

may find application in the early determination of those phases which can at best be but crudely approximated by (1.1).

4. Concluding remarks

Squared-tangent formulas have been found for the space groups $P1$ and $P2_12_12_1$. Analogous formulas exist for the remaining noncentrosymmetric space groups. It is anticipated that, at least for the space group $P2_12_12_1$ and other, selected, noncentrosymmetric space groups, these formulas will find application in facilitating the early determination of certain phases. The results obtained here raise two questions. First does (3.20) hold also in the space group $P1$? Secondly, does (3.20) retain its validity if the \mathbf{k} are restricted so

that the $|E_{\mathbf{k}}|$ and $|E_{\mathbf{h}-\mathbf{k}}|$ are large, say greater than unity? Although the available evidence indicates strongly that both of these questions are to be answered in the affirmative, rigorous proofs have been elusive so far. With respect to practical applications, the second question is particularly significant since, owing to a reduction of the errors arising from finite sampling, it is better to restrict the vectors \mathbf{k} so that the $|E_{\mathbf{k}}|$ and $|E_{\mathbf{h}-\mathbf{k}}|$ are large.

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Neutron and X-ray Diffraction Studies of Hydrazinium Sulfate, $\text{N}_2\text{H}_6\text{SO}_4^*$

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Hydrazinium sulfate has been studied by X-ray and neutron diffraction. The crystals are orthorhombic, space group $P2_12_12_1$, with four formula units in a cell of dimensions: $a=8.251$ (5), $b=9.159$ (1), $c=5.532$ (1) Å. Both the X-ray and neutron data were affected by extinction; this effect was very severe in the neutron case. By inclusion of six anisotropic extinction parameters in the least-squares refinement it was possible to obtain a good fit between observed and calculated structure factors. The structure consists of $\text{N}_2\text{H}_6^{2+}$ ions and SO_4^{2-} ions held together by a three-dimensional system of $\text{N-H}\cdots\text{O}$ hydrogen bonds. A number of the hydrogen bonds are weak and bifurcated or trifurcated. The $\text{N}_2\text{H}_6^{2+}$ ion has an almost perfectly staggered conformation. The neutron and X-ray diffraction results are in good agreement with respect to bond lengths involving the non-hydrogen atoms. Although the hydrogen atoms were located with a precision of 0.03 Å in the X-ray study, the mean N-H bond lengths were 0.2 Å shorter than those found from the neutron study, confirming the existence of large systematic errors in the location of hydrogen atoms from X-ray results when a spherical atomic electron distribution is assumed.

Introduction

The crystal structures of a number of hydrazine compounds have been studied; a review of some recent work has been given by Liminga (1968). These compounds often contain a quite complicated arrangement of hydrogen bonds, and an accurate location of the hydrogen atoms is thus essential. Only two hydrazine compounds studied by neutron diffraction have been reported: lithium hydrazinium sulfate, $\text{LiN}_2\text{H}_5\text{SO}_4$, by Padmanabhan & Balasubramanian (1967) and hydra-

zinium hydrogenoxalate, $\text{N}_2\text{H}_5\text{HC}_2\text{O}_4$, by Nilsson, Liminga & Olovsson (1968).

The present investigation involves the refinement of the hydrazinium sulfate structure by both X-ray and neutron diffraction methods. An X-ray diffraction study of this compound has been carried out by Nitta, Sakurai & Tomiie (1951); the accuracy of this determination was, however, rather low.

Crystal data

Hydrazinium sulfate, $\text{N}_2\text{H}_6\text{SO}_4$, F.W. 130.12. Orthorhombic, $a=8.251$ (5), $b=9.159$ (1), $c=5.532$ (1) Å. (Nit-

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* Numbers in parentheses here and throughout this paper are estimated standard deviations in the least significant digits.

ta, Sakurai & Tomiie, 1951) $V=418.1 \text{ \AA}^3$, $Z=4$, $D_x=2.067 \text{ g.cm}^{-3}$. Space group $P2_12_12_1$.

