ACTA CHEMICA SCANDINAVICA 23 (1969) 2764–2772

Hydrogen Bond Studies

38.* The Crystal Structure of Hydrazinium Acetate

SEHAM ABDEL HADY,** INGER NAHRINGBAUER, and IVAR OLOVSSON

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The crystal structure of hydrazinium acetate, $CH_3COON_2H_5$, has been determined from three-dimensional X-ray data. Four formula units crystallize in a monoclinic unit cell with the dimensions $a=7.791$, $b=8.386$, $c=7.073$ Å, and $\beta=104.00°$. The space group is *Cc*. The acetate and hydrazinium ions are joined by hydrogen bonds into puckered layers. The hydrazinium ions in adjacent layers are linked by hydrogen bonds of the type $N^+-H\cdots N$ into zig-zag chains. A three-dimensional hydrogen-bond system is thus formed.

The present analysis was undertaken as part of a study of the hydrogen bonds in compounds formed between simple carboxylic acids (formic acid, acetic acid) and ammonia or hydrazine. The crystal structures of the following compounds have been reported earlier: $HCOONH_4$,[1] CH_3COONH_4,[2] $CH_3COONH_4\cdot NH_3$,[3] $CH_3COONH_4\cdot 2NH_3$,[4] and $CH_3COONH_4\cdot CH_3COOH$.[5]

The thermal analysis of the binary system hydrazine—acetic acid indicates only the 1:1 compound.[6] The present structure determination of this compound, hydrazinium acetate, is based on single-crystal X-ray data.

EXPERIMENTAL

Hydrazinium acetate was prepared by mixing hydrazine monohydrate (*purum*) with 99—100 % acetic acid (*pro analysi*) in the ratio 1:1. Crystallization was induced by adding a small amount of chloroform-ethanol (1:1). By recrystallization from this solvent needle-formed crystals were obtained, with the *c* axis very close to the needle axis. The melting point was found to be 97—98°C in fair agreement with the value 96—97°C reported by Harris and Stone [7] (a melting point of 87.5°C has also been reported [6]). Chemical analysis of the crystals gave 49.94 mole % hydrazine (analyzed by titration, using the bromate method, at the Central Analytical Laboratory of this department).

* Part 37: *J. Chem. Phys. In press.*

** Permanent address: X-Ray Crystallographic Unit, National Research Centre, Dokki, Cairo, Egypt. Correspondence should be addressed to the coauthors.

As the crystals dissolve in all common adhesives, they were gently forced into glass capillaries (wall thickness 0.01–0.02 mm).

Equi-inclination Weissenberg photographs for the layers 0 to 6 were taken of a crystal set along the *c* axis using unfiltered Cu*K* radiation. The number of independent reflexions recorded was 376, corresponding to 77 % of the reflexions within the copper sphere. Of those recorded 35 were too weak to be measured. The relative intensities were estimated visually using the multiple-film technique (five films) by comparison with an intensity scale. The intensity range was 1 to 9000. The data were corrected for the Lorentz and polarization effects. No absorption correction was applied since the crystal was in the form of a very small needle with nearly circular cross-section. The μR value is approximately 0.77. No correction for extinction effects was applied.

The connection between the data from different layers was obtained by using another set of equi-inclination Weissenberg photographs from a crystal set along [101], layers 0 to 8. The calculations were based on the expression given by Rollett and Sparks.[8] As this method may give incorrect results [9] the inter-layer scale factors so obtained were used only in the determination of the structure and in the preliminary refinements. In the final refinements the inter-layer scaling was based on the least-squares calculations.

SPACE GROUP AND UNIT CELL

The data showed the diffraction symmetry $2/m$ indicating a monoclinic unit cell. The absence of reflexions hkl for $h+k=2n+1$, and $h0l$ for $l=2n+1$ suggests the space group Cc or $C2/c$. According to the subsequent refinements using both space groups, and the chemical arguments given below the structure is most appropriately described in Cc.

The cell dimensions were determined from quartz-calibrated rotation and zero-layer oscillation photographs around [100] and [101]. The following values were obtained: $a=7.806$, $b=8.387$, $c=7.074$ Å, and $\beta=103.95°$ ($a=4.913$ and $c=5.405$ Å for α quartz at 25°C; $\lambda(\mathrm{Cu}K\alpha_1)=1.54051$ Å, $\lambda(\mathrm{Cu}K\alpha_2)=1.54433$ Å, $\lambda(\mathrm{Cu}K\beta)=1.39217$ Å). Furthermore, a powder photograph was taken in a Guinier-Hägg camera with strictly monochromatized $\mathrm{Cu}K\alpha_1$ radiation using silicon as an internal standard ($a=5.43054$ Å). By least-squares treatment of 43 observations from this powder photograph the following cell dimensions were obtained (program CELSIUS; standard deviations given within parentheses refer to the last digit): $a=7.791(1)$, $b=8.386(1)$, $c=7.073(1)$ Å, $\beta=104{,}00(2)°$, $V=448{,}4$ Å^3. This last set of cell dimensions was finally used. With four formula units in the cell the calculated density of the solid is 1.364 g·cm^{-3} as compared to the value 1.36 g·cm^{-3} experimentally determined by weighing the specimen in air and in *m*-xylene.

