Hydrogen Bond Studies

24.* The Crystal Structure of Hydrazinium Hydrogen Oxalate, $N_2H_5HC_2O_4$

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The crystal structure of hydrazinium hydrogen oxalate has been determined from three-dimensional single-crystal X-ray data. The crystals are monoclinic, space group $P2_1/m$, with two formula units in a cell with the dimensions: $a = 3.583$, $b = 13.318$, $c = 5.103$ Å, $\beta = 102.72°$. The hydrogen oxalate ions are linked to each other end to end into infinite planar chains by short hydrogen bonds (2.450 Å). This O···H···O bond is either symmetrical with hydrogen at a centre of symmetry or in a disordered arrangement. The $N_2H_5{}^+$ ions are bonded to each other forming infinite zig-zag chains by $N^+ - H···N$ bonds (2.858 Å). The chains of $N_2H_5{}^+$ and $HC_2O_4{}^-$ ions are cross-linked by $N - H···O$ bonds.

Hydrazine forms two compounds with oxalic acid, $N_2H_4 \cdot H_2C_2O_4$ and $2N_2H_4 \cdot H_2C_2O_4$. Pratt and Richards [1] studied these substances with proton magnetic resonance and found that the spectra could be explained most satisfactorily if these compounds are formulated as $N_2H_5HC_2O_4$ and $(N_2H_5)_2C_2O_4$, respectively.

The crystal structures of some hydrazine compounds have been determined earlier at this Institute in a project involving systematic studies of hydrogen bonds in simple, closely related compounds. The purpose of the present investigation is to obtain further information about the hydrogen bond systems in hydrazine compounds. The phase $N_2H_4 \cdot H_2C_2O_4$ is also of particular interest as it probably contains $HC_2O_4{}^-$ ions, and very few studies of the $HC_2O_4{}^-$ ion have been reported earlier.[2,3] As will be shown below, the appropriate formulation of the present substance is $N_2H_5HC_2O_4$ (designated below as HHOx).

A neutron diffraction study of HHOx is in progress at this Institute in order to obtain more information about the details of the hydrogen bond system.

EXPERIMENTAL

HHOx was prepared according to Turrentine [4] by mixing suitable amounts of hydrazine hydrate (*purum*) and oxalic acid dihydrate (*pro analysi*). Recrystallization from water gave fine colourless needles. The crystals were dried to constant weight over a drying agent in a desiccator. Analysis of the compound was performed at the Central Analytical Laboratory at this Institute. The amount of N_2H_4 was determined using the bromate method, the sample containing 26.20 % by weight. For $N_2H_4 \cdot H_2C_2O_4$ the calculated value is 26.26 %.

Equi-inclination Weissenberg photographs of a crystal rotating around the a axis, layers zero to three, were taken with Ni-filtered CuK radiation. In order to obtain a connection between the layers and to determine the angle β, another set of photographs, layers zero to five, were taken with a crystal rotating around the b axis. The dimensions of the crystals were $0.15 \times 0.20 \times 0.18$ mm and $0.10 \times 0.15 \times 0.12$ mm, respectively. The intensities were measured visually by using the multiple-film technique (five films) and comparing with an intensity scale. The data were corrected for the Lorentz and polarization effects. No absorption correction was applied; the calculated linear absorption coefficient for $CuK\alpha$ radiation is 15 cm^{-1}. The number of independent reflexions recorded was 509, but 40 of these were too weak to be measured. About 89 % of the reflexions within the copper reflexion sphere were thus recorded.

The correlation of the intersecting layers was obtained using the program BAS, written by P. E. Werner, University of Stockholm. This program is based on a method devised by Rollett and Sparks. [5] The inter-layer scale factors so obtained were used 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, as the method used in the program BAS may give peculiar results. [6]

UNIT CELL

The unit cell dimensions were determined from quartz-calibrated zero-layer Weissenberg photographs for the crystal rotating around the a and b axes. About 70 reflexions with large θ values were used to determine a, b, c, and β using the method of least squares. The unit cell dimensions with estimated standard deviations are:

$a = 3.583 \pm 0.002$, $b = 13.318 \pm 0.002$, $c = 5.103 \pm 0.002$ Å, $\beta = 102.72 \pm 0.02°$.