X-ray study

Single crystals were obtained by recrystallization from an aqueous solution. Cell dimensions were determined from precession photographs taken with a small crystal fragment and recorded on Polaroid film with reflections from a NaCl crystal superimposed for calibration. The results agreed within their slightly larger standard deviations with the values of Nitta *et al.* (1951) quoted above.

An ellipsoidal crystal of dimensions $0.45 \times 0.55 \times 0.45 \text{ mm}$ was obtained by grinding. The intensity data were collected by the use of this crystal mounted with the a axis parallel to the φ axis on a computer-controlled Picker four-circle diffractometer. The θ - 2θ scan technique was employed with zirconium-filtered Mo K radiation to examine the equivalent reflections hkl and $h\bar{k}l$ out to a limit of $\sin \theta/\lambda=0.90 \text{ \AA}^{-1}$. A total of 2706 reflections were measured.

The data were corrected for background and assigned standard deviations based on Poisson counting statistics. The values of I and $\sigma(I)$ were then corrected for Lorentz-polarization effects and for absorption ($\mu=6.64 \text{ cm}^{-1}$). The ellipsoidal shape of the crystal was approximated by 128 boundary planes in the calculation of the absorption correction; the resulting transmission factors were in the range 0.77-0.81. The absorption program also calculated vector components of the incident and diffracted beam and the mean path length through the crystal; these quantities were later used to apply a correction for anisotropic extinction in the Zachariasen approximation as treated by Coppens & Hamilton (1970).

The solution of the structure was based on 718 reflections obtained by averaging together the equivalent reflections (anomalous dispersion effects were ignored at this stage) for an incomplete data set consisting mainly of reflections with $\sin \theta/\lambda$ less than 0.7 \AA^{-1} . Since an attempt to locate the hydrogen atoms from the neutron diffraction data using the heavy atom parameters of Nitta *et al.* (1951) had failed, it was decided to obtain an independent solution of the X-ray structure without using their results. The coordinates of all the non-hydrogen atoms except N(1) were obtained from a three-dimensional Patterson map. The remaining nitrogen atom was found in a difference electron density synthesis, and the structure was refined by a series of full-matrix least-squares refinements. The function minimized was $\sum w(|F_o^2| - |F_c^2|)^2$. Each reflection was assigned a weight w inversely proportional to the estimated variance of the observation

$$w^{-1} = \sigma^2(F^2)$$

and

$$\sigma^2(F^2) = \sigma^2_{\text{count}}(F^2) + k^2F^4$$

with k equal to 0.05 and σ^2_{count} being based on count-

ing statistics alone. In these preliminary refinements positional parameters and individual isotropic thermal parameters were refined for the non-hydrogen atoms. There was some evidence for secondary extinction, and some of the strongest reflections were therefore removed from the data. The refinement converged with agreement factors

$$R = \sum ||F_o^2| - |F_c^2|| / \sum |F_o^2| = 0.098$$

$$R_w = \{ \sum w(|F_o^2| - |F_c^2|)^2 / \sum w|F_o^4| \}^{1/2} = 0.116.$$

The parameters obtained from this refinement were used as initial parameters to determine the hydrogen atom positions from the neutron data as described below. The refinement of the X-ray data was continued when the final results from the neutron study became available; the positions of the hydrogen atoms as determined by neutron diffraction were taken as initial positions for the least-squares refinement. All reflections with F^2 values larger than $2\sigma(F^2)$ were now used as data; the total number of reflections was 2598. Each reflection was assigned a weight defined in the same way as in the preliminary refinement. In the first series of refinements, positional parameters for all atoms and anisotropic thermal parameters for the heavy atoms were varied together with a single scale factor. The thermal parameters for the hydrogen atoms were kept fixed at the values from the neutron study. The refinement converged with $R=0.170$, $R_w=0.161$. In subsequent cycles an isotropic extinction parameter was added to the parameter list. The R values now improved to $R=0.076$, $R_w=0.091$. Finally, six anisotropic extinction parameters for a type II crystal (Coppens & Hamilton, 1970) were varied together with positional parameters for all atoms and anisotropic thermal parameters for the heavy atoms and a scale factor. In the last cycle of least-squares refinement no parameter shifted by more than 0.1σ ; the final agreement factors were $R=0.057$ and $R_w=0.0876$. The corresponding conventional R value based on F was 0.032. The error in an observation of unit weight was 1.41. The final positional, thermal and extinction parameters are presented in Tables 1 and 2. The observed and calculated structure factors and the extinction corrections are listed in Table 3; observed values given in this Table are corrected for extinction. Scattering factors for S, O and N were those given by Hanson, Herman, Lea & Skillman (1964). The spherical scattering factor proposed by Stewart, Davidson & Simpson (1965) was used for the hydrogen atoms.