DETERMINATION OF THE CRYSTAL STRUCTURE

Localization of the atoms. The atomic coordinates were determined from three-dimensional Patterson maps considering the space group Cc. The data used were those collected around the *c* axis. The intramolecular O—O vector in the acetate group was found to be nearly parallel to the *a* axis. An examination of the Harker line $(0,2y,1/2)$ gave the y coordinates of O(1) and O(2). The position of the methyl carbon was determined from the indicated intramolecular C—O vectors. However, the coordinates of the carboxyl carbon had to be calculated from the known dimensions of the acetate group as no

appropriate vectors could be identified. Finally, the positions of the nitrogen atoms were obtained from the three-dimensional electron density based on the atomic coordinates determined so far.

The preliminary structure obtained was also consistent with the space group $C2/c$, with two carbon atoms on the twofold axis and one oxygen and one nitrogen atom in general eightfold positions. In this space group the nitrogen atoms belonging to the same $N_2H_5^+$ ion are virtually equivalent and this is also true for the two oxygen atoms of the CH_3COO^- ion.

Refinement of the structure. The preliminary atomic coordinates of all atoms except the hydrogen atoms were improved by three-dimensional electron density calculations assuming no centre of symmetry. As the structure remained pseudo-centrosymmetric the subsequent refinement of the atomic parameters was performed by the method of least squares using both Cc and $C2/c$. Refinement of inter-layer scale factors, coordinates and isotropic thermal parameters gave final discrepancy indices $R=\sum||F_o|-|F_c||/\sum|F_o|$ of 0.122 in Cc and 0.168 in $C2/c$. At this stage the shifts were less than 0.1σ. After that, the temperature factors were subjected to anisotropic refinement together with the atomic coordinates and an overall scale factor. The inter-layer scale factors were fixed to the values obtained from the final isotropic refinements. The total number of parameters varied increased from 29 to 53 in Cc and from 15 to 29 in $C2/c$. Two cycles of refinements made the shifts insignificant and reduced the R values to 0.116 and 0.154, respectively. Considering the R values the structure is most appropriately described in Cc. This is also the most reasonable choice from a chemical point of view as in the case of $C2/c$ the nitrogen atoms of the $N_2H_5^+$ ion are equivalent which is incompatible with an ordered arrangement of $N_2H_5^+$ ions.

An investigation of the deutero compound, $CD_3COON_2D_5$, by neutron diffraction is in progress at this Institute. By assuming the hydrogen and

Table 1. Atomic coordinates ($\times 10^4$) and thermal vibration tensor components ($\times 10^4$ Å^2) with standard deviations within parentheses. U_{ij} are coefficients in the expression $\exp[-2\pi^2(h^2a^{-2}U_{11}+\cdots+2hka^{-1}b^{-1}U_{12}+\cdots)]$. For the hydrogen atoms the Debye-Waller factors $B=4$ Å^2 were used.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	3481(14)	1065(5)	4658(14)	382(31)	440(24)	626(36)	−9(21)	208(21)	77(20)
O(2)	6408(13)	1193(5)	5300(14)	372(33)	432(21)	529(33)	−2(21)	101(22)	−1(19)
N(1)	5766(11)	4346(6)	5680(11)	350(33)	384(26)	278(34)	−46(20)	157(25)	−14(18)
N(2)	4345(12)	4563(6)	3921(12)	418(33)	415(26)	308(33)	−72(21)	107(22)	23(17)
C(1)	5000	417(6)	5000	404(28)	409(25)	234(32)	−32(34)	115(21)	−2(23)
C(2)	5074(17)	−1385(7)	5025(16)	546(41)	415(30)	614(46)	−5(39)	236(34)	0(33)

Probable atomic coordinates ($\times 10^3$) for the hydrogen atoms.

		x	y	z			x	y	z			x	y	z
	H(1)	526	468	682		H(4)	375	348	355		H(6)	428	−180	569
N(1)	H(2)	684	500	543	N(2)	H(5)	334	533	413	C(2)	H(7)	476	−179	365
	H(3)	619	311	570							H(8)	630	−173	569

deutero compounds to be isostructural the approximate positions of the hydrogen atoms were obtained from that study. A difference synthesis using the X-ray data and based on the parameters from the last cycle of anisotropic refinement in *Cc* indicated nearly the same hydrogen positions.