($a = 4.913$ Å for α quartz at 22°C; $\lambda CuK\alpha_1 = 1.54051$ Å, $\lambda CuK\alpha_2 = 1.54433$ Å).

The density, determined by weighing the specimen in air and in m-xylene, is 1.70 ± 0.02 g/cm^3. With two formula units per unit cell the calculated density is 1.705 g/cm^3.

SPACE GROUP AND STRUCTURE DETERMINATION

Preliminary considerations. The diffraction symmetry $2/m$ and systematic absences $0k0$ with k odd suggest the space groups $P2_1$ or $P2_1/m$.

1. *Space group $P2_1$*: In this case there are only general twofold equivalent positions and accordingly all the following three formulations of the compound are possible, namely $N_2H_4 \cdot H_2C_2O_4$, $N_2H_5HC_2O_4$ or $N_2H_6C_2O_4$.

2. *Space group* $P2_1/m$: In addition to the general fourfold positions there are twofold special positions in mirror planes as well as four different positions at centres of symmetry. These last four positions are immediately ruled out for the heavy atoms as they are not compatible with the dimensions of the molecules.

If the atoms in a hydrazine or oxalate group are in general fourfold positions it is evident that the midpoints of the N—N or C—C bonds, respectively, must lie either at centres of symmetry or in mirror planes. There are then several possibilities:

A. The atoms of both types of groups are in general fourfold positions. Possible formulations: $N_2H_4 \cdot H_2C_2O_4$ or $N_2H_6C_2O_4$.

B. Either the nitrogens in hydrazine *or* the carbons in the oxalate group lie in special twofold positions in the mirror planes. Both groups cannot simultaneously be located in the mirror planes, as this would give too large a separation of the atoms in the y direction (4.5—6.7 Å, depending on the orientation of the oxalate group). Both alternatives are compatible with the formulation $N_2H_4 \cdot H_2C_2O_4$ or $N_2H_6C_2O_4$. If the substance consists of $N_2H_5HC_2O_4$, one hydrogen in $N_2H_5^+$ as well as the single hydrogen in $HC_2O_4^-$ must be in twofold special positions (or effectively so if there is a disordered arrangement of hydrogen).

Atomic coordinates. The atomic coordinates were determined from three-dimensional Patterson maps with consideration taken to the above facts.

From the known dimensions of the oxalate group (assuming it to be planar), a vector model of the group was constructed. By rotation of this around the origin the orientation of the oxalate group was determined.

The next step to determine the positions of the atoms was less obvious as there were no isolated peaks in the Harker section $(u, \frac{1}{2}, w)$. Considering first the space group $P2_1/m$, a reasonable structure was obtained by placing the centre of the C—C bond at a centre of symmetry. From packing considerations hydrazine was placed in the mirror plane. This corresponds to one of the alternatives in *B* above.

A structure factor calculation based on the above structure indicated that the x and y coordinates were fairly correct while the z coordinate needed further adjustment. The space group $P2_1$ was now tried. Three-dimensional electron density calculations were made using the oxalate group only, with the previous x and y coordinates but with the z coordinates varied in steps of 0.3 Å in the range $0 \leq z \leq \frac{1}{2} c$. Examination of these maps for the alternative with the best nitrogen peaks revealed a structure very close to that already obtained using $P2_1/m$.

REFINEMENT OF THE STRUCTURE

The coordinates, individual isotropic thermal parameters and inter-layer scale factors were refined in a series of least-squares calculations, using both the space group $P2_1/m$ and $P2_1$. The discrepancy index $R = \sum ||F_o| - |F_c||/ \sum |F_o|$ after several cycles was 0.151 in $P2_1/m$ and 0.146 in $P2_1$.

The hydrogen atoms, obtained from the preliminary neutron diffraction study, were now included in the calculations with fixed parameters. After two

additional cycles the R values were 0.146 and 0.139, respectively (given in the same order as above). The number of parameters varied was 22 in $P2_1/m$ and 35 in $P2_1$. A comparison of the observed and calculated structure factors showed that some low-angle reflexions with high intensities had F_o much smaller than F_c, probably due to secondary extinction. Ten reflexions were excluded and two more cycles reduced the R values to 0.140 and 0.134, respectively.

