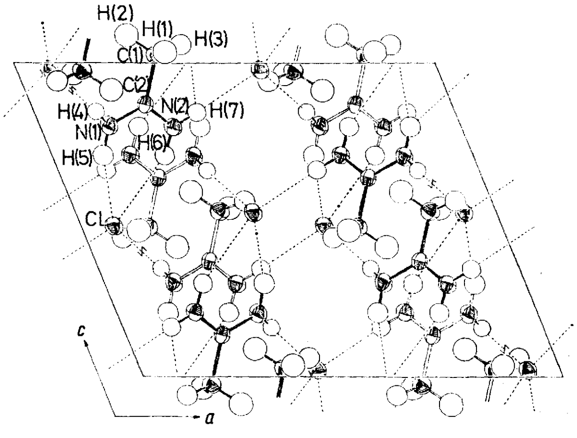
EXPERIMENTAL

Unit-cell calibration was carried out by a least squares fit of the angular parameters of 15 reflections (2θ *ca.* 25°) centred in the counter aperture of a Syntex P$\bar{1}$ four-circle diffractometer. A unique data set was gathered by a conventional 2θ—θ scan within the limit 2θ < 50°, yielding 905 independent reflections of which 855 with $I > \sigma(I)$ were considered observed and used in the structure solution and refinement. No correction was applied for absorption.

Crystal Data.—$C_2H_7ClN_2$, $M = 94.56$. Monoclinic, $a = 11.673(2)$, $b = 9.862(2)$, $c = 9.601(1)$ Å, $\beta = 111.71(2)°$, $U = 1\,026.8(4)$ Å^3, $D_m = 1.20(2)$, $Z = 8$, $D_c = 1.226$ g cm^{-3}, $F(000) = 400$. Mo-K_α radiation (monochromatic) $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 4.0 cm^{-1}. Space group $C2/c$, (C_{2h}^6, No. 15). Neutral-atom scattering factors, Cl^- excepted,[3,4] that for Cl^- being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[5]

The structure was solved by the heavy-atom method and refined by full-matrix least squares, the thermal parameters of the hydrogen atoms being refined isotropically with the remaining atoms anisotropic according to the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Refinement terminated with all parameter shifts $<0.05\sigma$ at $R = 0.037$ and $R'\{= [\Sigma w(||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]\}$ 0.048, the weighting scheme of the form $w = [\sigma^2(F_0) + n \times 10^{-4}(F_0)^2]^{-1}$ being found appropriate for $n = 4$.

Atomic numbering within the cation is shown in the Figure; results are presented in Tables 1 and 2. Structure amplitudes are deposited as Supplementary Publication No. SUP 21554 (4 pp, 1 microfiche).† Computation was carried out on a CDC 6200 machine using a local variant of the ' *X*-Ray '72 ' program system.[6]



Unit cell contents projected down *b*, showing 20% thermal ellipsoids. Bonds of molecules in the upper half of the cell are shown solid; hydrogen bonds are shown as dotted lines, with breaks indicating intercellular contacts

DISCUSSION

As expected, the structure is comprised of acetamidinium $[MeC(NH_2)_2]^+$ and chloride ions. The CCN_2

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† For details, see Notice to Authors No. 7, *J.C.S. Perkin II*, 1975, Index issue.

[1] A. W. Dox, *Org. Synth.*, Coll. Vol. I, 1941, 5.

[2] H. M. Barnes, D. Kundiger, and S. M. McElvain, *J. Amer. Chem. Soc.*, 1940, **62**, 1281.

[3] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[4] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, *A***24**, 321.

[5] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[6] ' *X*-Ray ' program system, Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A., June 1972.

skeleton is a good plane (Table 3) and has approximate *mm* symmetry with only trivial deviations. The structure of the cation clearly supports the mesomeric configuration, equal C–N bond lengths being observed; the mean (1.30_7 Å) is longer than that found in $[MeClC{:}NH_2]^+Cl^-$ (1.26_5 Å) and related compounds with only one $C{:}NH_2^+$ linkage, as expected,[7] but much shorter than the C–N single-bond distance (1.47 Å). The C–C bond is also considerably shorter than the normal single-bond value. While the amino-hydrogen atoms are also approximately coplanar, H(5) and H(6), which chelate the adjacent chloride ion, may be twisted slightly out of the plane towards that ion so that the NH_2 groups are rotated slightly about the C–N bonds. This constraint is also presumably instrumental in maintaining the angle N(1)–C(2)–N(2) close to 120°; likewise the angle between the hydrogen atoms at each nitrogen is unexpectedly large. H(3) of the methyl group lies approximately in the plane of the cation on the side of N(2).