Table 2. Root-mean-square components R_i (Å) of thermal displacement along the principal axes of the ellipsoids.

	O(1)	O(2)	N(1)	N(2)	C(1)	C(2)
R_1	0.172	0.187	0.136	0.162	0.141	0.203
R_2	0.207	0.208	0.182	0.186	0.190	0.206
R_3	0.250	0.224	0.204	0.219	0.207	0.250

Table 3. Observed and calculated structure factors. Reflexions which were too weak to be measured are indicated with an asterisk and were assigned the intensity $1/2I_{min}$. The reflexion 002 was excluded from the least-squares refinement as it was not measured accurately due to its high intensity.

h	k	l	$\|F_o\|$	$\|F_c\|$
2	0	0	50.5	52.1
4	0	0	19.4	18.2
6	0	0	9.5	9.2
8	0	0	3.4	3.5
1	1	0	14.8	13.3
3	1	0	14.4	13.0
5	1	0	18.5	16.6
7	1	0	23.5	20.9
9	1	0	4.5	4.4
0	2	0	51.8	56.6
2	2	0	27.4	24.6
4	2	0	1.1	1.3
6	2	0	1.4	1.9
8	2	0	2.1	2.4
1	3	0	41.4	35.5
3	3	0	10.2	10.1
5	3	0	4.5	5.5
7	3	0	1.1	0.9 *
9	3	0	3.5	3.1
0	4	0	31.3	30.5
2	4	0	7.8	8.3
4	4	0	14.4	14.8
6	4	0	8.5	8.6
8	4	0	4.0	4.2
1	5	0	11.3	12.5
3	5	0	15.6	15.6
5	5	0	1.0	1.0 *
7	5	0	7.3	6.7
0	6	0	7.9	8.6
2	6	0	0.9	1.3 *
4	6	0	6.8	7.4
6	6	0	1.1	1.0 *
1	7	0	10.9	11.9
3	7	0	4.9	5.2
5	7	0	1.6	1.6
7	7	0	0.7	1.0 *
0	8	0	1.5	1.5
2	8	0	4.5	4.7
4	8	0	3.0	3.0
6	8	0	6.3	5.5
1	9	0	5.5	6.0
3	9	0	5.7	5.1
5	9	0	3.7	3.3
0	10	0	4.3	3.6
2	10	0	6.7	5.9
-7	1	1	4.1	5.0
-5	1	1	10.6	8.1
-3	1	1	22.0	20.8
-1	1	1	31.7	31.1
1	1	1	10.2	11.0
3	1	1	29.5	29.6
5	1	1	6.4	5.7
7	1	1	4.3	3.8
9	1	1	2.2	2.2
-8	2	1	9.9	8.2
-6	2	1	10.3	12.1
-4	2	1	35.1	32.0
-2	2	1	38.4	36.8
0	2	1	10.9	9.2
2	2	1	24.8	24.9
4	2	1	8.8	9.2
6	2	1	13.8	15.6
8	2	1	4.1	3.4
-7	3	1	6.1	5.5
-5	3	1	5.5	5.2
-3	3	1	7.1	7.4
-1	3	1	63.0	54.2
1	3	1	32.6	30.5
3	3	1	23.6	24.2
5	3	1	6.8	6.9
7	3	1	3.6	4.0
-8	4	1	9.5	8.7
-6	4	1	8.8	10.7
-4	4	1	5.1	4.4
-2	4	1	14.2	11.3
0	4	1	4.8	4.4
4	4	1	4.7	4.2
6	4	1	8.8	10.8
8	4	1	4.7	4.6
1	5	1	13.1	12.7
3	5	1	5.1	5.0
5	5	1	3.5	2.8
7	5	1	9.0	8.5
-3	5	1	31.5	27.3
-1	5	1	26.9	24.3
1	5	1	20.7	18.9
3	5	1	10.2	12.4
5	5	1	2.4	2.8
7	5	1	4.0	3.0
-8	6	1	4.4	4.1
-6	6	1	5.9	4.9
-4	6	1	11.8	13.2
-2	6	1	3.1	3.1
0	6	1	13.6	13.5
2	6	1	10.0	12.5
4	6	1	15.8	17.6
6	6	1	5.5	4.8
-7	7	1	4.3	4.1
-5	7	1	6.5	6.2
-3	7	1	16.1	16.4
