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Hydrogen Bond Studies

25.* A Neutron Diffraction Study of Hydrazinium Hydrogen Oxalate, $N_2H_5HC_2O_4$

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A study of the crystal structure of hydrazinium hydrogen oxalate, $N_2H_5HC_2O_4$, has been made, based on three-dimensional single-crystal neutron diffraction data. The parameters of the heavy atoms are in good agreement with those obtained in the previous X-ray investigation by Ahmed, Liminga and Olovsson. The hydrogen oxalate ions are linked end to end by short hydrogen bonds (2.448 Å) across centres of symmetry and these bonds are either truly symmetric or with statistically disordered hydrogens. The $N_2H_5^+$ ions have a perfectly staggered configuration with the nitrogens and one hydrogen of the NH_3^+ end situated in the mirror plane. This hydrogen links the $N_2H_5^+$ ions into zig-zag chains, while the rest of the hydrogen atoms are involved in "bifurcated" and "trifurcated" hydrogen bonds involving the oxygens of surrounding hydrogen oxalate ions.

Oxalic acid and hydrazine form two compounds, $N_2H_4 \cdot H_2C_2O_4$ and $2N_2H_4 \cdot H_2C_2O_4$. The structure of the first compound has been determined using X-rays by Ahmed, Liminga and Olovsson,[1] and was found to consist of $N_2H_5^+$ and $HC_2O_4^-$ ions. The same conclusions were drawn from the proton magnetic resonance investigation by Pratt and Richards.[2] The present neutron diffraction investigation was undertaken to obtain detailed information about the geometry of the ions and also to study the virtually symmetric hydrogen bond of 2.45 Å between the hydrogen oxalate ions. The $N_2H_5^+$ and $HC_2O_4^-$ ions have previously been studied by neutron diffraction only in the following cases: $N_2H_5^+$ in $LiN_2H_5SO_4$[3] and $HC_2O_4^-$ in ammonium tetraoxalate dihydrate.[4] For information and further references to X-ray studies of compounds containing these ions, see Refs. 5—8. A study of the compound $2N_2H_4 \cdot H_2C_2O_4$ is in progress at this Institute.

* The preceding paper in this series: *Hydrogen Bond Studies 24. The Crystal Structure of Hydrazinium Hydrogen Oxalate* by N.A.K. Ahmed, R. Liminga and I. Olovsson appeared in *Acta Chem. Scand.* **22** (1968) 88.

EXPERIMENTAL

The hydrazinium hydrogen oxalate was prepared as described earlier.[1] Large crystals were grown from the aqueous solution. After drying in a desiccator the crystals were held for a while above liquid nitrogen to reduce extinction effects (complete immersion shatters the crystal). Two crystals, with the dimensions 5.1 × 5.9 × 7.0 mm and 1.9 × 2.2 × 2.5 mm, respectively, were used for the collection of the data.

The three-dimensional neutron intensity data were collected at room temperature with a Hilger-Ferranti single crystal diffractometer at the Swedish Atomic Energy Company reactor R2 at Studsvik. The monochromatic neutron beam, reflected from the (331) planes of a large copper crystal, had a wavelength of 1.18 Å. The diffractometer was an automatic four circle instrument and ω-2θ stepscan was employed. The intensities were measured with a high pressure BF_3 proportional counter. Another similar counter was used to monitor the beam in order to eliminate the effect of variations in the neutron flux. The reflection 400 was used as a standard. A total of 711 independent reflections with 2θ less than 113° was measured twice for the large crystal and mean values of the intensities were taken. The number of reflections with intensities greater than the background was 438. The integrated intensity range was 50 to 11 700. Furthermore, the 108 strongest reflections were measured twice using the small crystal. The intensities in this case ranged from 225 to 3975, and the counting time for each reflection was about 50 min. The corresponding time for the large crystal was 25 min.

Lorentz factors were applied but no absorption or extinction corrections were made. The linear absorption coefficient for neutrons was experimentally found to be 1.7 cm^{-1}. This value corresponds to an empirical incoherent scattering cross-section for hydrogen of about 33 barns.

In order to obtain information about possible phase transformations some X-ray photographs were taken at several temperatures in a low-temperature Weissenberg camera. A new phase appeared on cooling below about −100°C. The preliminary photographs indicated no change in space group but a doubling of the c axis. The transition between the two phases appears to be completely reversible, but the crystal is evidently subjected to considerable strain in the transition process.

UNIT CELL

The dimensions of the monoclinic unit cell were determined from powder photographs recorded in a Guinier-Hägg camera using Cu$K\alpha_1$ radiation, (λ = 1.54051 Å) with silicon (a = 5.43054 Å at 25°C) as an internal standard. The cell dimensions were calculated from 48 reflections by the method of least squares using a program named CELSIUS. The cell dimensions, with estimated standard deviations within parentheses, are at 25°C: a = 3.580(1) Å, b = 13.321(2) Å, c = 5.097(1) Å, β = 102.62(1)°. U = 237.2 Å^3.

With two formula units per unit cell the calculated density is 1.709 g/cm^3. The density observed by Ahmed *et al.*[1] was 1.70 ± 0.02 g/cm^3.

SPACE GROUP AND STRUCTURE DETERMINATION

The diffraction symmetry, $2/m$, and systematic absences, $0k0$ with k odd, were the same as those observed in the X-ray case.[1] The space group is accordingly either $P2_1/m$ or $P2_1$, and the first was found to be the most probable in the previous investigation. The preference for $P2_1/m$ was based on the final least-squares refinements.

The approximate coordinates of the hydrogen atoms were obtained from Fourier maps based on the parameters of the heavy atoms obtained in the

previous X-ray study. These approximate hydrogen positions, as well as those of the heavy atoms, were compatible with both space groups (*cf.* above) and the choice of the most probable space group was again based on the final least-squares refinements.

In the space group $P2_1/m$ thus chosen, the hydrogen atom of $HC_2O_4^-$ is at a centre of symmetry (2*a*), one hydrogen atom of $N_2H_5^+$ in a mirror plane (2*e*) while the rest are in general fourfold positions.

The preliminary atomic parameters were refined by least-squares methods using the full-matrix program LALS using both space groups. In the first cycles only the data of the large crystal were utilized. After some cycles of isotropic refinement the agreement factors $R = \sum||F_o|-|F_c||/\sum|F_o|$ were about 0.15 and 0.13 in $P2_1/m$ and $P2_1$, respectively.

A comparison of the observed and calculated structure factors at this stage indicated the presence of extinction effects. However, it was found that the agreement was significantly better between the calculated structure factors and those observed from the smaller crystal. The 108 strongest reflections were therefore exchanged with those obtained from the smaller crystal. Different scale factors were used for the two sets of data, and the R values dropped to 0.129 in $P2_1/m$ and 0.103 $P2_1$. The number of parameters varied was 32 and 57, respectively. In the last cycle the shifts were smaller than 0.2σ. The standard deviations of the atomic positions were for some atoms two or three times larger in the latter space group.

