BERMAN, H. M., ROSENSTEIN, R. D. & SOUTHWICK, J. (1971). *Acta Cryst.* B**27**, 7–10.

CHEN, C. M. (1981). To be published.

CHU, S. S. C. & JEFFREY, G. A. (1968). *Acta Cryst.* B**24**, 830–838.

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

FRIDRICHSONS, J. & MATHIESON, A. McL. (1962). *Acta Cryst.* **15**, 119–128.

FRIES, D. C., RAO, S. T. & SUNDARALINGAM, M. (1971). *Acta Cryst.* B**27**, 994–1005.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

HILL, R. & VAN HEYNINGEN, R. (1951). *Biochem. J.* **49**, 332–337.

HOLLENBEAK, K. H. & KUEHNE, M. E. (1974). *Tetrahedron*, **30**, 2307–2316.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

JEFFREY, G. A., POPLE, J. A. & RADOM, L. (1974). *Carbohydr. Res.* **38**, 81–95.

JEFFREY, G. A., ROSENSTEIN, R. D. & VLASSE, M. (1967). *Acta Cryst.* **22**, 725–733.

MATHIESON, A. McL. (1963). *Tetrahedron Lett.* **2**, 81–84.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

REYNOLDS, T. (1975). *Chem. Ind.* (*London*), **19**, 603–605.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, p. 457. London: Macmillan.

TSCHESCHE, R., HOPPE, H.-J., SNATZKE, G., WULFF, G. & FEHLHABER, H.-W. (1971). *Chem. Ber.* **104**, 1420–1428.

Acta Cryst. (1981). B**37**, 2098–2100

Acetamide Hemihydrochloride, by Neutron Diffraction at 120 K

BY J. C. SPEAKMAN

*Chemistry Department, The University, Glasgow G*12 8*QQ, Scotland*

M. S. LEHMANN AND J. R. ALLIBON

Institut Laue–Langevin, 38042 *Grenoble, France*

AND D. SEMMINGSEN

Chemistry Department, University of Oslo, Blindern, Oslo 3, *Norway*

(*Received* 13 *April* 1981; *accepted* 7 *May* 1981)

Abstract. $C_2H_5NO.\frac{1}{2}HCl$, monoclinic, $P2_1/c$, $Z = 4$, $a = 6{\cdot}291\ (6)$, $b = 8{\cdot}300\ (7)$, $c = 7{\cdot}931\ (8)$ Å, $\beta = 113{\cdot}43\ (4)°$, $V = 380{\cdot}0$ Å^3, $D_c = 1{\cdot}35$ Mg m^{-3}. $R = 0{\cdot}038$, $R_w = 0{\cdot}023$ for 882 reflexions. Room-temperature X-ray work has verified [Muir & Speakman (1979). *J. Chem. Res.* (*M*), pp. 3401–3424; (*S*), p. 277] the crystallographically symmetrical cation $[C_2H_5NO\cdots H\cdots ONC_2H_5]^+$ and found O···O to be 2·451 (1) Å. Low-temperature neutron diffraction work now finds 2·426 (3) Å, which is significantly shorter. Inter- and intramolecular vibrations have also been analysed.

Introduction. Carboxylic acids, H*X*, often form acid salts of compositions such as *MX*.H*X*, where *M* is a univalent metal. Some have structures of type *A* (Speakman, 1972): they have crystallographically symmetrical XHX^- anions embodying 'very short' OHO bonds (*e.g.* Bacon, Walker & Speakman, 1977). Organic bases, *B*, sometimes form analogous, type *A* basic salts, such as the chloride $BHB^+.Cl^-$ with a similarly symmetrical cation. The simplest example, and the first to be discovered, is acetamide hemihydrochloride (AHHCl). This compound is properly represented by the formula $[C_2H_5NO\cdots H\cdots ONC_2H_5]^+.Cl^-$, with each ion centred on a point of inversion, as was found by diffraction work with X-rays (Hughes & Takei, 1955) and with neutrons (Peterson & Worsham, 1959). Details of these early analyses were never published.

The preparation of AHHCl from aqueous solution was described by Muir & Speakman (1979). Crystals large enough for neutron diffraction (ND) work are hard to grow because, in acid solution, acetamide is rapidly decomposed to acetic acid and ammonium chloride. However, some large single crystals of moderate quality were grown at Oslo. Pieces cut from these were studied on the D9 diffractometer at the ILL, Grenoble. Two sets of data were collected. They led to almost identical atomic coordinates. We preferred the

0567-7408/81/112098-03$01.00

Table 1. *Fractional atomic coordinates* ($\times 10^5$, *for* H $\times 10^4$) *and isotropic thermal parameters* (Å^2 $\times 10^4$) *for AHHCl at* 120 K, *with e.s.d.'s in parentheses*