Some cycles of least-squares calculations were then run to refine the atomic coordinates and anisotropic thermal parameters, together with an overall scale factor. The inter-layer scale factors were fixed as the values obtained from the final isotropic refinement. The total number of parameters varied was 40 in $P2_1/m$ and 72 in $P2_1$. When the structure was described in terms of $P2_1/m$, the R value was 0.083 after four cycles, and the shifts were less than one tenth of their estimated standard deviations. A corresponding refinement in $P2_1$ gave an approximately equal R value, namely 0.080. Considering the number of parameters in the two cases, the structure is accordingly most appropriately described in terms of $P2_1/m$. The same choice is suggested by the standard deviations of the atomic coordinates: those of x and z were about three times greater and those of y about five times greater in $P2_1$ than in $P2_1/m$. The distances within the oxalate group also appeared more reasonable in $P2_1/m$.

Table 1. Atomic coordinates with estimated standard deviations (within parentheses), each multiplied by 10^4.

Atom			
C	6191(7)	247(2)	6280(5)
N(1)	2956(11)	2500	810(8)
N(2)	1014(10)	2500	3006(8)
O(1)	5911(7)	1153(2)	6668(4)
O(2)	8368(6)	−363(1)	7847(4)
H(1)[a]	2080	1890	−200
H(2)	2040	1880	4150
H(3)	8040	2500	2290
H(4)	0	0	0

[a] Hydrogen coordinates from the preliminary neutron diffraction study.

Table 2. Anisotropic thermal parameters with estimated standard deviations, each multiplied by 10^4. The expression used is: $\exp[-(h^2\beta_{11} + hk\beta_{12} + \cdots)]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C	170(28)	27(1)	163(11)	30(7)	18(23)	4(5)
N(1)	381(36)	34(2)	280(15)	0	277(33)	0
N(2)	246(33)	29(2)	312(15)	0	299(32)	0
O(1)	549(26)	27(1)	240(10)	47(7)	−147(21)	−34(5)
O(2)	322(23)	29(1)	201(9)	36(6)	−226(18)	− 5(5)

The isotropic thermal parameters B used for the hydrogen atoms H(1) to H(4) were: 4.9, 4.2, 4.0, and 2.7 Å^2, respectively.

Table 3. Root-mean-square components, R_i, of thermal displacement along the principal axes of the ellipsoids of vibration.

	R_1	R_2	R_3
C	0.140 Å	0.175 Å	0.191 Å
N(1)	0.105	0.161	0.200
N(2)	0.142	0.147	0.228
O(1)	0.099	0.160	0.207
O(2)	0.097	0.148	0.158

Table 4. Bond distances and angles with estimated standard deviations. (*cf.* Figs. 2 and 3).

1. Within the $N_2H_5^+$ and $HC_2O_4^-$ ions.

N(1)—N(2)	1.443(5) Å		
C—C	1.542(5)	C—C—O(1)	120.4° (3)
C—O(1)	1.230(3)	—O(2)	113.9 (3)
C—O(2)	1.279(3)	O(1)—C—O(2)	125.7 (2)

2. Hydrogen bonds.

a) Distances between the ions in the chains.

O(2)...O(2)	2.450(4) Å
N(1)...N(2)	2.858(5)

b) N···O contacts which are possible hydrogen bonds.

N(1)···O(1)	3.129(4) Å
···O(2)	2.989(2)
N(2)···O(1)	2.889(4)
···O(2)	2.894(2)

c) Angles around N(1).

N(2)—N(1)···N(2)	108.3° (3)
···O(1)	144.8 (1)
···O(2)	72.2 (1)
N(2)···N(1)···O(1)	78.6 (1)
···O(2)	96.2 (1)
O(1)···N(1)···O(1)	70.0 (1)
···O(2)	142.7 (1)
···O(2)	72.8 (1)
O(2)···N(1)···O(2)	144.3 (2)

d) Angles around N(2).