Anisotropic thermal parameters were now introduced for all atoms together with the above parameters. The scale factors for the two different sets of data were fixed to the values obtained from the final isotropic refinement and an overall scale factor was refined. The total number of parameters varied was now 70 and 126 for the two space groups. After a few cycles a final R value of 0.060 was obtained in $P2_1/m$ and the shifts of all parameters were less than one tenth of their estimated standard deviations. For the non-centrosymmetric space group $P2_1$ the R value was 0.054 after two cycles. The standard deviations were this time three to seven times larger, except for the nitrogen atoms, and in addition some temperature factor coefficients were not of positive-definite form.

In the X-ray study the structure was described in terms of $P2_1/m$, and the preference for this space group was based on the least-squares refinement. A significance test on the R values according to Hamilton [17] also indicated that this choice was satisfactory. In the neutron diffraction case significance tests indicate that 1) the atoms vibrate anisotropically in both space groups, but 2) that the space group $P2_1$ should be preferred. However, the refinement could not be successfully performed in the latter space group when using anisotropic thermal parameters as mentioned above. Furthermore, the dimensions of the ions based on the parameters from the isotropic as well as anisotropic refinement in $P2_1/m$ were more reasonable than those obtained using $P2_1$. Finally, a difference Fourier synthesis based on the final parameters in $P2_1/m$ showed only negligible spurious peaks (absolute values less than 0.16×10^{-12} cm Å^{-3}; in comparison, a hydrogen peak had a density of -1.94). The above facts make it reasonable to consider the centrosymmetric space group as the most satisfactory choice.

Table 1. Hydrazinium hydrogen oxalate positional parameters with standard deviations ($\times 10^4$).

		This work	X-ray work [1]			This work	X-ray work [1]
C	x	6189(9)	6191(7)	H(1)	x	2068(31)	
	y	246(2)	247(2)		y	1876(7)	—
	z	6279(5)	6280(5)		z	−238(20)	
N(1)	x	2930(10)	2956(11)	H(2)	x	1998(27)	
	y	2500	2500		y	1877(6)	—
	z	804(7)	810(8)		z	4121(19)	
N(2)	x	1029(9)	1014(10)	H(3)	x	−1913(30)	
	y	2500	2500		y	2500	—
	z	3020(7)	3006(8)		z	2305(28)	
O(1)	x	5873(13)	5911(7)	H(4)	x	0	
	y	1155(2)	1153(2)		y	0	—
	z	6658(7)	6668(4)		z	0	
O(2)	x	8375(11)	8368(6)				
	y	−364(2)	−363(1)				
	z	7847(7)	7847(4)				

Table 2. Anisotropic temperature factor coefficients with estimated standard deviations, each multiplied by 10^4. The form of the temperature factor used is:

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)].$$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C	423(20)	16(1)	134(9)	13(8)	−121(23)	−9(5)
N(1)	601(27)	24(2)	235(12)	0	158(28)	0
N(2)	432(26)	27(2)	289(13)	0	181(29)	0
O(1)	817(35)	15(1)	234(13)	41(11)	−166(34)	−42(7)
O(2)	630(33)	21(2)	221(12)	36(11)	−218(32)	0(7)
H(1)	1378(103)	47(5)	541(42)	−114(35)	369(113)	−144(23)
H(2)	1093(81)	38(4)	574(40)	52(28)	755(95)	68(21)
H(3)	591(87)	44(5)	644(64)	0	441(122)	0
H(4)	679(73)	31(4)	339(37)	64(29)	25(83)	35(19)

Table 3. Root-mean-square components, R_i, of thermal vibration along principal axes of the ellipsoids of vibration, calculated from the β_{ij} values in Table 2 with the program OR FFE. Standard deviations $\times 10^3$ are given within parentheses.

Atom	R_1	R_2	R_3
C	0.110(8) Å	0.121(6) Å	0.189(8) Å
N(1)	0.147(6)	0.172(5)	0.193(5)
N(2)	0.156(6)	0.162(6)	0.190(5)
O(1)	0.105(9)	0.158(9)	0.255(9)
O(2)	0.128(10)	0.144(9)	0.237(9)
H(1)	0.165(19)	0.280(23)	0.300(19)
H(2)	0.175(14)	0.218(21)	0.295(17)
H(3)	0.183(19)	0.199(13)	0.284(16)
H(4)	0.149(21)	0.203(21)	0.230(22)

Table 4. Observed and calculated structure factors. An asterisk indicates reflections observed from the smaller crystal. Reflections too weak to be measured are given with $F_o = 0$.