Absolute configuration

The effects of anomalous scattering were included in the structure factor calculations (Ibers & Hamilton, 1964). The anomalous scattering contributions were those given in *International Tables for X-ray Crystallography* (1962). A refinement of the structure with an absolute configuration opposite to that in Table 1 converged with $R(-)=0.060$, $R_w(-)=0.0953$. The

ratio of the two agreement factors $\mathcal{R} = R_w(+)/R_w(-)$ is 1.088. Use of the \mathcal{R} test (Hamilton, 1965) indicates that the difference is significant and that the choice of handedness implied by the parameters in Table 1 with a right-handed coordinate system is correct for the crystal studied.

Neutron study

A crystal with a volume of 3.6 mm³ was mounted with the *a* axis parallel to the φ axis on a four-circle diffractometer at the Brookhaven National Laboratory High Flux Beam Reactor. The data were collected automatically using the computer-controlled Multi-Spectrometer Control System (Beaucage, Kelley, Ophir, Rankowitz, Spinrad & van Norton, 1966). Using a neutron

wavelength of 1.073 Å monochromatized by the 331 reflection of a single crystal of germanium a portion of reciprocal space extending out to $\sin \theta/\lambda = 0.65 \text{ \AA}^{-1}$ was examined. A θ - 2θ step scan technique was used with $\Delta(2\theta) = 0.1^\circ$. To provide a check on crystal symmetry more than one of the equivalent reflections were measured for part of the data set. A set of F^2 and $\sigma(F^2)$ values was derived from the observed intensities as described for the X-ray data except that no polarization correction was applied. The crystal shape was defined by 19 rational crystal boundary planes in the calculation of the absorption correction ($\mu = 2.00 \text{ cm}^{-1}$). The resulting transmission factors were in the range 0.73–0.82. The total number of reflections with F^2 values greater than $\sigma(F^2)$ was 858. The equivalent reflections

Table 1. Final fractional coordinates and thermal parameters

For each atom, the neutron result is given on the first line and the X-ray result on the second. The vibration tensor components (in 10^{-4} \AA^2) are defined as