-1	7	1	2.3	2.8
1	7	1	2.3	3.4
3	7	1	10.0	11.2
5	7	1	1.7	0.9 *
-6	8	1	1.3	0.9 *
-4	8	1	3.5	3.1
-2	8	1	3.6	3.4
0	8	1	6.1	6.4
2	8	1	5.0	5.3
4	8	1	4.2	4.1
-5	9	1	1.6	3.8 *
-3	9	1	2.3	1.3 *
-1	9	1	2.5	1.5 *
1	9	1	2.5	0.9 *
3	9	1	3.1	2.5
-2	10	1	2.6	2.5
0	10	1	4.8	4.1
2	10	1	4.2	3.7
-2	0	2	73.0	79.9
0	0	2	56.5	101.3**
2	0	2	20.5	20.8
4	0	2	18.0	18.4
6	0	2	8.9	8.9
8	0	2	3.5	3.9
-5	1	2	3.0	3.6
-3	1	2	31.5	25.5
-1	1	2	36.0	26.5
1	1	2	39.3	32.9
3	1	2	11.5	10.7
5	1	2	20.0	20.8
7	1	2	11.3	11.8
-6	2	2	6.1	5.5
-4	2	2	14.0	13.1
-2	2	2	39.1	30.7
0	2	2	33.4	26.2
2	2	2	6.3	6.9
4	2	2	6.4	8.0
6	2	2	3.8	1.3 *
8	2	2	3.2	1.3 *
-5	3	2	2.4	1.2 *
-3	3	2	5.2	5.4
-1	3	2	38.8	29.7
1	3	2	4.7	5.1
3	3	2	17.3	18.6
5	3	2	3.6	4.3
7	3	2	2.7	1.6 *
-6	4	2	3.7	4.4
-4	4	2	20.9	17.6
-2	4	2	3.9	4.4
0	4	2	32.5	25.8
2	4	2	8.9	9.8
4	4	2	5.0	4.7
6	4	2	9.1	8.5
8	4	2	1.7	0.8 *
-7	5	2	7.8	7.9
-5	5	2	3.7	4.7
-3	5	2	13.1	12.2
-1	5	2	15.1	14.4
1	5	2	6.3	6.1
3	5	2	10.5	11.5
5	5	2	3.9	3.6
7	5	2	3.2	4.0
-6	6	2	5.2	5.9
-4	6	2	5.2	5.8
-2	6	2	3.5	3.8
0	6	2	5.9	6.1
2	6	2	5.1	6.1
4	6	2	5.6	6.2
6	6	2	3.8	2.1 *
-5	7	2	3.9	3.3
-3	7	2	6.6	8.2
-1	7	2	8.9	10.0
1	7	2	7.3	7.2
3	7	2	3.9	4.4
5	7	2	2.6	2.9 *
-4	8	2	7.7	7.6
-2	8	2	3.8	4.0
0	8	2	3.9	3.5
2	8	2	2.8	1.0 *
4	8	2	2.5	1.6 *
-5	9	2	1.7	2.4 *
-3	9	2	2.5	2.2 *
-1	9	2	5.4	6.3
1	9	2	2.6	0.2 *
3	9	2	7.5	8.1
-2	10	2	7.5	5.7
0	10	2	2.0	1.8 *
2	10	2	3.0	3.0
-3	1	3	7.7	8.3
-1	1	3	23.0	19.5
1	1	3	9.2	9.3
3	1	3	20.8	19.7
5	1	3	2.5	2.6
7	1	3	3.0	2.8
-4	2	3	35.1	36.1
-2	2	3	9.8	9.0
0	2	3	22.1	22.8
2	2	3	9.1	8.6
4	2	3	1.9	2.0
6	2	3	7.7	8.7
8	2	3	1.6	1.6
-5	3	3	6.9	7.7
-3	3	3	7.8	7.7
-1	3	3	31.1	29.2
1	3	3	6.3	5.5
3	3	3	21.8	21.7
5	3	3	1.1	2.1 *
7	3	3	4.8	4.4
-4	4	3	12.1	11.5
-2	4	3	8.3	7.0
0	4	3	15.4	14.6
2	4	3	13.3	13.0
4	4	3	12.6	12.1
6	4	3	6.9	6.7
-5	5	3	14.6	17.0
-3	5	3	26.5	22.9
-1	5	3	9.5	8.6
1	5	3	2.6	2.8
3	5	3	3.5	3.5
5	5	3	3.5	3.1
7	5	3	1.3	1.5
-4	6	3	10.0	9.9
-2	6	3	4.7	4.6
0	6	3	1.0	0.8 *
2	6	3	19.0	18.7
4	6	3	11.7	12.5
6	6	3	0.8	0.9
-5	7	3	10.7	10.5
-3	7	3	10.8	12.4
-1	7	3	4.7	4.6
1	7	3	1.1	0.9 *
3	7	3	2.4	2.5
5	7	3	2.1	2.0
-4	8	3	2.1	1.5 *
-2	8	3	3.8	4.0
0	8	3	5.8	5.3
2	8	3	3.7	3.5