h	k	l	$\|F_o\|$	$\|F_c\|$
0	2	0	3.44	3.21 *
0	4	0	3.56	3.45 *
0	6	0	4.28	4.13 *
0	8	0	6.27	6.44 *
0	10	0	4.46	4.45 *
0	12	0	1.62	1.82
0	14	0	5.01	5.30 *
0	16	0	1.14	1.29
0	18	0	2.05	2.05
0	0	1	2.28	2.46 *
0	1	1	0.48	0.35
0	2	1	2.87	2.92 *
0	3	1	2.72	2.80 *
0	4	1	0	0.18
0	5	1	3.54	3.63 *
0	6	1	2.18	2.25 *
0	7	1	0	0.07
0	8	1	1.50	1.26
0	9	1	1.68	1.56
0	10	1	2.14	2.08
0	11	1	3.70	3.62 *
0	12	1	0.93	0.99
0	13	1	0	0.01
0	14	1	0	0.00
0	15	1	0	0.91
0	16	1	0	0.42
0	17	1	0	0.20
0	18	1	0	0.51
0	0	2	4.92	5.26 *
0	1	2	3.38	3.42 *
0	2	2	1.49	1.54 *
0	3	2	2.21	2.22 *
0	4	2	0	0.77
0	5	2	1.47	1.46
0	6	2	1.98	1.72
0	7	2	2.14	2.00
0	8	2	0	0.45
0	9	2	2.50	2.50
0	10	2	1.57	1.00
0	11	2	4.06	4.14 *
0	12	2	1.37	1.49
0	13	2	2.00	2.08
0	14	2	2.22	2.06
0	15	2	0	0.98
0	16	2	0	0.17
0	17	2	0	0.94
0	0	3	2.27	2.43 *
0	1	3	0	0.03
0	2	3	0.67	0.53
0	3	3	2.63	2.62 *
0	4	3	0	0.08
0	5	3	1.12	0.93
0	6	3	2.38	2.31
0	7	3	4.21	4.13 *
0	8	3	3.74	3.78 *
0	9	3	1.61	1.55
0	10	3	0	0.17
0	11	3	2.67	2.70
0	12	3	0	0.35
0	13	3	0.82	0.65
0	14	3	1.57	1.61
0	15	3	0	0.79
0	16	3	0	0.55
0	0	4	2.89	3.01 *
0	1	4	2.07	2.02
0	2	4	1.19	0.98
0	3	4	4.75	4.76 *
0	4	4	1.42	1.13
0	5	4	1.29	1.53
0	6	4	0	0.95
0	7	4	1.60	1.61
0	8	4	2.43	2.23
0	9	4	0	0.02
0	10	4	1.07	0.87
0	11	4	3.12	3.19 *
0	12	4	0	0.23
0	13	4	1.14	1.04
0	14	4	0.82	0.60
0	15	4	0	0.60
0	0	5	1.15	1.02
0	1	5	1.82	1.66
0	2	5	4.06	3.98 *
0	3	5	1.79	1.40
0	4	5	0	0.21
0	5	5	1.45	1.28
0	6	5	2.18	2.11
0	7	5	0	0.43
0	8	5	1.69	1.68
0	9	5	2.57	2.24
0	10	5	0	0.16
0	11	5	2.36	2.13
0	12	5	2.66	2.53
0	13	5	1.20	1.20
0	0	6	0	0.24
0	1	6	0	0.51
0	2	6	0	0.26
0	3	6	0	0.37
0	4	6	1.72	1.58
0	5	6	0	0.63
0	6	6	0	0.02
0	7	6	0	0.10
0	8	6	0	0.33
0	9	6	1.75	1.51
0	0	7	2.93	2.70 *
1	0	-1	5.78	6.65 *
1	1	-1	0.55	0.39
1	2	-1	2.47	2.36 *
1	3	-1	1.54	1.63
1	4	-1	2.54	2.27 *
1	5	-1	0	0.02
1	6	-1	2.00	1.15
1	7	-1	0	0.06
1	8	-1	2.84	2.85 *
1	9	-1	0	0.58
1	10	-1	2.50	2.04
1	11	-1	1.40	1.51
1	12	-1	2.54	2.52
1	13	-1	0	0.14
1	14	-1	3.92	4.27 *
1	15	-1	0	0.28
1	16	-1	1.28	1.25
1	17	-1	0	0.69
1	18	-1	1.76	1.71
1	0	-2	1.44	1.71
1	1	-2	0	0.04
1	2	-2	2.43	2.68 *
1	3	-2	1.28	1.14
1	4	-2	1.93	1.99
1	5	-2	0	0.09
1	6	-2	0.91	0.87
1	7	-2	4.02	4.10 *
1	8	-2	1.92	1.95
1	9	-2	2.56	2.56
1	10	-2	0	0.43
1	11	-2	0.98	1.00
1	12	-2	0	0.08
1	13	-2	1.33	1.28
1	14	-2	0	0.21
1	15	-2	0	0.12
1	16	-2	0	0.69
1	17	-2	0	0.92
1	0	-3	2.73	3.03 *
1	1	-3	0	0.02
1	2	-3	3.24	3.40 *
1	3	-3	3.01	3.08 *
1	4	-3	1.30	1.28
1	5	-3	0	0.68
1	6	-3	2.45	2.47
1	7	-3	3.08	3.12 *
1	8	-3	0.96	0.77
1	9	-3	0	0.66
1	10	-3	1.87	1.90
1	11	-3	3.55	3.68 *
1	12	-3	2.48	2.48
1	13	-3	0	0.38
1	14	-3	1.20	1.10
1	15	-3	1.09	0.97
1	16	-3	0	0.78
1	0	-4	4.75	4.79 *
1	1	-4	1.02	1.03
1	2	-4	2.08	1.90
1	3	-4	1.64	1.75
1	4	-4	1.60	1.47
1	5	-4	1.69	1.54
1	6	-4	1.50	1.28
1	7	-4	3.33	3.26 *
1	8	-4	2.39	2.33
1	9	-4	1.75	1.75
1	10	-4	0	0.43
1	11	-4	1.60	1.52
1	12	-4	0	0.14
1	13	-4	0	0.19
1	14	-4	2.70	2.54
1	15	-4	1.37	1.40
1	0	-5	0	1.09
1	1	-5	0.96	0.83
1	2	-5	0.97	1.06
1	3	-5	2.40	2.59
1	4	-5	0	0.82
1	5	-5	0	0.51
1	6	-5	1.44	1.39
1	7	-5	0	0.05
1	8	-5	0.85	0.89
1	9	-5	0	0.45
1	10	-5	0	0.69
1	11	-5	2.15	2.12
1	12	-5	0	0.23
1	13	-5	0	0.74
1	0	-6	0.83	0.94
1	1	-6	0	0.68
1	2	-6	0	0.66
1	3	-6	1.20	1.13
1	4	-6	1.58	1.75
1	5	-6	1.11	1.10
1	6	-6	0	0.50
1	7	-6	1.02	0.97
1	8	-6	0	0.62
1	9	-6	1.94	1.89
1	10	-6	0	0.91
1	0	-7	0	0.79
1	1	-7	0	0.98
1	2	-7	0	0.71
1	3	-7	0	0.70
1	0	0	3.10	3.32 *
1	1	0	0.64	0.50
1	2	0	1.89	1.82 *
1	3	0	2.97	2.93 *
1	4	0	1.10	0.90
1	5	0	5.18	5.05 *
1	6	0	1.99	1.92 *
1	7	0	3.61	3.75 *
1	8	0	2.03	1.60
1	9	0	3.89	3.97 *
1	10	0	2.88	3.00 *
1	11	0	4.38	4.56 *
1	12	0	0.95	0.80
1	13	0	0.88	0.72
1	14	0	0	0.39
1	15	0	1.39	1.37
1	16	0	0	0.55
1	17	0	0	0.35
1	18	0	0	0.77
1	0	1	4.97	5.05 *
1	1	1	3.82	3.84 *
1	2	1	1.50	0.95
1	3	1	1.96	1.80 *
1	4	1	4.72	4.69 *
1	5	1	4.22	4.11 *
1	6	1	2.40	2.49 *
1	7	1	0	0.53
1	8	1	3.34	3.21 *