$$\exp \{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
S	−0.05125 (61)	0.06917 (49)	0.21345 (84)	116 (23)	115 (19)	47 (19)	−10 (17)	11 (18)	−11 (15)
	−0.05034 (3)	0.06919 (2)	0.21259 (4)	182 (1)	153 (1)	139 (1)	−9 (1)	7 (1)	0 (1)
O(1)	0.07963 (32)	0.08617 (28)	0.02780 (45)	130 (13)	159 (11)	121 (11)	−16 (9)	41 (9)	7 (8)
	0.07947 (10)	0.08637 (9)	0.02723 (15)	225 (3)	218 (3)	194 (3)	−14 (2)	55 (2)	6 (2)
O(2)	0.02541 (40)	0.07221 (28)	0.45427 (44)	314 (17)	211 (11)	86 (12)	−28 (12)	−63 (11)	8 (9)
	0.02637 (13)	0.07187 (10)	0.45495 (14)	398 (5)	255 (3)	150 (3)	−48 (4)	−56 (3)	9 (2)
O(3)	−0.16308 (36)	0.19281 (28)	0.19338 (58)	163 (14)	198 (13)	307 (16)	58 (10)	2 (14)	20 (11)
	−0.16332 (12)	0.19240 (11)	0.19335 (21)	234 (4)	249 (3)	384 (5)	74 (3)	43 (4)	38 (4)
O(4)	−0.13238 (36)	−0.07091 (26)	0.17444 (52)	228 (15)	170 (13)	178 (13)	−106 (11)	25 (11)	−42 (9)
	−0.13161 (13)	−0.07145 (10)	0.17401 (17)	318 (4)	221 (3)	245 (3)	−103 (3)	35 (3)	−30 (3)
N(1)	0.00953 (22)	0.33392 (15)	0.76654 (29)	136 (10)	149 (9)	146 (9)	8 (5)	−13 (7)	5 (5)
	0.00904 (13)	0.33380 (10)	0.76683 (17)	219 (4)	201 (3)	196 (3)	1 (3)	−8 (3)	5 (3)
N(2)	−0.15386 (22)	0.31239 (20)	0.69043 (40)	131 (10)	263 (10)	247 (11)	−14 (7)	−2 (9)	−71 (7)
	−0.15340 (13)	0.31199 (13)	0.69114 (21)	200 (4)	300 (4)	282 (4)	−5 (3)	3 (3)	−49 (4)
H(1)	0.0776 (7)	0.3574 (6)	0.6141 (11)	257 (27)	396 (27)	336 (30)	−79 (23)	108 (26)	31 (21)
	0.0630 (28)	0.3518 (25)	0.6595 (39)						
H(2)	0.0112 (7)	0.4235 (6)	0.8876 (9)	379 (31)	308 (20)	308 (25)	−66 (25)	−61 (24)	−85 (19)
	0.0122 (27)	0.4053 (28)	0.8644 (40)						
H(3)	0.0512 (8)	0.2398 (6)	0.8509 (12)	389 (31)	295 (26)	407 (31)	97 (22)	−111 (26)	107 (20)
	0.0480 (33)	0.2579 (25)	0.8145 (42)						
H(4)	−0.1591 (12)	0.2329 (10)	0.5698 (26)	500 (49)	655 (47)	1493 (116)	21 (39)	−268 (63)	−752 (66)
	−0.1599 (44)	0.2459 (35)	0.6148 (71)						
H(5)	−0.1916 (12)	0.4026 (11)	0.6100 (24)	638 (55)	668 (48)	1158 (93)	291 (44)	−588 (63)	−171 (52)
	−0.1847 (34)	0.3848 (40)	0.6280 (76)						
H(6)	−0.2209 (13)	0.2969 (23)	0.8281 (27)	455 (54)	2596 (207)	644 (68)	−588 (95)	173 (58)	32 (99)
	−0.2139 (37)	0.2939 (64)	0.8484 (63)						

Table 2. Extinction parameters*

Isotropic extinction	<i>g</i> '					
X-ray	2.93 (0.10)					
Neutron	20.5 (1.4)					
Type I extinction	<i>Z</i> ₁₁ '	<i>Z</i> ₂₂ '	<i>Z</i> ₃₃ '	<i>Z</i> ₁₂ '	<i>Z</i> ₁₃ '	<i>Z</i> ₂₃ '
Neutron	470 (59)	275 (52)	96 (26)	−56 (19)	−72 (16)	132 (26)
Neutron, constrained	463 (60)	305 (54)	118 (29)	0	0	0
Type II extinction	<i>W</i> ₁₁ '	<i>W</i> ₂₂ '	<i>W</i> ₃₃ '	<i>W</i> ₁₂ '	<i>W</i> ₁₃ '	<i>W</i> ₂₃ '
X-ray	0.585 (98)	0.062 (11)	0.048 (7)	−0.045 (31)	−0.062 (19)	0.022 (7)
Neutron	0.00568 (86)	0.00224 (30)	0.00234 (30)	−0.00092 (21)	0.00029 (16)	−0.00108 (18)
Neutron, constrained	0.00535 (84)	0.00173 (24)	0.00251 (34)	0.0	0.0	0.0

* See Coppens & Hamilton (1970) for an explanation of the notation.

were sorted together and the values of F^2 were averaged. The total number of independent reflections thus obtained was 543.