-3	9	3	1.8	2.3
-1	9	3	3.4	3.1
1	9	3	1.3	0.9
3	9	3	1.3	0.9
0	10	3	4.4	4.0
0	0	4	15.7	19.2
2	0	4	21.4	21.6
4	0	4	2.7	2.5
6	0	4	12.0	11.1
-3	1	4	9.6	8.9
-1	1	4	31.1	34.2
1	1	4	22.4	24.6
3	1	4	9.1	8.6
5	1	4	9.3	10.0
7	1	4	2.3	2.3
-4	2	4	11.9	11.7
-2	2	4	13.8	11.6
0	2	4	1.2	1.2 *
2	2	4	9.2	9.2
4	2	4	2.7	3.0
6	2	4	4.1	3.6
-5	3	4	4.5	3.7
-3	3	4	8.0	6.6
-1	3	4	9.1	8.0
1	3	4	8.8	8.9
3	3	4	9.8	10.8
5	3	4	2.1	1.2 *
7	3	4	2.6	2.1
-4	4	4	11.2	10.6
-2	4	4	11.5	10.3
0	4	4	14.6	13.7
2	4	4	6.8	6.6
4	4	4	3.0	2.6
6	4	4	4.3	4.0
-5	5	4	7.7	7.1
-3	5	4	5.9	5.6
-1	5	4	12.3	10.7
1	5	4	2.6	2.5
3	5	4	5.1	5.2
5	5	4	4.8	3.6
7	5	4	2.2	1.2 *
-6	6	4	4.1	4.3
-4	6	4	2.1	2.0 *
-2	6	4	5.5	5.3
0	6	4	2.0	1.7 *
2	6	4	5.9	6.9
4	6	4	4.0	3.1
-5	7	4	4.9	4.7
-3	7	4	5.2	4.8
-1	7	4	5.2	4.9
1	7	4	5.2	4.9
3	7	4	4.0	3.9
-4	8	4	8.0	6.7
-2	8	4	2.1	1.6
0	8	4	5.8	5.5
2	8	4	1.8	1.1 *
-1	9	4	1.6	1.9 *
1	9	4	5.0	4.7
-5	1	5	6.5	6.5
-3	1	5	2.0	2.4
-1	1	5	7.8	7.3
1	1	5	8.3	8.5
3	1	5	7.0	7.4
5	1	5	3.4	3.2
-4	2	5	19.0	17.5
-2	2	5	11.1	10.8
0	2	5	13.6	14.5
2	2	5	4.8	4.8
4	2	5	1.2	1.0 *
6	2	5	2.2	2.1
-5	3	5	6.1	5.8
-3	3	5	1.8	2.5
-1	3	5	9.1	9.2
1	3	5	11.1	10.4
3	3	5	6.9	7.3
5	3	5	6.3	5.4
-6	4	5	4.1	4.6
-4	4	5	4.7	4.5
-2	4	5	9.6	10.0
0	4	5	15.1	15.3
2	4	5	8.5	8.8
4	4	5	3.7	4.5
-5	5	5	13.0	13.3
-3	5	5	8.0	8.9
-1	5	5	3.1	3.4
1	5	5	2.8	3.2
3	5	5	4.6	4.7
5	5	5	3.5	3.2
-6	6	5	3.7	3.4
-4	6	5	10.4	9.4
-2	6	5	4.1	4.2
0	6	5	6.7	7.6
2	6	5	12.9	12.5
4	6	5	4.1	3.9
-5	7	5	9.8	8.5
-3	7	5	4.5	4.1
-1	7	5	3.8	4.7
1	7	5	2.9	2.8
3	7	5	4.8	4.5
-4	8	5	3.8	3.4
-2	8	5	1.5	1.4
0	8	5	2.0	1.9
2	8	5	3.6	3.6
0	0	6	8.9	8.9
2	0	6	5.3	5.6
4	0	6	7.4	7.3
-3	1	6	10.8	10.3
-1	1	6	21.0	23.6
1	1	6	9.8	9.7
3	1	6	2.0	1.7
5	1	6	2.2	2.7
-4	2	6	2.8	2.8
-2	2	6	5.1	4.6
0	2	6	6.0	5.5
2	2	6	2.6	2.9
4	2	6	5.0	4.1
-5	3	6	2.7	4.4
-3	3	6	3.2	3.2
-1	3	6	3.4	3.4
1	3	6	6.0	6.7
3	3	6	2.8	2.6
5	3	6	2.7	2.3
-4	4	6	4.3	3.5
-2	4	6	7.0	7.7
0	4	6	3.2	3.6
2	4	6	5.3	5.4
4	4	6	1.6	1.6
-5	5	6	6.7	6.7
-3	5	6	2.0	2.2
-1	5	6	5.5	5.7
1	5	6	2.0	1.7
3	5	6	2.9	2.1
-4	6	6	2.6	3.0
-2	6	6	3.4	3.5
0	6	6	3.4	2.6
2	6	6	4.0	3.9
-5	7	6	2.0	2.2
-3	7	6	1.7	1.7
-1	7	6	4.2	3.7
1	7	6	2.9	2.8
-2	8	6	4.6	4.3