1	9	1	5.54	5.53 *
1	10	1	2.82	2.82 *
1	11	1	2.91	3.04 *
1	12	1	1.17	1.23
1	13	1	2.82	3.05 *
1	14	1	2.37	2.19
1	15	1	1.35	1.52
1	16	1	0.94	0.93
1	17	1	0.98	0.92
1	18	1	1.36	1.39
1	0	2	2.14	2.15 *
1	1	2	3.60	3.62 *
1	2	2	2.76	2.60 *
1	3	2	0	0.45
1	4	2	3.97	3.79 *
1	5	2	2.91	2.81 *
1	6	2	0	0.41
1	7	2	1.17	1.11
1	8	2	1.67	1.33
1	9	2	3.16	3.19 *
1	10	2	1.98	1.96
1	11	2	1.85	1.94
1	12	2	1.75	1.74
1	13	2	2.28	2.33
1	14	2	0	0.64
1	15	2	1.15	1.12
1	16	2	1.06	1.17
1	17	2	0	0.95
1	0	3	3.16	3.28 *
1	1	3	1.98	1.95
1	2	3	2.54	2.65 *
1	3	3	1.65	1.49
1	4	3	0	0.26
1	5	3	1.26	0.98
1	6	3	1.43	1.33
1	7	3	1.57	1.36
1	8	3	2.49	2.47
1	9	3	1.45	1.24
1	10	3	1.84	1.76
1	11	3	1.68	1.48
1	12	3	1.03	0.96
1	13	3	1.07	1.03
1	14	3	1.09	0.79
1	15	3	1.45	1.40
1	16	3	0	0.05
1	0	4	0.84	0.88
1	1	4	1.87	1.79
1	2	4	4.23	4.08 *
1	3	4	1.82	1.62
1	4	4	0	0.43
1	5	4	1.06	0.98
1	6	4	1.69	1.72
1	7	4	0	0.31
1	8	4	0	0.77
1	9	4	2.18	2.07
1	10	4	1.14	0.83
1	11	4	2.49	2.43
1	12	4	2.45	2.49
1	13	4	1.25	1.09
1	14	4	1.15	0.95
1	0	5	0	0.24
1	1	5	2.13	2.11
1	2	5	1.20	1.22
1	3	5	0.94	0.90
1	4	5	2.26	2.16
1	5	5	0.85	0.80
1	6	5	0	0.22
1	7	5	1.10	1.00
1	8	5	0	0.05
1	9	5	1.58	1.83
1	10	5	0.94	1.04
1	11	5	0	0.49
1	0	6	2.83	2.93 *
1	1	6	1.07	1.06
1	2	6	2.70	2.94 *
1	3	6	0.96	1.18
1	4	6	0	0.47
1	5	6	0	0.24
1	6	6	1.64	1.43
1	7	6	2.21	2.53 *
2	0	-1	2.33	2.46 *
2	1	-1	1.58	1.64
2	2	-1	1.40	1.25
2	3	-1	1.54	1.46
2	4	-1	0.89	0.66
2	5	-1	1.21	1.11
2	6	-1	1.11	1.03
2	7	-1	1.08	0.83
2	8	-1	2.26	2.09
2	9	-1	1.65	1.49
2	10	-1	2.27	2.20
2	11	-1	0	0.03
2	12	-1	0	0.16
2	13	-1	1.42	1.50
2	14	-1	0	0.41
2	15	-1	0	0.16
2	16	-1	0	0.91
2	17	-1	1.33	1.69
2	0	-2	2.40	2.39 *
2	1	-2	1.51	1.46
2	2	-2	4.14	4.06 *
2	3	-2	1.17	1.05
2	4	-2	1.72	1.64
2	5	-2	1.18	1.17
2	6	-2	4.28	4.27 *
2	7	-2	0	0.85
2	8	-2	3.17	3.10 *
2	9	-2	1.80	1.81
2	10	-2	2.32	2.18
2	11	-2	1.24	1.19
2	12	-2	4.10	4.13 *
2	13	-2	0	0.82
2	14	-2	1.25	1.06
2	15	-2	0	0.89
2	16	-2	2.16	2.15
2	0	-3	2.69	2.92 *
2	1	-3	2.35	2.48
2	2	-3	0	0.47
2	3	-3	1.59	1.49
2	4	-3	3.56	3.63 *
2	5	-3	2.19	2.17
2	6	-3	0	0.09
2	7	-3	3.60	3.76 *
2	8	-3	1.60	1.60
2	9	-3	3.12	3.32 *
2	10	-3	1.51	1.58
2	11	-3	0	0.36
2	12	-3	0	0.77
2	13	-3	2.24	2.16
2	14	-3	1.23	1.00
2	15	-3	1.12	0.83
2	0	-4	0	0.98
2	1	-4	1.69	1.83
2	2	-4	2.72	3.10
2	3	-4	2.33	2.30
2	4	-4	0.98	0.95
2	5	-4	0	0.38
2	6	-4	1.21	1.11
2	7	-4	1.78	1.80
2	8	-4	0	0.41
2	9	-4	0	0.82
2	10	-4	0	0.86
2	11	-4	2.26	1.91
2	12	-4	1.92	1.76
2	13	-4	0	0.18
2	14	-4	0	0.36
2	0	-5	1.97	2.20
2	1	-5	0	0.45
2	2	-5	0	0.23
2	3	-5	0	0.49
2	4	-5	0	0.47
2	5	-5	1.48	1.68
2	6	-5	0	0.62
2	7	-5	1.84	1.77
2	8	-5	0	0.39
2	9	-5	1.81	1.52
2	10	-5	0	0.05
2	11	-5	0	0.42
2	12	-5	0	0.50
2	0	-6	0	0.53
2	1	-6	1.46	1.40
2	2	-6	0	0.66
2	3	-6	0	0.32
2	4	-6	0	0.90
2	5	-6	0	0.73
2	6	-6	0.96	0.99
2	7	-6	0	0.77
2	8	-6	0	0.34
2	9	-6	0	0.92
2	0	-7	1.22	1.39
2	1	-7	0	0.17
2	0	0	0.76	0.68
2	1	0	2.01	1.89
2	2	0	1.89	1.68
2	3	0	2.62	2.41 *
2	4	0	2.11	1.96
2	5	0	3.69	3.51 *
2	6	0	0	0.55
2	7	0	0	0.21
2	8	0	1.30	1.12
2	9	0	4.98	5.03 *
2	10	0	1.95	1.68
2	11	0	2.75	2.69 *
2	12	0	0	0.50
2	13	0	2.14	2.13
2	14	0	0	0.45
2	15	0	0	0.38
2	16	0	0	0.46
2	17	0	0	0.04
2	0	1	2.10	2.11
2	1	1	2.05	1.97
2	2	1	1.84	1.67
2	3	1	1.65	1.40
2	4	1	3.89	3.75 *
2	5	1	2.33	1.99
2	6	1	2.38	2.25
2	7	1	0	0.46
2	8	1	1.31	1.19
2	9	1	2.91	2.97 *
2	10	1	2.59	2.78 *
2	11	1	2.12	2.12
2	12	1	1.59	1.55
2	13	1	1.75	1.64
2	14	1	1.13	1.00
2	15	1	0	0.66
2	16	1	0	0.84
2	0	2	4.00	3.85 *
2	1	2	4.03	4.05 *
2	2	2	2.93	3.06 *
2	3	2	1.89	1.88
2	4	2	0.83	0.62
2	5	2	3.73	3.75 *
2	6	2	1.15	1.12
2	7	2	0	0.04
2	8	2	2.69	2.60
2	9	2	2.73	2.72 *
2	10	2	1.48	1.33
2	11	2	0	0.66
2	12	2	1.18	1.23
2	13	2	1.84	1.99
2	14	2	1.27	1.20
2	15	2	1.91	2.19
2	0	3	5.24	5.38 *
2	1	3	0	0.46
2	2	3	0	0.87
2	3	3	2.08	2.06
2	4	3	2.63	2.37
2	5	3	0	0.34
2	6	3	0	0.30
2	7	3	0	0.09
2	8	3	1.60	1.12
2	9	3	0	0.89
2	10	3	1.93	1.87