A difference map was now calculated where the calculated structure factors were based on the heavy atom

positions from the preliminary X-ray refinement. The positions of the hydrogen atoms attached to N(1) were clearly visible. A new difference map now based on calculated structure factors including the three hy-

Table 3. Observed and calculated X-ray structure amplitudes for N2H6SO4

The five columns are, in order, the indices k and l, |100|F0, |100|Fc (in electrons) and the extinction correction (x1000). The true for the extinction correction is blank when no extinction was indicated. The |F0| values have been corrected for extinction, the true observed values can be obtained by multiplication with the square root of the extinction correction.

Table with multiple columns containing numerical data for X-ray structure amplitudes. The table is organized into several sections based on the indices k and l, such as 0 0 0, 0 0 1, 0 0 2, etc., with corresponding values for |100|F0, |100|Fc, and extinction correction.

eters. The models tried were isotropic extinction and anisotropic extinction for type I and type II crystals. The anisotropic extinction refinements were also carried out with the anisotropic extinction tensors constrained to have orthorhombic symmetry. The parameters refined were positional and anisotropic thermal parameters for all atoms, a scale factor and one, three or six extinction parameters. The function minimized and the weighting scheme were the same as in the X-ray study. The un-averaged set of 858 reflections was now used as data since the extinction components were not equal for the equivalent forms of a reflection. A summary of the resulting R values is given in Table 4; the final values of the extinction parameters are presented in Table 2. A discussion of the physical interpretation of the extinction parameters is given in the paper by Coppens & Hamilton (1970). The unconstrained type II model, particle-size dominated, was concluded to be the most appropriate for this crystal. The final positional and thermal parameters for the unconstrained type II model are presented in Table 1,* and the observed and calculated structure factors together with the extinction coefficients are listed in Table 5. In the last cycle of least-squares refinement no parameter shifted by more than 0.1σ ; the final agreement indices were $R=0.074$ and $R_w=0.096$. The corresponding conventional R index based on F was 0.040. The error in an observation of unit weight was 1.46. The neutron scattering lengths used were $b_S=0.28$, $b_O=0.58$, $b_N=0.94$, $b_H=-0.372$ (10^{-12} cm).

* There was little correlation of the positional and thermal parameters with the type of crystal assumed for the extinction refinement.

Table 4. R values (based on F^2) for neutron data

	R	R_w
Isotropic extinction	0.085	0.109
Constrained Type I	0.081	0.103
Type I	0.074	0.097
Constrained Type II	0.081	0.103
Type II	0.074	0.096

Computer programs

The calculations were carried out on the CDC 6600 computer at the Brookhaven National Laboratory. The following programs from the BNL crystallographic program library were used: *DATAPH* for absorption correction, *FORDAP* for Patterson and Fourier calculations, *LINUS* for least-squares refinement, *NANOVA* for analysis of the weighting scheme at the end of the least-squares refinement, and *ORFFE* and *ORTEP* for structure description.

Comparison of the neutron and X-ray results

Only a few compounds have been studied by both neutron and X-ray diffraction using counter methods; a comparison of the results of the two determinations is therefore of some interest.

There is very satisfactory agreement between the neutron and X-ray results for the positional parameters of the heavy atoms, as can be seen from the values in Table 1. The estimated standard deviations are lower in the X-ray results for the heavy atoms; this reflects the larger number of observations in the X-ray study. The thermal parameters for the two methods are also compared in Table 1; there are clearly differences. The corresponding diagonal elements of the thermal vibratio-