For all atoms $U_{\rm eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
C(1)	28671 (19	4650 (12)	64137 (14)	129 (6)
C(2)	35888 (22)	−10924 (13)	73972 (16)	166 (7)
N	14630 (14)	14060 (9)	68119 (10)	168 (4)
O	36207 (24)	9021 (14)	52285 (17)	197 (6)
Cl	0	0	100000	178 (5)
H(0)	5000	0	5000	327 (13)
H(1)	3300 (7)	−2059 (3)	6442 (4)	503 (18)
H(2)	2707 (6)	−1316 (4)	8275 (5)	663 (20)
H(3)	5419 (5)	−1046 (4)	8222 (5)	453 (17)
H(4)	1050 (5)	2516 (3)	6224 (3)	325 (13)
H(5)	909 (4)	1065 (3)	7798 (3)	320 (13)

second set whose vibrational parameters seemed better; and it is this latter analysis only that we now report. The crystal was mounted on its *a* axis and had dimensions 0·92 × 1·75 × 4·88 mm. The wavelength was 0·8402 Å. Absorption factors, derived from the calculated coefficient μ = 1·63 mm^{-1}, ranged from 0·75 to 0·88, and corrections were applied. Intensities were measured for 2074 reflexions out to $\theta = 35°$; they were merged to yield 983 independent terms, further reduced to 882 by the criterion $I > 3\sigma(I)$. The internal consistency of the merged data corresponded to R = 0·029. Full-matrix refinement with *SHELX* (Sheldrick, 1976), all atoms anisotropic, converged at R = 0·038, R_w = 0·023. A formal extinction coefficient had been included in the later cycles. Neutron-scattering amplitudes were 6·55 (C), −3·72 (H), 9·40 (N), 5·83 (O) and 9·60 (Cl) fm. Final coordinates are in Table 1.*

The report on the room-temperature (RT) study drew attention to an alternative choice of axes, leading to a cell with similar dimensions, in the space group $P2_1/n$. At 120 K the dimensions of the two cells become almost indistinguishable: β = 113·43, 113·32°. Such an 'ambiguity', in the monoclinic system, occurs whenever *a* and *c* are nearly the same; or $|2c\cos\beta| \simeq a$, where $a \lesseqgtr c$ if $\beta \lesseqgtr 120°$.

Discussion. The *ORTEP* drawing (Johnson, 1965) in Fig. 1 gives a general view of the structure, and the atom numbering. The principal interatomic distances and angles are in Table 2. The mean plane of the atoms C(1), C(2), N and O is defined by the equation 0·54219X' + 0·44758Y + 0·71113Z' = 3·3795 Å. The small deviation [0·006 (1) Å] of C(1) from this plane is significant. All the other atoms shown in Fig. 1 are within 0·09 Å of this plane, except for H(1) and H(3) which are 0·79 and 0·88 Å away, on opposite sides. The C—O and C—N distances differ from those in crystalline acetamide (Jeffrey, Ruble, McMullan, DeFrees, Blinkley & Pople, 1980; see also Ottersen, 1975), the differences being in the sense attributable to some transfer of double-bond character from the C—O bond to C—N, when the cation is formed. The

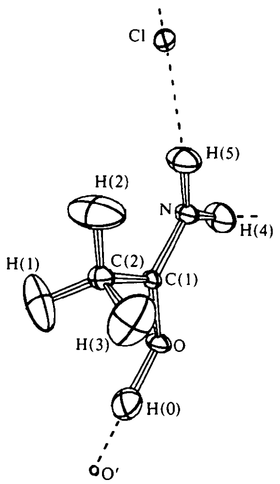

Fig. 1. The structure and atom numbering in AHHCl at 120 K; ellipsoids represent the 50% probability level. H(0) and Cl lie on centres of symmetry.

Table 2. *Some geometrical details* (Å *and* deg) *of AHHCl at* 120 K, *with standard deviations in parentheses*

A single prime denotes an atom at $1-x, -y, 1-z$; a double prime one at $x, \frac{1}{2}-y, -\frac{1}{2}+z$.

C(1)–C(2)	1·4845 (15)	C(2)–H(1)	1·069 (3)
C(1)–O	1·2627 (16)	C(2)–H(2)	1·065 (4)
C(1)–N	1·3084 (13)	C(2)–H(3)	1·075 (3)
N–C(1)–C(2)	119·19 (9)	H(1)–C(2)–H(2)	110·3 (3)
O–C(1)–C(2)	120·96 (10)	H(2)–C(2)–H(3)	108·6 (3)
O–C(1)–N	119·84 (10)	H(3)–C(2)–H(1)	107·3 (3)
(Sum	359·99)	(Sum	326·2)
H(4)–N–H(5)	120·1 (2)		
C(1)–N–H(4)	119·4 (2)		
C(1)–N–H(5)	120·2 (2)	C(1)–O–H(0)	115·9 (1)
(Sum	359·7)		
Hydrogen bonds			
O···O′	2·4260 (26)		
O–H(0)	1·2130 (13)	H(0)–O	(1·2130)
	O–H(0)–O′	(180)	
Cl″···N	3·2800 (7)		
N–H(5)	1·015 (2)	H(5)···Cl	2·226 (2)
	Cl″···H(5)–N	171·7 (2)	
Cl···N	3·2331 (7)		
N–H(4)	1·018 (2)	H(4)···Cl′	2·263 (2)
	Cl···H(4)–N	176·8 (2)	

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36170 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

conformation at the methyl group is also different: one C—H bond lies in the molecular plane in AHHCl; in acetamide it is normal to the plane.