2	11	3	2.30	2.26
2	12	3	1.13	1.02
2	13	3	0	0.52
2	14	3	3.11	3.48 *
2	0	4	1.13	1.00
2	1	4	1.13	1.04
2	2	4	0	0.23
2	3	4	0	0.75
2	4	4	0	0.50
2	5	4	0	0.39
2	6	4	0	0.54
2	7	4	0	0.32
2	8	4	0	0.39
2	9	4	0	0.78
2	10	4	0	0.33
2	11	4	2.06	2.18
2	0	5	2.47	2.97 *
2	1	5	0	0.42
2	2	5	2.67	3.15 *
2	3	5	1.59	1.59
2	4	5	0	0.34
2	5	5	1.01	0.90
2	6	5	1.19	1.12
2	7	5	2.15	2.09
2	8	5	1.08	0.87
3	0	-1	1.87	2.02
3	1	-1	0	0.77
3	2	-1	1.55	1.70
3	3	-1	3.46	3.46 *
3	4	-1	0	0.44
3	5	-1	0	0.52
3	6	-1	1.99	1.88
3	7	-1	3.06	3.03 *
3	8	-1	1.99	1.83
3	9	-1	1.73	1.62
3	10	-1	1.01	0.67
3	11	-1	3.11	3.27 *
3	12	-1	0	0.42
3	13	-1	0	0.23
3	14	-1	1.37	1.53
3	15	-1	0.84	1.04
3	0	-2	2.22	2.39
3	1	-2	1.05	1.01
3	2	-2	0	0.14
3	3	-2	1.94	1.89
3	4	-2	1.04	0.95
3	5	-2	2.88	2.87 *
3	6	-2	0	0.31
3	7	-2	1.96	1.89
3	8	-2	2.51	2.50
3	9	-2	3.27	3.17 *
3	10	-2	0	0.43
3	11	-2	1.43	1.52
3	12	-2	0	0.73
3	13	-2	1.64	1.76
3	14	-2	0	0.53
3	0	-3	0	0.65
3	1	-3	0	0.59
3	2	-3	2.61	2.60
3	3	-3	1.54	1.34
3	4	-3	0	0.53
3	5	-3	0	0.16
3	6	-3	2.44	2.44
3	7	-3	0	0.49
3	8	-3	1.61	1.66
3	9	-3	0	0.67
3	10	-3	0.94	0.85
3	11	-3	1.45	1.43
3	12	-3	2.24	2.10
3	13	-3	0	0.33
3	0	-4	1.17	1.19
3	1	-4	1.08	0.98
3	2	-4	1.17	1.16
3	3	-4	0	0.07
3	4	-4	1.36	1.38
3	5	-4	0	0.14
3	6	-4	1.34	1.39
3	7	-4	0	0.17
3	8	-4	0	0.62
3	9	-4	0	0.62
3	10	-4	0	0.06
3	11	-4	1.11	0.92
3	12	-4	0	0.25
3	0	-5	1.37	1.38
3	1	-5	0	0.54
3	2	-5	0	0.64
3	3	-5	0	0.60
3	4	-5	0	0.70
3	5	-5	1.51	1.41
3	6	-5	0	0.45
3	7	-5	0	0.14
3	8	-5	1.36	1.30
3	9	-5	1.55	1.58
3	10	-5	0	0.46
3	0	-6	0	0.61
3	1	-6	0	0.23
3	2	-6	1.96	2.06
3	3	-6	0	0.16
3	4	-6	0	0.67
3	5	-6	1.20	1.22
3	6	-6	1.54	1.46
3	0	0	1.16	1.00
3	1	0	0	0.13
3	2	0	1.86	1.80
3	3	0	2.12	1.95
3	4	0	0	0.34
3	5	0	0	0.42
3	6	0	0	0.14
3	7	0	0	0.15
3	8	0	0	0.36
3	9	0	1.63	1.60
3	10	0	0	0.19
3	11	0	1.99	2.03
3	12	0	0	0.63
3	13	0	0	0.62
3	14	0	0	0.44
3	0	1	3.57	3.49 *
3	1	1	0	0.51
3	2	1	2.77	2.83 *
3	3	1	0	0.32
3	4	1	1.01	0.83
3	5	1	2.19	2.11
3	6	1	1.73	1.60
3	7	1	0	0.72
3	8	1	1.66	1.38
3	9	1	1.56	1.50
3	10	1	1.12	0.90
3	11	1	0	0.39
3	12	1	1.15	1.15
3	13	1	0	0.28
3	14	1	1.28	1.25
3	0	2	5.12	5.22 *
3	1	2	0	0.30
3	2	2	0	0.24
3	3	2	0	0.77
3	4	2	2.26	2.12
3	5	2	0	0.25
3	6	2	1.04	0.80
3	7	2	0	0.07
3	8	2	1.78	1.48
3	9	2	0	0.48
3	10	2	1.49	1.33
3	11	2	0.99	1.07
3	12	2	0	0.89
3	0	3	1.17	1.24
3	1	3	0	0.67
3	2	3	0	0.28
3	3	3	2.19	2.26
3	4	3	0	0.71
3	5	3	1.17	1.10
3	6	3	0	0.65
3	7	3	0	0.62
3	8	3	0	0.07
3	9	3	0	0.23
3	10	3	0.95	1.07
3	0	4	3.04	3.18 *
3	1	4	0.98	1.05
3	2	4	1.91	1.71
3	3	4	1.20	1.06
3	4	4	1.17	1.08
3	5	4	1.77	1.82
3	6	4	0	0.22
3	7	4	0.99	1.05
4	0	-1	0	0.76
4	1	-1	0	0.51
4	2	-1	1.28	1.39
4	3	-1	1.80	1.70
4	4	-1	1.17	1.19
4	5	-1	0.92	0.81
4	6	-1	0	0.73
4	7	-1	1.09	1.12
4	8	-1	0	0.81
4	9	-1	0	0.05
4	10	-1	0	0.76
4	11	-1	1.77	1.85
4	0	-2	1.24	1.14
4	1	-2	0	0.00
4	2	-2	0	0.51
4	3	-2	1.35	1.38
4	4	-2	0	0.61
4	5	-2	0.94	0.64
4	6	-2	1.43	1.41
4	7	-2	2.08	2.09
4	8	-2	1.70	1.65
4	9	-2	0.94	0.95
4	10	-2	0.93	0.90
4	11	-2	1.64	1.67
4	0	-3	0	0.54
4	1	-3	0	0.10
4	2	-3	0	0.71
4	3	-3	0	0.19
4	4	-3	0	0.32
4	5	-3	0	0.83
4	6	-3	0	0.41
4	7	-3	0	0.38
4	8	-3	0.95	1.00
4	9	-3	0.90	0.89
4	10	-3	0	0.41
4	0	-4	0.96	1.06
4	1	-4	0	0.48
4	2	-4	0	0.27
4	3	-4	0	0.53
4	4	-4	1.30	1.34
4	5	-4	0	0.18
4	6	-4	0	0.37
4	7	-4	0	0.49
4	8	-4	1.08	0.80
4	0	-5	0	0.12
4	1	-5	0	0.62
4	2	-5	0.98	1.13
4	3	-5	0.97	1.05
4	4	-5	0	0.34
4	5	-5	0	0.81
4	0	0	3.04	3.09 *
4	1	0	1.48	1.39
4	2	0	1.57	1.39
4	3	0	0.85	0.94
4	4	0	1.66	1.73
4	5	0	0	0.05
4	6	0	0.99	0.71
4	7	0	1.43	1.42
4	8	0	1.22	1.16
4	9	0	0	0.14
4	10	0	0	0.16
4	0	1	1.93	2.04
4	1	1	0	0.23
4	2	1	1.60	1.44
4	3	1	0	0.23
4	4	1	0	0.42
4	5	1	0	0.26
4	6	1	0	0.15
4	7	1	0	0.15
4	8	1	0	0.54
4	9	1	0	0.09
4	0	2	0	0.70
4	1	2	0	0.38
4	2	2	0	0.23
4	3	2	1.50	1.59
4	4	2	0	0.88
4	5	2	0	0.34
4	6	2	0	0.43
4	7	2	0	0.77
4	0	3	2.34	2.46
5	0	-1	1.31	1.54
5	1	-1	1.09	1.32
5	0	-2	0	0.33
5	1	-2	0	0.15