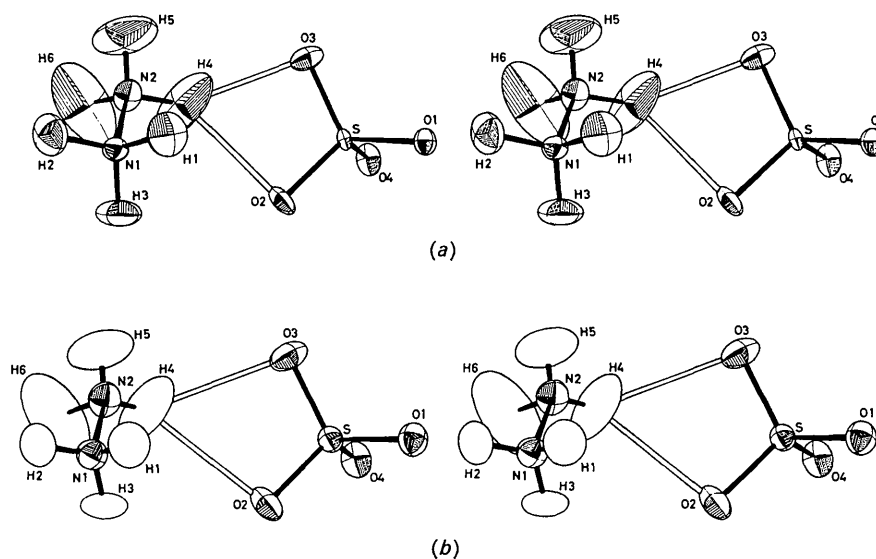


Fig. 1. Stereoscopic illustration of an asymmetric unit of $N_2H_6SO_4$. Thermal ellipsoids are scaled to include 50% probability. (a) Neutron results, (b) X-ray results; the boundary ellipsoids for the hydrogen atoms are taken from the neutron study.

Table 5. Observed and calculated neutron structure amplitudes for N₂H₆SO₄

The five columns are, in order, the indices k and l, 100|F_o|, 100|F_c| (in units of 10⁻¹² cm) and the extinction correction (× 1000). The entry for the extinction correction is blank when no extinction was indicated. The |F_o| values have been corrected for extinction, the true observed values can be obtained by multiplication with the square root of the extinction correction.

Table with multiple columns containing numerical data for neutron structure amplitudes, including indices k and l, observed and calculated values, and extinction corrections.

nal tensor are without exception larger for the X-ray values. In a comparison of X-ray and neutron diffraction structural results it was pointed out by Hamilton (1969) that for all but one of the diffractometer experiments, mean diagonal elements of the thermal vibration tensor were larger for X-rays than for neutrons. This reflects the inadequacy of the free-atom approximation for the X-ray scattering factors as discussed in detail by Coppens (1969).

The principal axes of thermal motion for the heavy atoms are compared in Table 6. The agreement between the shapes of the thermal motion ellipsoids can be seen from an examination of Fig. 1.

Bond lengths and bond angles are compared in Table 7; the agreement is satisfactory when only the heavy atoms are involved. The mean N-H bond length from the X-ray study is 0.83 Å as compared with the

Table 6. Comparison of heavy atom principal axes of thermal motion ellipsoids

The directions are most clearly seen by an examination of Fig. 1. The neutron values are given on the first line in each case and the X-ray values on the second. The units are 10⁻³ Å.

Table with columns for Axis 1, Axis 2, and Axis 3, listing S, O(1), O(2), O(3), O(4), N(1), and N(2) values for X-ray and Neutron.

mean of the neutron results of 1.01 Å. The differences in individual bond lengths are in all but one case much larger than those to be expected from the calculated standard deviations. Similar results have been encountered in other cases where a structure containing hydrogen atoms has been studied by both neutron and X-ray diffraction methods. Stewart, Davidson & Simpson (1965) have given justification for an apparent contrac-

tion for C-H and N-H bond lengths determined by least-squares procedures from X-ray data when a spherical scattering factor for hydrogen is assumed. In the following discussion, only the neutron diffraction values will be used for the hydrogen parameters.

Discussion of the structure

The structure is composed of $N_2H_5^+$ and SO_4^{2-} ions held together by a three-dimensional system of hydrogen bonds. The structure is essentially the same as that found in the investigation by Nitta *et al.* (1951), but since the differences in the atomic positions are as large as 0.05–0.20 Å, no comparison of bond lengths seems to be justified here.