The ellipsoids in Fig. 1 suggest that the acetamide unit is undergoing considerable vibrational motion. Analysis of the U_{ij} by the Schomaker & Trueblood (1968) method was carried out by the program *THMI* (Trueblood, 1977). Agreement between observed and calculated U was satisfactory (r.m.s. Δ, 0·004 Å^2). The intramolecular torsional oscillation of the methyl group has a r.m.s. amplitude of 14·0 (6)°, compared with 22° at RT; the rest of the molecule, taken as rigid, has a librational amplitude of 6·4 (4)° about the axis of minimum moment of inertia, approximately parallel to C(1)—C(2), against ~4° about the other principal axes.

The Cl^- ion lies at a centre of symmetry and is involved in two pairs of N—H···Cl bonds, details of which are in Table 2. The most interesting feature of AHHCl is the type *A* hydrogen bond. The O···O distance diminishes by 0·0247 (30) Å between RT and 120 K. (However, though significant, this difference is not necessarily due to the change of temperature alone.) One of us (JCS) has held the view that OHO bonds in type *A* structures, where O···O is less than 2·50 Å, may have the proton moving in a single-minimum potential field, perhaps of flattened shape. This has been questioned, for instance by Thomas & Liminga (1978) who, from a consideration of difference-density distributions, have argued that the limit ought to be lower: at 2·50 Å there is disorder between inherently unequal O—H and H···O; only when the overall distance approaches 2·40 Å do the distances become equal. If this be true, AHHCl could be an example where the hydrogen bond becomes genuinely symmetrical on cooling.

With certain assumptions, the U_{ij} derived by ND may be used to assess the relative motion of the proton within the OHO unit (*e.g.* Bacon, Walker & Speakman, 1977). In AHHCl we find the characteristic inversion of the ellipsoid representing the relative proton motion; the principal r.m.s. amplitudes are 0·15 (1) Å parallel to the hydrogen bond, and 0·08 Å transversely.

Groth (1977) has reported accurate X-ray work at 113 K on the hemihydrobromide, AHHBr, which is isomorphous with AHHCl. Where comparable, his results agree with ours; notably, the OHO bond is similarly short [2·438 (5) Å]. There is one important exception: our ND results give no support to his finding that H(0) is disordered as two half-atoms, 0·4 Å apart, on either side of the centre of symmetry and well off the O···O line. This apparent splitting is attributable to a KKM (Kanters–Kroon–McAdam) effect (*e.g.* Macdonald, Speakman & Hadži, 1972).

For the spectroscopy of AHHCl see Spinner (1980).

Thanks are due to Dr P. R. Mallinson for help with computing.

References

Bacon, G. E., Walker, C. R. & Speakman, J. C. (1977). *J. Chem. Soc. Perkin Trans.* 2, pp. 979–983.

Groth, P. (1977). *Acta Chem. Scand. Ser. A*, **31**, 607–609.

Hughes, E. W. & Takei, W. J. (1955). *Struct. Rep.* **19**, 509.

Jeffrey, G. A., Ruble, J. R., McMullan, R. K., DeFrees, D. J., Binkley, J. S. & Pople, J. A. (1980). *Acta Cryst.* B**36**, 2292–2299.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Macdonald, A. L., Speakman, J. C. & Hadži, D. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 825–832.

Muir, K. M. & Speakman, J. C. (1979). *J. Chem. Res.* (*M*), pp. 3401–3424; (*S*), p. 277.

Ottersen, T. (1975). *Acta Chem. Scand. Ser. A*, **29**, 939–944.

Peterson, S. W. & Worsham, J. E. (1959). Report ORNL-2782. Oak Ridge National Laboratory, Tennessee.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

Sheldrick, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.

Speakman, J. C. (1972). *Struct. Bonding* (*Berlin*), **12**, 141–199.

Spinner, E. (1980). *J. Chem. Soc. Perkin Trans.* 2, pp. 395–400.

Thomas, J. O. & Liminga, R. (1978). *Acta Cryst.* B**34**, 3686–3690.

Trueblood, K. N. (1977). Program *THMI*. Univ. of California at Los Angeles, USA.