The above refinements were based on F, minimizing the function $\sum w(|F_o|-|F_c|)^2$. The weights for all observed reflections were unity and the weight analysis indicated that this choice was satisfactory. Reflections too weak to be measured were omitted in the calculations.

The coherent nuclear scattering amplitudes used were those for C, N, O, and H as given in the *International Tables*.[9]

Some cycles of least-squares calculations were made with refinement of scattering amplitudes (except for that of nitrogen) as well as the atomic coordinates, scale factor and anisotropic temperature factors. No further improvement of the R factor was obtained.

The atomic coordinates with standard deviations are compared with those obtained in the X-ray investigation [1] in Table 1. The thermal parameters from the final least-squares refinement are found in Table 2 and the root-mean-square components of thermal displacement along principal axes of the ellipsoids are given in Table 3. The observed and calculated structure factors are compared in Table 4.

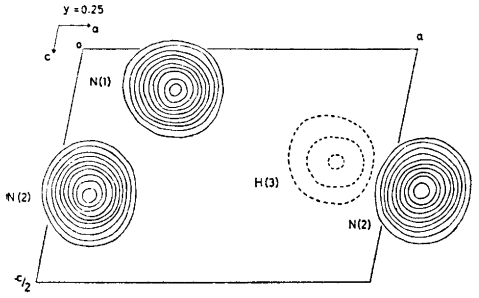

Fig. 1. Observed neutron scattering density function $\varrho(x, 0.25, z)$. The contour interval is 0.53×10^{-12} cm Å^{-3}; zero contours are omitted and negative contours are dashed.

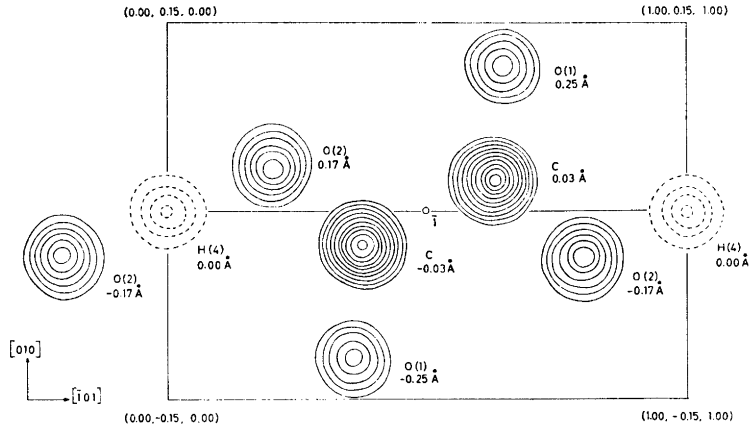

Fig. 2. Observed neutron scattering density in the plane parallel to (1̄01) passing through the origin. Contours are drawn as in Fig. 1 with an interval of 0.46×10^{-12} cm Å^{-3}. The distance of each atom from the plane is given. Notice the circular cross-section of the hydrogen atom H(4), located at a centre of symmetry.

Computing. Most calculations were made on the CD 3600 computer in Uppsala, using programs briefly presented in an earlier paper.[18]

DISCUSSION OF THE STRUCTURE

A stereoscopic illustration of the heavy atom structure was given in the previous X-ray report.[1] As mentioned earlier, the crystal is composed of $N_2H_5^+$ and $HC_2O_4^-$ ions. The $HC_2O_4^-$ ions are linked together end to end across centres of symmetry by short hydrogen bonds (2.448 Å); these hydrogen oxalate chains are slightly puckered and run parallel to the [$\bar{1}$01] direction. The chains are crosslinked by N—H···O bonds from the $N_2H_5^+$ ions, thus forming a three-dimensional network. The $N_2H_5^+$ ions are also linked to each other into zig-zag chains extending along [100], with the nitrogen atoms and H(3) situated in the mirror plane. The observed neutron scattering density is illustrated in Figs. 1 and 2.

The bonding situation around the $N_2H_5^+$ and $HC_2O_4^-$ ions is illustrated in detail in Figs. 3 and 4. Bond distances and angles are given in Table 5 and Figs. 5—7. These values are based on the parameters listed in Table 1. The distances have also been corrected for thermal "riding" motion in the cases where such a model is reasonable.

THE HYDRAZINIUM ION

The N—N distance of 1.440 Å in the $N_2H_5^+$ ion is in good agreement with earlier reported values for this type of ion. Thus values of 1.440 Å and 1.427 Å have been found in $(N_2H_5)_2SO_4$,[5] 1.438 Å in $N_2H_5H_2PO_4$,[6] and 1.42 Å in $LiN_2H_5SO_4$[3] (for further references consult these papers).

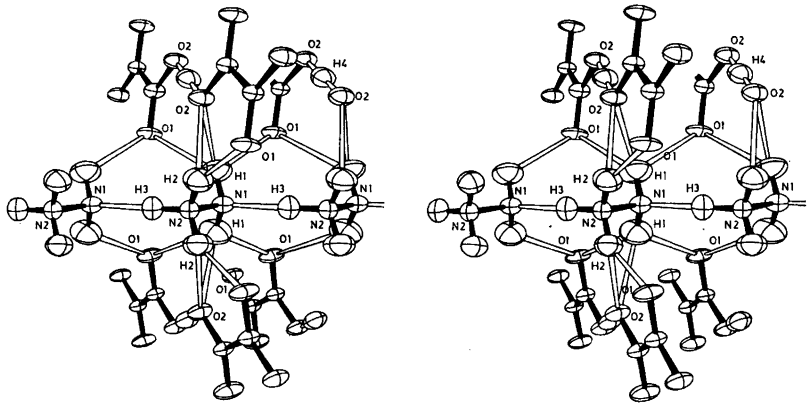

Fig. 3. A stereoscopic pair of drawings showing the bonding situation around an $N_2H_5^+$ ion. The thermal ellipsoids are scaled to enclose 50 % probability. The three principal ellipses per ellipsoid correspond to the three principal planes. The orientation is approximately the same as in Fig. 4.

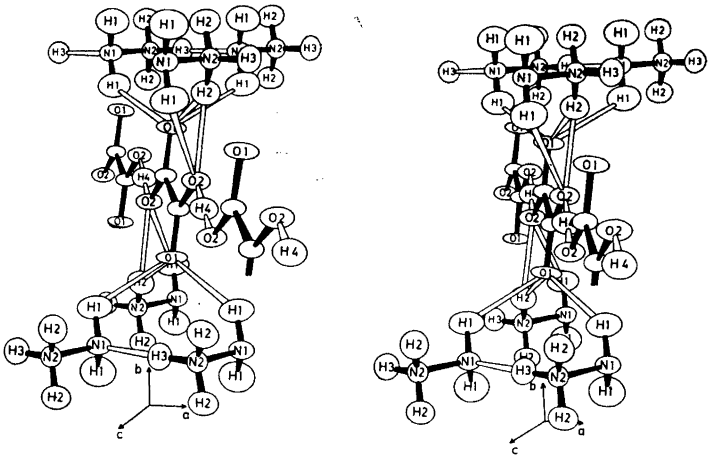

Fig. 4. A stereoscopic pair of drawings showing the bonding situation around an $HC_2O_4^-$ ion. Only the boundary ellipses are drawn, scaled to enclose 50 % probability. Figs. 3 and 4 were drawn with the program OR TEP.