Hydrogen bonding

The environments of the two NH_3 groups in the hydrazinium ion show a marked difference. Fig. 2 illustrates the sulfate group neighbors around a hydrazinium ion; all sulfate groups where the $H \cdots O$ distance is less than 2.4 Å have been included. Table 8 gives values for the N-H \cdots O bond lengths and angles. In this Table all $H \cdots O$ distances less than 2.65 Å have been included. The longest $H \cdots O$ distances in this Table should not be regarded as defining hydrogen bonds if we accept that the criterion for hydrogen bonding is a hydrogen atom-heavy atom distance that is 0.2 Å or more shorter than the sum of the van der Waals radii (Hamilton & Ibers, 1968). If we take the van der Waals radii of H and O atoms as 1.2 and 1.4 Å, $H \cdots O$ distances longer than about 2.4 Å should not be regarded as defining hydrogen bonds. An examination of Table 8 reveals that if the longer $H \cdots O$ contacts were accepted as hydrogen bonds this would lead to large deviations from linearity in such hydrogen bonds, the N-H \cdots O angles being close to 90° in some cases. A good correlation between N-H \cdots O angles and $H \cdots O$ distances is seen in Fig. 3. The tendency for short hydrogen bonds to be linear is marked. We prefer

Table 7. Covalent bond lengths and angles

(a) Bond lengths (Å). Distances given within brackets are corrected for thermal riding motion.

	Neutron	X-ray
S—O(1)	1.498 [1.503] (5)	1.491 [1.497] (1)
S—O(2)	1.475 [1.486] (5)	1.483 [1.494] (1)
S—O(3)	1.465 [1.478] (5)	1.468 [1.481] (1)
S—O(4)	1.463 [1.474] (5)	1.468 [1.478] (1)
N(1)—N(2)	1.426 (3)	1.418 (2)
N(1)—H(1)	1.036 [1.061] (6)	0.76 (2)
N(1)—H(2)	1.059 [1.083] (5)	0.85 (2)
N(1)—H(3)	1.039 [1.069] (5)	0.81 (2)
N(2)—H(4)	0.989 [1.086] (7)	0.74 (3)
N(2)—H(5)	0.989 [1.068] (11)	0.80 (4)
N(2)—H(6)	0.952 [1.106] (13)	1.02 (4)

(b) Angles (degrees)

	Neutron	X-ray
O(1)—S—O(2)	107.9 (0.4)	108.3 (0.1)
O(1)—S—O(3)	108.8 (0.3)	109.0 (0.1)
O(1)—S—O(4)	108.6 (0.3)	108.7 (0.1)
O(2)—S—O(3)	108.9 (0.3)	108.9 (0.1)
O(2)—S—O(4)	110.2 (0.3)	109.9 (0.1)
O(3)—S—O(4)	112.2 (0.4)	112.0 (0.1)
N(2)—N(1)—H(1)	107.5 (0.4)	110.7 (1.9)
N(2)—N(1)—H(2)	107.8 (0.4)	109.0 (1.5)
N(2)—N(1)—H(3)	109.3 (0.4)	110.5 (1.8)
N(1)—N(2)—H(4)	110.0 (0.6)	110.6 (2.8)
N(1)—N(2)—H(5)	108.4 (0.6)	108.6 (2.2)
N(1)—N(2)—H(6)	109.5 (0.8)	103.6 (1.7)
H(1)—N(1)—H(2)	110.3 (0.5)	108.1 (2.1)
H(1)—N(1)—H(3)	111.0 (0.5)	102.0 (2.3)
H(2)—N(1)—H(3)	110.8 (0.5)	116.3 (1.8)
H(4)—N(2)—H(5)	107.3 (1.1)	114.3 (3.5)
H(4)—N(2)—H(6)	113.9 (1.3)	108.6 (3.9)
H(5)—N(2)—H(6)	107.6 (1.4)	110.7 (4.1)