A new series of least-squares refinements (isotropic and anisotropic) analogous to that described previously was now performed in *Cc*, including the hydrogen atoms with fixed parameters. The Debye-Waller factors used for the hydrogen atoms were 4 Å^2. When the shifts were less than 0.1σ the final R value for the anisotropic refinement was 0.092.

Table 1 lists the final atomic coordinates and vibration tensor components U_{ij}. The latter were transformed from the anisotropic thermal parameters β_{ij} according to Scheringer.[10] The r.m.s. components of thermal displacement along the principal axes of the ellipsoids are given in Table 2. The observed and calculated structure factors are compared in Table 3.

Table 4. Distances (Å) with standard deviations ($\times 10^3$) within parentheses.

Covalent bonds.

C(1)–O(1) = 1.271(10)	N(1)–N(2) = 1.462(12)
–O(2) = 1.249(9)	
–C(2) = 1.513(7)	

Intermolecular bond distances less than 3.3 Å (*cf.* Fig. 2).

N(1)–H(1)···N(2) = 2.923(11)	N(2)–H(4)···O(1) = 3.081(8)
–H(2)···O(1) = 2.796(12)	–H(5)···O(2) = 3.022(12)
–H(3)···O(2) = 2.716(7)	···O(2) = 3.060(13)
···O(1) = 3.103(13)	···O(2) = 3.280(9)
···O(1) = 3.261(9)	

The Fourier calculations were performed with the program DRF. In the least-squares refinements the full-matrix program LALS was used with minimization of the function $\sum w(|F_o|-|F_c|)^2$. The weights were calculated according to the expression $w=1/(a+|F_o|+c|F_o|^2+d|F_o|^3)$. Final values

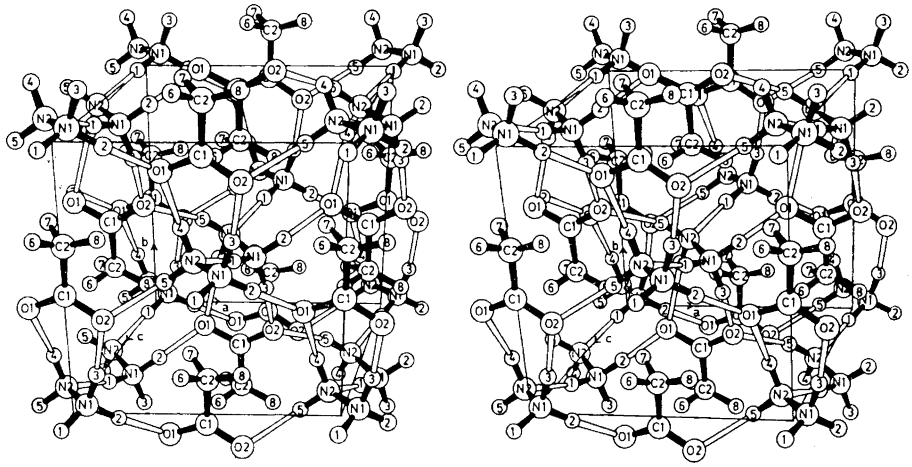

Fig. 1. A stereoscopic pair of drawings showing the hydrogen-bond pattern in hydrazinium acetate. Covalent bonds are filled and probable hydrogen bonds are open.

used for a, c, and d were 1.1, 0.02, and 0.005, respectively. Reflexions too weak to be measured were given zero weight, and were also omitted in all calculations of R values. The atomic scattering factors used were those of neutral O, N, C, and H given in the *International Tables* (Vol. III, p. 202).[11] Distances (Table 4 and Fig. 2) and angles (Figs. 3—5) together with standard deviations were calculated from the atomic coordinates and standard