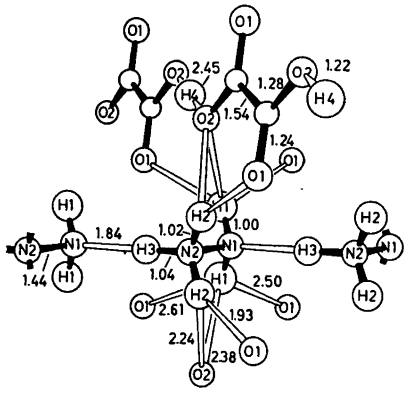

Fig. 5. Bond distances (in Å units).

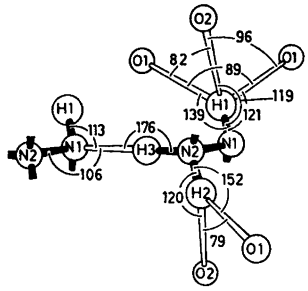

Fig. 6. Bond angles around the hydrogen atoms of $N_2H_5^+$.

The uncorrected N—H distances are slightly longer at the NH_3^+ end than at the NH_2 end as might have been expected (Table 5). However, the differences are at the limit of significance and correction for thermal riding motion makes them almost identical. A comparison of N—H distances in related bonds is made in Table 6. The reported values (not corrected for thermal motion) fall in the interval 1.00 to 1.04 Å and the differences between the N—H distances in neutral and positively charged ions are hardly significant.

The bond angles within the $N_2H_5^+$ ion are all fairly close to tetrahedral and there seems to be no significant difference between the two ends in this

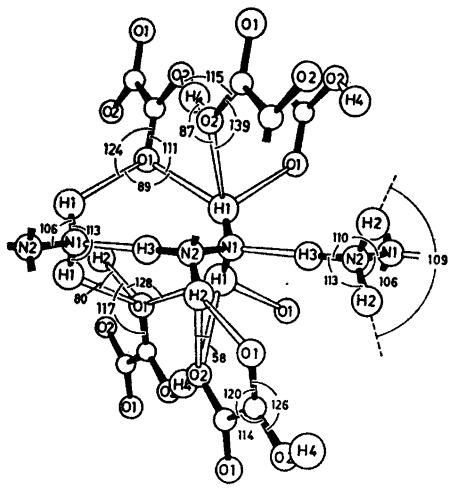

Fig. 7. Bond angles within the $N_2H_5^+$ and $HC_2O_4^-$ ions and around the oxygen atoms.

respect. The arrangement of hydrogen bouds around $N_2H_5^+$ is discussed in the next two sections.

The conformation of the $N_2H_5^+$ ion is perfectly staggered (a perfectly eclipsed or staggered conformation is required by symmetry in the present case). A nearly staggered form was also reported in $LiN_2H_5SO_4$,[3] with a dihedral angle of 66°.

The motion of the hydrogens in $N_2H_5^+$, as indicated by the thermal ellipsoids is consistent with the picture of N—H bonds which resist stretching but permit bending or torsional vibrations (Fig. 3).

(*A*) *Hydrogen bonds from the NH_3^+ end of the hydrazinium ion.* As mentioned previously, the $N_2H_5^+$ ions are hydrogen-bonded to each other into zig-zag chains extending along the *a* axis, with the nitrogens and H(3) situated in the mirror plane (Fig. 1). The hydrogen bond, N(2)—H(3)···N(1) (2.872 Å) is almost linear, 176.1°, and of normal type with the lone pair of N(1) participating in this bond. Similar zig-zag chains were found in N_2H_5Cl and N_2H_5Br [11] and also in $N_2H_5H_2PO_4$.[6] The hydrogen-bond distances were around 2.90—2.95 Å in these cases.

The situation is considerably more complicated for the rest of the hydrogen atoms. The remaining two hydrogens of the NH_3^+ end, H(2), are related to each other by the mirror plane passing through the hydrazinium ion. These hydrogen atoms have each two oxygens at distances of 1.933 and 2.242 Å, The corresponding N···O distances are 2.872 and 2.894 Å and the N—H···O bond angles are 151.8 and 120.4°. The bond with the shortest H···O distance is also the least bent and evidently the stronger of the two. According to current nomenclature the hydrogen bond should here be classified as bifurcated. This type of bonding situation is in fact considerably more common than generally realized. It occurs frequently in hydrogen-bonded compounds containing positive ions like $R—NH_3^+$ and negative ions like carboxylate, sulfate,

Table 5. Distances and angles with their standard deviations. (Standard deviations of distances are multiplied by 10^3).

A. Covalent distances and angles.

1. Within the $HC_2O_4^-$ ion.

	This work		X-ray work [1]
	Uncorrected	Corrected for thermal "riding" motion.	(uncorrected)
C—C	1.539(5) Å		1.542(5) Å
C—O(1)	1.236(4)	1.253(5) Å	1.230(3)
C—O(2)	1.280(4)	1.291(5)	1.279(3)
O(2)···H(4) [a]	1.224(4)		
C—C—O(1)	119.8(0.3)°		120.4(0.3)°
C—C—O(2)	114.1(0.3)		113.9(0.3)
O(1)—C—O(2)	126.1(0.3)		125.7(0.2)
C—O(2)—H(4)	114.5(0.3)		

2. Within the $N_2H_5^+$ ion.

N(1)—N(2)	1.440(5) Å		1.443(5) Å
N(1)—H(1)	0.998(9)	1.051(10) Å	
N(2)—H(2)	1.020(8)	1.053(9)	
N(2)—H(3)	1.037(11)	1.063(12)	
N(1)—N(2)—H(2)	105.6(0.6)°		
N(1)—N(2)—H(3)	110.0(0.8)		
N(2)—N(1)—H(1)	105.8(0.6)		
H(1)—N(1)—H(1)	112.7(1.1)		
H(2)—N(2)—H(2)	109.0(1.0)		
H(2)—N(2)—H(3)	113.0(0.7)		

[a] part of the "symmetrical" O···O bond.