N(1)—N(2)···N(1)	108.3° (3)
···O(1)	100.0 (2)
···O(2)	79.5 (1)
N(1)···N(2)···O(1)	132.1 (1)
···O(2)	92.6 (1)
O(1)···N(2)···O(1)	76.8 (1)
···O(2)	130.7 (1)
···O(2)	55.3 (1)
O(2)···N(2)···O(2)	158.9 (2)

e) Angles around the oxygen atoms.

C—O(1)···N(1)	136.3° (2)
···N(2)	124.3 (2)
N(1)···O(1)···N(2)	80.4 (1)

C—O(2)···O(2)	114.5° (2)
···N(1)	130.0 (2)
···N(2)	126.0 (2)
O(2)···O(2)···N(1)	103.8 (1)
···N(2)	119.1 (1)
N(1)···O(2)···N(2)	28.4 (1)

The above refinements were based on F, minimizing the function $\sum w(|F_o| - |F_c|)^2$. The weights were calculated according to the equation: $w = 1/(a + |F_o| + c|F_o|^2)$. The final values used for a and c were 0.6 and 0.069, respectively. Reflexions too weak to be measured were given zero weight in all calculations. Ten strong reflexions were also excluded from the final refinement, which was thus based on 459 observations.

Table 5. Observed and calculated structure factors. Reflexions not included in the refinement are marked with asterisks. One asterisk indicates reflexions which were too weak to be measured. The F_0 values for these are given as 0.0. Two asterisks indicate omitted strong reflexions.

h	k	l	$|F_o|$	$|F_c|$

(Table of observed and calculated structure factors, arranged in six column groups of h, k, l, $|F_o|$, $|F_c|$.)

Atomic scattering factors for neutral C, N, O, and H were taken from the *International Tables* (Vol. III, p. 202).[7]

Computer programs: Most calculations were made on the CD 3600 computer in Uppsala, using programs briefly described in an earlier paper.[8]

Atomic coordinates and thermal parameters from the last cycle of refinement in space group $P2_1/m$ are listed in Tables 1 and 2. The root-mean-square components of thermal displacement along the principal axes of the ellipsoids are given in Table 3. Distances and angles are listed in Table 4. The standard deviations in these were calculated from the standard deviations of the atomic coordinates. The errors in the unit cell dimensions were also considered. The observed and calculated structure factors are compared in Table 5.

DESCRIPTION OF THE STRUCTURE

The location of hydrogen will be discussed in detail in a subsequent paper. It is immediately clear, however, that the structure contains $N_2H_5^+$ and $HC_2O_4^-$ ions (Fig. 1). The hydrazinium ions are linked into zig-zag chains, situated in the mirror planes, and extending along the a axis. The $HC_2O_4^-$ ions are bonded end to end across centres of symmetry by short hydrogen bonds (2.450 Å). These $O\cdots H\cdots O$ bonds are accordingly either symmetrical
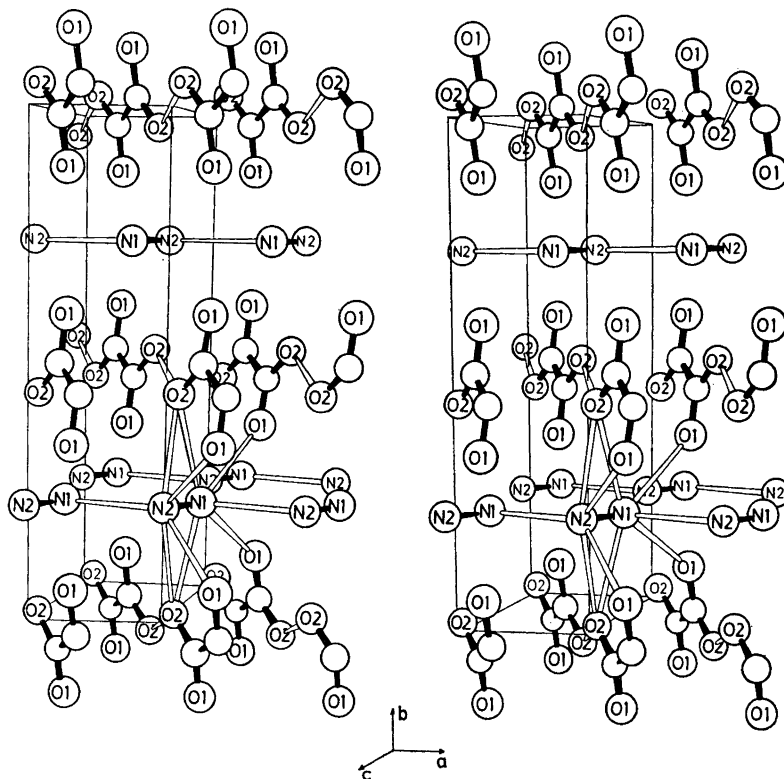