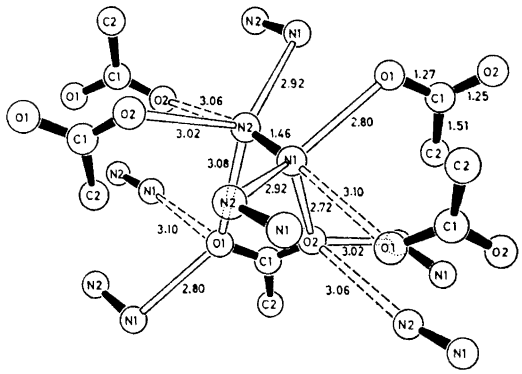

Fig. 2. Bond distances around the nitrogen and the oxygen atoms and within the hydrazinium and the acetate ions. Covalent bonds are filled. Hydrogen bond distances are represented by full lines and other short N···O distances are drawn as broken lines.

deviations obtained from the final least-squares calculation, using the program DISTAN. The errors in the cell dimensions were also included. No correction was made for thermal motion. The illustrations were prepared by means of the plot program OR TEP. All calculations were performed on the CD 3600 computer in Uppsala. A more detailed description of the programs used has been given in an earlier paper.[2]

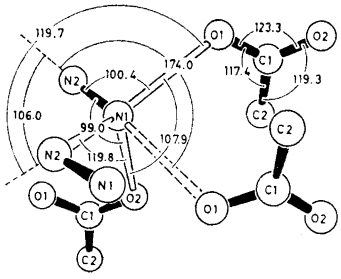

Fig. 3. Bond angles around N(1) and within the acetate ion. The standard deviations range from 0.3 to 0.6°. The notation is the same as in Fig. 2.

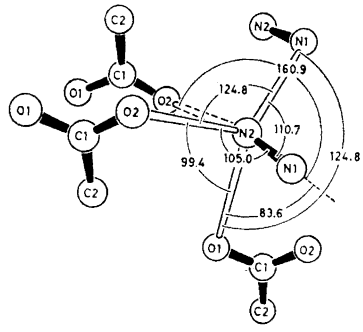

Fig. 4. Bond angles around N(2). Standard deviations 0.3—0.6°. Notation as in Fig. 2.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The packing arrangement is illustrated in Fig. 1. The structure is built up from $N_2H_5^+$ and CH_3COO^- ions which are joined by hydrogen bonds into puckered layers parallel to (001). The acetate groups deviate only slightly

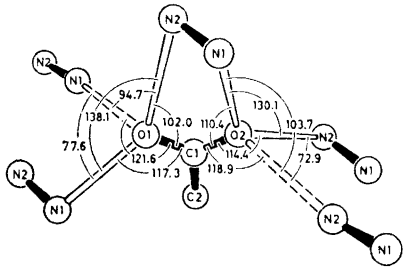

Fig. 5. Bond angles around the oxygen atoms. Standard deviations 0.3—0.5°. Notation as in Fig. 2.

from this plane. The hydrazinium ions in adjacent layers are linked by hydrogen bonds, of the type $N^+—H\cdots N$, into zig-zag chains extending along the *c* axis. A three-dimensional hydrogen-bond system is thus formed.

The hydrazinium ion

The N—N distance, 1.462(12) Å is somewhat longer but not significantly different from earlier reported values (the standard deviation within the parenthesis refers to the last digits). The mean value in four compounds studied by Liminga is 1.444 Å.[12] As seen from Fig. 1 the orientation of the hydrazinium ion is approximately eclipsed.

Hydrogen bonds from the NH_3^+ end of the hydrazinium ion. One of the three hydrogen atoms belonging to N(1) is involved in a hydrogen bond to the lone pair of N(2) in an adjacent $N_2H_5^+$ ion. Zig-zag chains of $N_2H_5^+$ ions are thus formed extending along the *c* axis. The bond length, 2.923(11) Å, is comparable to the values found in other hydrazinium compounds with similar chains: 2.896(8) Å in $N_2H_5H_2PO_4$,[13] 2.858(5) Å in $N_2H_5HC_2O_4$,[14] 2.95 Å in N_2H_5Cl,[15] and 2.93 Å in N_2H_5Br.[16]

The other two hydrogen atoms connected to N(1) participate in hydrogen bonds to two oxygen atoms, O(1) and O(2), in different acetate ions. The bond lengths, 2.796(12) and 2.716(7) Å, respectively, may be compared with the hydrogen bond, of the type $N^+—H\cdots O^-$, joining an ammonium ion and an acetate ion. In the compounds $CH_3COONH_4\cdot nNH_3 (n=0, 1, 2)$, and $CH_3COONH_4\cdot CH_3COOH$ the N···O distance ranges from 2.80 to 2.95 Å.[2-5]