B. Hydrogen-bond distances and angles.

Atom				Distances (Å) This work		Distances (Å) X-ray work [1]
1	2	3	Angle (°)	2—3	1—3	1—3
O(2)	H(4)	O(2)	180	1.224(4)	2.448(7)	2.450(4)
N(2)	H(3)	N(1)	176.1(1.2)	1.837(11)	2.872(5)	2.858(5)
N(1)	H(1)	O(1)	120.6(0.8)	2.495(11)	3.124(5)	3.129(4)
N(1)	H(1)	O(1)	138.8(0.8)	2.609(11)	3.424(5)	3.422(4)
N(1)	H(1)	O(2)	118.7(0.7)	2.377(10)	2.988(3)	2.989(2)
N(2)	H(2)	O(1)	151.8(0.8)	1.933(10)	2.872(5)	2.889(4)
N(2)	H(2)	O(2)	120.4(0.7)	2.242(9)	2.894(3)	2.894(2)

C. Some selected bond angles involving hydrogen atoms.

For angles involving only the heavy atoms, see the X-ray work.[1]

N(2)—N(1)···H(3)	106.1(0.5)°	H(1)···O(1)···H(1)	89.1(0.3)°
H(1)—N(1)···H(3)	112.8(0.7)	H(1)···O(1)···H(2)	79.7(0.4)
		H(1)···O(1)···H(2)	127.9(0.3)
O(1)···H(1)···O(1)	89.1(0.3)	C—O(1)···H(1)	123.9(0.3)
O(1)···H(1)···O(2)	81.7(0.3)	C—O(1)···H(1)	111.2(0.3)
O(1)···H(1)···O(2)	96.1(0.3)	C—O(1)···H(2)	117.4(0.4)
O(1)···H(2)···O(2)	79.4(0.3)	C—O(2)···H(1)	139.3(0.4)
		H(4)···O(2)···H(1)	87.0(0.3)
		H(1)···O(2)···H(2)	57.6(0.3)

Table 6. Selected N—H distances as determined by neutron diffraction.

Compound	Type of bond	Distance uncorrected	Distance corrected for thermal "riding" motion	Reference [a]
NH_3SO_3	N^+—H···O	1.032(26) Å 1.028(20) 1.013(22)		Sass [23]
N_2H_4	N—H···N	1.01(3)		Busing, Zocchi and Levy [24] (See also Ref.10)
KNH_2SO_3	N—H···O	1.007(6)	1.044	Cox *et al.*[25] (See also Ref. 26)
NH_3OHCl	N^+—H···O	1.024(11) 1.017(9) 1.019(9)	1.047(11) 1.046(10) 1.039(10)	Padmanabhan, Smith and Peterson [26]
$LiN_2H_5SO_4$	N—H···O N—H···N N^+—H···O	1.02(2) 1.02(2) 1.01(2) 1.03(2) 1.04(2)		Padmanabhan and Balasubramanian [3]
$N_2H_5HC_2O_4$	N—H···O N^+—H···O N^+—H···N	0.998(9) 1.020(8) 1.037(11)	1.051(10) 1.053(9) 1.063(12)	This work

[a] Further references are given in papers 10 and 26.

phosphate etc. Examples are glycine ($NH_3^+CH_3COO^-$),[12,13,28] $(N_2H_5)_2SO_4$,[5] $N_2H_6SO_4$,[14] and $LiN_2H_5SO_4$.[3] In the last investigation some short hydrogen-oxygen distances are not listed, and the complete hydrogen-bond situation is not presented in that paper.

(*B*) *Hydrogen bonds from the NH_2 end of the hydrazinium ion.* The two hydrogens H(1) of the NH_2 end are related to each other by the mirror plane. Each hydrogen H(1) has no less than three oxygen neighbours, namely O(2) and two atoms O(1), which are arranged fairly symmetrically around H(1). All of these may be considered as acceptors in a hydrogen bond. The H···O distances are 2.377, 2.495, and 2.609 Å; the N(1)—H(1)···O angles are 118.7, 120.6, and 138.8°, and the N(1)···O distances are 2.988, 3.124, and 3.424 Å, respectively. The O···H···O angles are about the same: 96.1, 81.7, and 89.1° (see Fig. 3). There are evidently reasons for considering this hydrogen bond as "trifurcated", although the H···O distances are rather long. Such hydrogen bonds have previously also been reported in some other cases.[15,27] As pointed out above, however, similar situations probably exist in many other compounds, particularly in hydrogen-bonded compounds composed of ions. Cases like the one now discussed illustrate the difficulties in giving a satisfactory definition of the hydrogen bond. It may be argued that the term should not include all cases like those above, particularly as a definite interaction between hydrogen and the acceptor oxygens has not been demonstrated.

THE HYDROGEN OXALATE ION

The hydrogen oxalate ion and its surroundings are illustrated in Fig. 4. The $HC_2O_4^-$ ions are linked together into infinite chains by O···H···O bonds of 2.448 Å. According to our choice of space group there is a crystallographic centre of symmetry in the middle of the C—C bond and in the middle of the hydrogen bond. The $C_2O_4^{2-}$ skeleton is perfectly planar: the deviations of the carbon and oxygen atoms from the least-squares plane defined by these atoms are <0.001 Å. The hydrogen atom H(4) in the middle of the O···H···O bond deviates by 0.128 Å from the least-squares plane just mentioned.

The covalent bond distances and angles within the $HC_2O_4^-$ ion (C—C: 1.539, C—O(1): 1.236, and C—OH: 1.280 Å) are in good agreement with those generally found in carboxyl compounds. The bond distances in the same ion as found in the neutron diffraction study of ammonium tetraoxalate [4] are: C—C: 1.549, C=O: 1.212, C—OH: 1.291, and C—O: 1.247, 1.230 Å. A comparison of bond lengths and angles within the carboxyl group in a number of compounds has been made by Nahringbauer.[16] The distances and angles in the $HC_2O_4^-$ ion in the present study are between the values found in $R—COO^-$ and R—COOH groups, as might have been expected.

The thermal ellipsoids of the atoms in the oxalate ion are strongly prolate, with the longest axis directed along the normal of the oxalate plane (Fig. 3).

The short hydrogen bond O···H···O is either symmetrical (with hydrogen in a crystallographic centre of symmetry) or with a statistically disordered hydrogen. The anisotropic thermal parameters obtained in the present investigation reveal no elongation of the thermal ellipsoid in the direction of the hydrogen bond, which might otherwise have been taken as an indication of a disordered arrangement of hydrogen (*cf.* Fig. 2). The largest principal axis of the thermal ellipsoid of H(4) is approximately directed along the normal to the oxalate plane while the shortest axis lies in this plane and at right angles to the O···O bond. Finally, the component along the O···O bond is between these two extreme values.

The shortness of the hydrogen bond (2.448 Å) together with the symmetrical environment of the hydrogen atom (which is true even if space group $P2_1$ is used) makes it reasonable to assume a very flat, possibly symmetrical, potential energy curve or a double-minimum potential in which the barrier is small compared to the ground state energy of hydrogen. Even in the latter case the hydrogen bond may accordingly be considered as effectively symmetrical. The situation is similar to that in other acid salts, like potassium hydrogen maleate,[19] potassium hydrogen diphenylacetate,[20] potassium hydrogen chloromaleate,[21] and potassium hydrogen diformate,[22] where the O···O distances are 2.44, 2.54, 2.40, and 2.45 Å, respectively.

COMPARISON WITH THE X-RAY WORK

A comparison of the atomic coordinates obtained in the X-ray and neutron diffraction investigations is made in Table 1. The agreement is in most cases very good and the only more pronounced differences are the x coordinates of the N(1) and O(1) atoms. Even in these cases, however, the values fall within

3σ. The bond lengths and angles in the two investigations are compared in Table 5. The hydrogen bond N···N is 0.014 Å shorter and N(2)···O(1) is 0.017 Å longer in the X-ray work while all other distances and angles are within two standard deviations.

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