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Short Communications

Refinement of the Acetamide Hemihydrobromide Crystal Structure at −160 °C

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The crystal structure of acetamide hemihydrobromide, $(CH_3CONH_2)_2$. HBr, was determined (at room temperature) in 1969 by film methods.[1] However, the accuracy of that investigation was relatively poor, and in particular the hydrogen atoms could not be localized. With the main purpose of trying to establish whether the short intermolecular O···O′ hydrogen bond is symmetrical or not, a redetermination has been carried out at − 160 °C.

The crystals belong to the monoclinic system with space group $P2_1/n$, cell dimensions $a=6.443(2)$ Å, $b=8.632(3)$ Å, $c=7.979(3)$ Å, $\beta=112.40(3)°$, and $Z=2$ ($D_m=1.59$ g cm^{-3}, $D_x=1.61$ g cm^{-3}).

With $2\theta_{max}=50°$ and Mo$K\alpha$-radiation 1584 independent reflections were measured on an automatic four circle diffractometer at − 160 °C. Using an observed-unobserved cutoff at $2.5\sigma(I)$, 1165 reflections were recorded as observed. The crystal size was $(0.2\times0.2\times0.15)$ mm^3 and no absorption corrections were applied ($\mu=52.5$ cm^{-1}).

The structure was solved by the heavy atom method and refined by full-matrix least-squares technique.[2]* Hydrogen atom positions were localized in a difference Fourier map. Anisotropic temperature factors were introduced for the non-hydrogen atoms and weights in least-squares were calculated from the standard deviations in intensities, $\sigma(I)$, taken as

$$\sigma(I)=[C_T+(0.02\ C_N)^2]^{\frac{1}{2}}$$

where C_T is the total number of counts and C_N the net count.

The hydrogen atom HO, being localized at a position close to that of Table 1, was refined with multiplicity factor 0.5. No shifts towards the centre of inversion (to give a more symmetric hydrogen bond) occurred. When forcing it closer to the centre of symmetry and refining, the B-value increased rapidly.

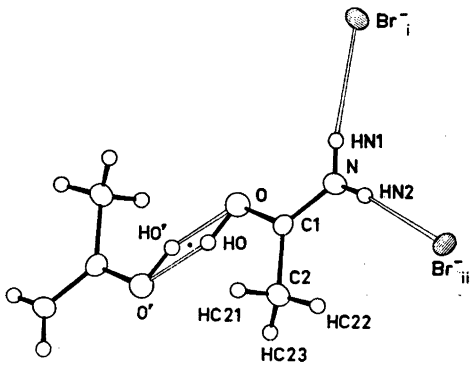

Fig. 1. Schematic drawing showing the numbering of atoms. The atoms labelled HO and HO′ correspond to 'half' hydrogen atoms.

* All programs used (except for ORTEP) are included in this reference.

Table 1. Final fractional coordinates and thermal parameters with estimated standard deviations. The expression for anisotropic vibration is $\exp[-2\pi^2(h^2a^{*2}U11+\cdots+2klb^*c^*U23)]$.

ATOM	x	y	z	U11	U22	U33	U12	U13	U23
BR-	.00000	.00000	.00000	.0167(2)	.0177(2)	.0211(2)	.0032(2)	.0031(1)	-.0027(2)
O	.15649(42)	.06881(29)	.52625(35)	.0176(11)	.0231(12)	.0277(13)	-.0011(10)	.0029(10)	.0014(10)
N	.51908(48)	.13548(35)	.67936(42)	.0187(13)	.0184(13)	.0246(14)	-.0002(10)	.0057(11)	.0035(11)
C1	.34502(54)	.04414(39)	.63842(47)	.0185(14)	.0173(13)	.0205(15)	.0010(11)	.0061(12)	-.0012(11)
C2	.37232(62)	-.11047(43)	.72921(55)	.0218(15)	.0208(16)	.0303(18)	-.0014(13)	.0119(14)	.0031(14)

ATOM	x	y	z	B	ATOM	x	y	z	B
HO	.064(17)	.085(11)	.528(14)	2.5(21)	HN1	.583(9)	.229(6)	.639(7)	3.3(12)
HN2	.644(8)	.189(6)	.752(7)	2.6(11)	HC21	.318(8)	-.193(5)	.648(7)	2.8(11)
HC22	.521(8)	-.135(5)	.794(6)	1.2(9)	HC23	.286(8)	-.199(6)	.882(6)	3.4(11)

Table 2. Bond distances and angles with estimated standard deviations. i: $\frac{1}{2}+x$, $\frac{1}{2}+y$, $\frac{1}{2}+z$. ii: $1+x$, y, $1+z$. Values from the earlier investigation are also included.