TABLE 1

Atomic fractional cell for Cl × 10^5, C and N × 10^4, and H × 10^3 and thermal parameters (× 10^3 Å^2) with least-squares estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	*U*
Cl	07 765(4)	18 761(4)	47 839(5)	*
C(1)	3 440(2)	0 666(2)	10 255(2)	*
H(1)	368(3)	−026(3)	1 035(4)	110(9)
H(2)	294(3)	084(3)	1 088(3)	110(9)
H(3)	413(2)	118(3)	1 059(3)	83(7)
C(2)	2 707(2)	0 983(2)	8 670(2)	*
N(1)	1 645(2)	0 391(2)	7 992(2)	*
H(4)	147(2)	−017(2)	844(2)	56(6)
H(5)	121(2)	063(2)	704(3)	82(7)
N(2)	3 139(2)	1 844(2)	7 948(2)	*
H(6)	267(3)	201(2)	704(3)	73(7)
H(7)	385(2)	220(2)	842(3)	68(6)

*Anisotropic thermal parameters:

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	58.9(4)	69.6(4)	66.5(4)	16.0(2)	17.1(2)	3.9(2)
C(1)	71(1)	66(1)	65(1)	−4(1)	23(1)	5(1)
C(2)	54(1)	48(1)	62(1)	2(1)	26(1)	−1(1)
N(1)	58(1)	77(1)	72(1)	−13(1)	21(1)	12(1)
N(2)	59(1)	64(1)	61(1)	−11(1)	19(1)	5(1)

The chloride ion has only four close contacts, all to amino-hydrogens, and two of these are to the same cation, so that the resulting geometry is highly distorted. In spite of this, the Cl ··· H distances are surprisingly even and while very much longer than that of H–Cl (1.274 Å), they are nevertheless much less than the van der Waal's contact distance (3.0 Å) and clearly represent a strong interaction. The mean Cl ··· H distance (2.40 Å) is appreciably longer than that found in $[MeClC{:}NH_2]^+Cl^-$ (2.02 Å), the chloride ion in the latter having only two neighbouring amino-groups.

TABLE 2

Interatomic distances (Å) and angles (°) with least-squares estimated standard deviations in parentheses

(*a*) Cation geometry

C(1)–H(1)	0.95(3)	H(1)–C(1)–H(3)	108(3)
C(1)–H(2)	0.99(3)	H(1)–C(1)–C(2)	110(2)
C(1)–H(3)	0.90(3)	H(2)–C(1)–H(3)	110(3)
C(1)–C(2)	1.477(3)	H(2)–C(1)–C(2)	110(2)
H(1)–C(1)–H(2)	109(3)	H(3)–C(1)–C(2)	110(2)
C(2)–N(1)	1.305(2)	C(1)–C(2)–N(1)	120.0(2)
C(2)–N(2)	1.310(3)	C(1)–C(2)–N(2)	119.5(2)
N(1)–C(2)–N(2)	120.5(2)	C(2)–N(1)–H(4)	116(1)
N(1)–H(4)	0.77(2)	C(2)–N(1)–H(5)	118(2)
N(1)–H(5)	0.90(3)	H(4)–N(1)–H(5)	126(2)
N(2)–H(6)	0.86(2)	C(2)–N(2)–H(6)	116(2)
N(2)–H(7)	0.86(2)	C(2)–N(2)–H(7)	118(2)
		H(6)–N(2)–H(7)	126(2)

(*b*) Anion environment

Cl ··· H(5)	2.38(3)	Cl ··· H(5)–N(1)	156(2)
Cl ··· H(6)	2.46(2)	Cl ··· H(6)–N(2)	156(3)
Cl ··· H(4^{I})	2.43(2)	Cl ··· H(4^{I})–N(1^{I})	176(2)
Cl ··· H(7^{II})	2.33(2)	Cl ··· H(7^{II})–N(2^{II})	178(2)
H(5) ··· Cl ··· H(6)	53.4(9)	H(6) ··· Cl ··· H(4^{I})	98.0(8)
H(5) ··· Cl ··· H(4^{I})	97.2(9)	H(6) ··· Cl ··· H(7^{II})	147.1(8)
H(5) ··· Cl ··· H(7^{II})	123.5(9)	H(4^{I}) ··· Cl ··· H(7^{II})	114.4(7)

Transformations of the asymmetric unit.

I $x, \bar{y}, z - \frac{1}{2}$ II $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$

TABLE 3

Equation of least-squares plane defined by the CCN_2 skeleton in the orthogonal (Å) frame defined by $X = ax + cz \cos \beta$, $Y = by$, $Z = cz \sin \beta$

$$-0.6014X + 0.7466Y + 0.2844\,Z = 2.870$$

σ of defining atoms: 0.003 Å

χ^2 (3° of freedom) 6.87

Atom deviations (Å): C(1) −0.002, C(2) 0.005, N(1) −0.002, N(2) −0.002, H(1) −0.81, H(2) 0.77, H(3) 0.05, H(4) −0.08 H(5) 0.03, H(6) 0.03, H(7) −0.02, Cl 0.202

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[7] J. M. Williams, S. W. Peterson, and G. M. Brown, *Inorg. Chem.*, 1968, **7**, 2577, and refs. therein.