Fig. 1. A stereoscopic pair of drawings of the structure of $N_2H_5HC_2O_4$. Covalent bonds are filled, hydrogen bonds and $N\cdots O$ contacts (possible $N-H\cdots O$ bonds with distances less than 3.14 Å) are open. The latter are shown only around one $N_2H_5^+$ ion. To decrease the overlap in the figure parts of the oxalate groups are omitted in some cases. Atom labels on carbon are omitted. This figure was drawn with the program OR TEP.

with hydrogen in a centre of symmetry or in a disordered arrangement. The oxalate chains are parallel to the (1̄01) plane. The two types of chains described above are crosslinked by N—H···O bonds, thus forming a three-dimensional network. Bond distances and angles are listed in Table 4 and illustrated in Fig. 2.
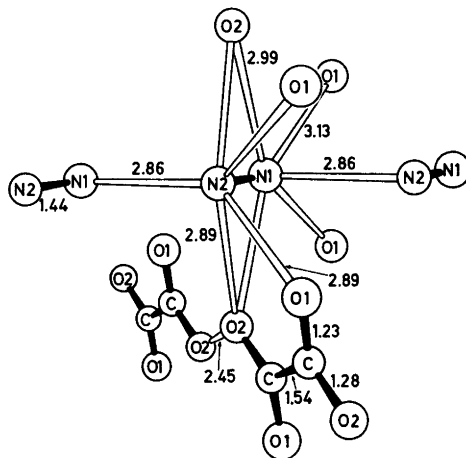
Fig. 2. Bond distances. The orientation is approximately the same as in the left part of Fig. 1. The $N_2H_5^+$ ions lie in a mirror plane, and the centre of the O(2)···O(2) bond at a centre of symmetry.
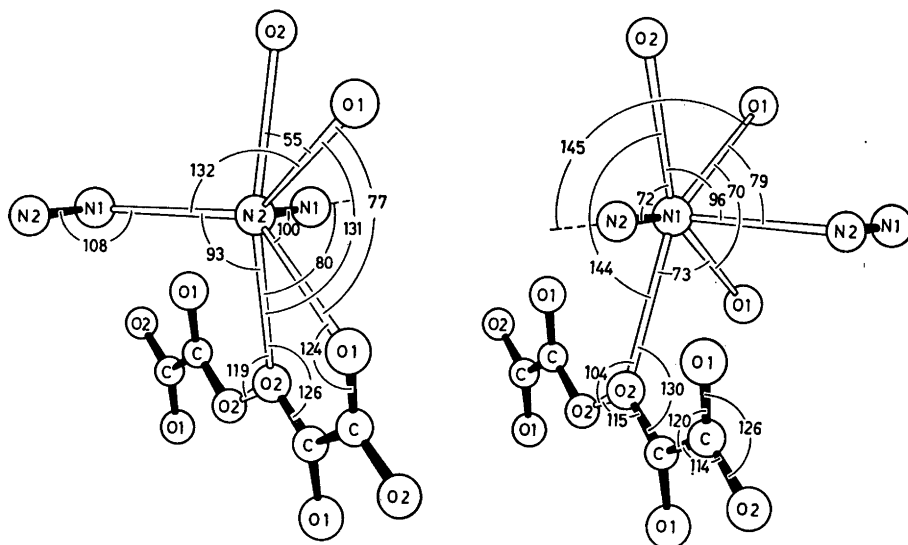
Fig. 3. Bond angles. Orientation as in Fig. 2.

A detailed discussion of the structure and comparison with earlier reported results will be made when the results from the neutron diffraction study are published.

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