Distance	(Å)	(Å)	Distance	(Å)	(Å)
O – C1	1.264(4)	1.27(9)	N – C1	1.307(4)	1.35(11)
C1 – C2	1.497(5)	1.56(12)	N···Br^-_{ii}	3.388(3)	3.41(8)
N···Br^-_{i}	3.439(3)	3.41(8)	O···O′	2.438(5)	2.48
O – HO	0.93(8)		N – HN1	0.86(5)	
N – HN2	0.83(5)		C2 – HC21	0.94(5)	
C2 – HC22	0.92(4)		C2 – HC23	0.95(5)	
HO···O′	1.55(9)		HN1···Br^-_{i}	2.59(5)	
HN2···Br^-_{ii}	2.57(5)				
Angle	(°)	(°)	**Angle**	(°)	(°)
O – C1 – N	119.7(3)	117(1)	O – C1 – C2	121.3(3)	123(1)
N – C1 – C2	119.0(3)	118(1)	C1 – N···Br^-_{ii}	115.6(2)	114(1)
C1 – N···Br^-_{i}	123.8(2)	114(1)	C1 – O···O′	116.0(2)	113(1)
C1 – O – HO	103(7)		C1 – N – HN1	120(3)	
C1 – N – HN2	122(4)		HN1 – N – HN2	118(3)	
C1 – C2 – HC21	114(3)		C1 – C2 – HC22	112(3)	
C1 – C2 – HC23	103(3)		HC21 – C2 – HC22	107(4)	
HC21 – C2 – HC23	107(4)		HC22 – C2 – HC23	114(4)	
O – HO···O′	159(11)		N – HN1···Br^-_{i}	172(5)	
N – HN2···Br^-_{ii}	171(5)				

The form factors used were those of Doyle *et al.*[3] except for hydrogen.[4] The final R-value was 4.5 % ($R_w = 4.9$ %) for 1165 observed reflections.

Final fractional coordinates and thermal parameters are listed in Table 1. From the thermal parameters of this table the principal axes of the thermal vibration ellipsoids for the non-hydrogen atoms were calculated. Maximum r.m.s. amplitudes range from 0.145 to 0.185 Å (corresponding B-values are 1.65 and 2.70 Å^2). Bond distances and angles with estimated standard deviations (calculated from the correlation matrix of the final least-squares refinement cycle) are given in Table 2. Fig. 1 is a schematic drawing showing the numbering of atoms, and the stereoscopic illustration of Fig. 2 indicates the hydrogen bonding system.

The refining scheme for HO mentioned above strongly suggests that the O···O′ hydrogen bond of length 2.438(5) Å is in fact asymmetric. However, the uncertainty in the proton position is large, and the degree of asymmetry is not significantly larger than that of a corre-

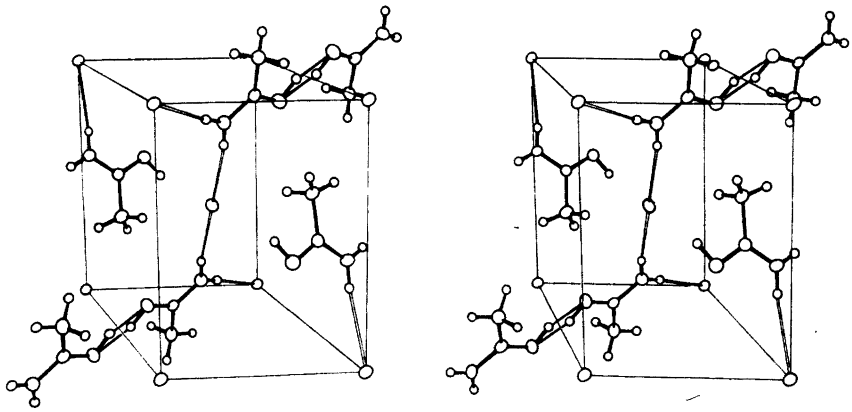

Fig. 2. Stereoscopic illustration showing the hydrogen bonding system [Johnson, C. K. *ORTEP* ORNL-3794, Oak Ridge National Laboratory, Oak Ridge 1965]. a-axis is across, b-axis down the page.

spondingly short intramolecular hydrogen bond in the enol form of 5,6-diacetyl-2,9-dimethyl-4,7-decanedione,[5] where O···O′ = 2.439(1) Å, O – HO = 1.08(2) Å, and HO···O = 1.42(2) Å.

Bond distances and angles of the acetamide molecule in the present structure may be compared with those of a recent low temperature crystal structure redetermination of the separate molecule.[6] The C1 – N bond of the present compound (1.307(4) Å) is somewhat shorter than that of acetamide itself (1.330(1) Å), and the angle C2 – C1 – N is more open (119.0(3)°; 116.8(1)°). As to be expected, the C1 – O bond is elongated (1.264(4) Å; 1.247(1) Å). No other geometrical parameters show significant differences. The four non-hydrogen atoms are coplanar to within 0.008 Å.

The two N···Br^- distances of length 3.388(3) Å and 3.439(3) Å are normal for hydrobromides of this type,[7] and the N – HN···Br^- bonds are, within error limits, linear.

1. Wiemann, J., Gillier-Pandrau, M., Thoai, N. and Beauté, C. *Bull. Soc. Chim. Fr.* (1969) 2147.
2. Groth, P. *Acta Chem. Scand. 27* (1973) 1837.
3. Doyle, P. A. and Turner, P. S. *Acta Crystallogr. A 24* (1968) 392.
4. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys. 43* (1965) 3175.
5. Groth, P. and Semmingsen, D. *Acta Chem. Scand. B 30* (1976) 737.
6. Ottersen, T., Hope, H. and Almlöf, J. *To be published.*
7. Ernst, S. R. and Cagle, Jr., F. W. *Acta Crystallogr. B 29* (1973) 1543.

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