In addition to the neighbours of N(1) mentioned above there is an atom O(1) at 3.10 Å from N(1). The angle $N(2)—N(1)\cdots O(1)$ is 174° and thus O(1) is close to the extension of the N—N axis. A similar situation is found in several other compounds, *e.g.* $N_2H_5H_2PO_4$,[14] $(N_2H_5)_2SO_4$,[17] and $LiN_2H_5SO_4$.[19]

Hydrogen bonds from the NH_2 end of the hydrazinium ion. As mentioned previously, N(2) accepts one hydrogen bond from N(1). Further neighbours to N(2) are one O(1) and two O(2) at the distances 3.081(8),

3.022(12), and 3.060(13) Å, respectively. According to the location of the two hydrogen atoms connected to N(2) only the first two distances represent hydrogen bonds. Both of the bonds are bent, especially the first one ($\angle$N(2)—H(4)···O(1)=143°). The bond lengths seem reasonable if compared with the distances of the hydrogen bonds formed between the ammonia and the acetate ion in the mono and diammine of ammonium acetate (N···O=3.15—3.22 Å).[3,4] The oxygen atom, 3.060 Å from N(2), lies near to the extension of the N—N axis; the angle N(2)—N(1)···O(2) is 161°. (Compare the situation at the NH_3^+ end).

The acetate ion

The least-squares plane defined by O(1), O(2), C(1), and C(2) (max. deviation 0.01 Å) is nearly parallel to (001); the angle between the planes is 6°. The carbon-oxygen distances are hardly significantly different C(1)—O(1)=1.271(10) Å and C(1)—O(2)=1.249(9) Å. The C(1)—C(2) bond length is 1.513(7) Å. The corresponding bond angles are C(2)—C(1)—O(1)=117.4(6)°, C(2)—C(1)—O(2)=119.3(6)°, and O(1)—C(1)—O(2)=123.3(5)°. These dimensions of the acetate ion are comparable with the values found in related compounds.[2–5].

The environment is similar for O(1) and O(2); both are surrounded by three nitrogen atoms but for each oxygen atom only two of the N···O contacts represent hydrogen bonds, one from an NH_3^+ end and the other from an NH_2 end. Most of the corresponding bond angles are also about the same (*cf.* Fig. 5).

The orientation of the methyl group is shown in Fig. 1. The hydrogen atom H(8) is situated close to the plane defined by C(1), C(2), O(1), and O(2), in an eclipsed position to O(2).

Acknowledgements. The authors wish to express their gratitude to the head of the Institute, Prof. G. Hägg, for all the facilities put at their disposal.

This work has been supported by grants from the *Swedish Natural Science Research Council* and the *Malmfonden — Swedish Foundation for Scientific Research and Industrial Development*, which are here gratefully acknowledged.

REFERENCES

1. Nahringbauer, I. *Acta Cryst.* **B 24** (1968) 565.
2. Nahringbauer, I. *Acta Cryst.* **23** (1967) 956.
3. Nahringbauer, I. *Acta Chem. Scand.* **22** (1968) 1141.
4. Nahringbauer, I. *Acta Chem. Scand.* **22** (1968) 2981.
5. Nahringbauer, I. *Acta Chem. Scand.* **23** (1969) 1653.
6. Semiskin, V. I. *J. Gen. Chem. USSR* **13** (1943) 632.
7. Harris, W. C. and Stone, K. G. *J. Org. Chem.* **23** (1958) 2032.
8. Rollett, J. S. and Sparks, R. A. *Acta Cryst.* **13** (1960) 273.
9. Hamilton, W. C., Rollett, J. S. and Sparks, R. A. *Acta Cryst.* **18** (1965) 129.
10. Scheringer, C. *Acta Cryst.* **20** (1966) 316.
11. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
12. Liminga, R. *Arkiv Kemi* **28** (1968) 483.
13. Liminga, R. *Acta Chem. Scand.* **19** (1965) 1629.

14. Ahmed, N. A. K., Liminga, R. and Olovsson, I. *Acta Chem. Scand.* **22** (1968) 88.
15. Sakurai, K. and Tomiie, Y. *Acta Cryst.* **5** (1952) 293.
16. Sakurai, K. and Tomiie, Y. *Acta Cryst.* **5** (1952) 289.
17. Liminga, R. and Lundgren, J.-O. *Acta Chem. Scand.* **19** (1965) 1612.
18. Nilsson, Å., Liminga, R. and Olovsson, I. *Acta Chem. Scand.* **22** (1968) 719.
19. Padmanabhan, V. M. and Balasubramanian, R. *Acta Cryst.* **22** (1967) 532.

Received March 1, 1969.