Table 8. Hydrogen bonds N-H \cdots O and short van der Waals contacts*

N	H	O	N \cdots O	N-H	H \cdots O	< N-H \cdots O	< H \cdots O-S
N(1)	H(1)	O(4)	2.782 (3)	1.036 (6)	1.784 (7)†	160.4 (0.6)°	109.8 (0.3)°
N(1)	H(1)	O(3)	2.721 (4)	1.036 (6)	2.434 (7)	94.6 (0.4)	112.0 (0.3)
N(1)	H(1)	O(1)	2.921 (3)	1.036 (6)	2.586 (7)	98.3 (0.4)	76.3 (0.2)
N(1)	H(2)	O(2)	2.689 (3)	1.059 (5)	1.646 (6)†	167.0 (0.5)	112.7 (0.3)
N(1)	H(2)	O(4)	3.369 (3)	1.059 (5)	2.622 (6)	127.2 (0.4)	72.9 (0.2)
N(1)	H(3)	O(1)	2.752 (3)	1.039 (5)	1.730 (6)†	166.9 (0.6)	112.0 (0.3)
N(1)	H(3)	O(3)	2.721 (4)	1.039 (5)	2.449 (8)	93.7 (0.4)	144.0 (0.3)
N(1)	H(3)	O(3)	3.045 (4)	1.039 (5)	2.627 (8)	103.7 (0.4)	76.0 (0.2)
N(2)	H(4)	O(3)	2.961 (4)	0.989 (7)	2.115 (14)†	142.5 (1.2)	92.9 (0.4)
N(2)	H(4)	O(2)	2.955 (4)	0.989 (7)	2.212 (9)†	130.9 (0.8)	88.8 (0.4)
N(2)	H(4)	O(4)	2.830 (3)	0.989 (7)	2.344 (12)†	109.4 (1.0)	158.0 (0.3)
N(2)	H(5)	O(1)	2.850 (3)	0.989 (11)	2.064 (13)†	134.9 (0.8)	119.4 (0.4)
N(2)	H(5)	O(2)	2.960 (4)	0.989 (11)	2.373 (10)†	117.3 (0.9)	106.8 (0.4)
N(2)	H(6)	O(1)	2.851 (3)	0.952 (13)	2.119 (16)†	132.6 (1.6)	110.8 (0.5)
N(2)	H(6)	O(3)	2.991 (4)	0.952 (13)	2.285 (17)†	130.4 (1.2)	121.4 (0.5)
N(2)	H(6)	O(4)	2.830 (3)	0.952 (13)	2.544 (17)	97.5 (1.2)	151.9 (0.4)

* H \cdots O distances which correspond to hydrogen bonds according to the Hamilton-Ibers criterion are indicated by the dagger.

to classify $H \cdots O$ contacts longer than 2.4 \AA as van der Waals contacts. However, it is clear that there is no clear distinction between weak hydrogen bonds and van der Waals 'bonds'.

It is apparent from the values in Table 8 that a precise determination of the hydrogen positions is essential in revealing the hydrogen bonding scheme in a structure like this one, where most of the hydrogen bonds are far from linear. Conclusions drawn only from $N \cdots O$ contacts can be misleading. An example is the second shortest $N \cdots O$ distance in the Table, 2.721 \AA ; the two contacts at this distance do not represent hydrogen bonds if the Hamilton-Ibers criterion is accepted.

The hydrazinium ($2+$) ion

The N–N distances of $1.426(3) \text{ \AA}$ from the neutron study and $1.418(2) \text{ \AA}$ from the X-ray study are in good agreement with the value of $1.432(6) \text{ \AA}$ found by Liminga (1966) in $N_2H_6(H_2PO_4)_2$. The hydrazinium ion has a staggered conformation with the dihedral angles close to 60° ; the maximum deviation from this value is less than 3σ .

The mean apparent N(1)–H bond length is 1.045 \AA , whereas the mean apparent N(2)–H bond length is 0.976 \AA . There is a marked contrast in anisotropic thermal parameters between the hydrogen atoms at the two ends of the hydrazinium ion, as can be seen from Fig. 1; numerical values for the thermal motion ellipsoids are presented in Table 9. The ellipsoids indicate a very large amplitude of vibration for the N(2)H₃ group around the N(2)–N(1) axis. A correction for thermal riding motion according to Busing & Levy (1964), where the hydrogen atoms were assumed to ride on the nitrogen atom, gave corrected mean values of 1.071 \AA for the N(1)–H bonds and 1.086 \AA for the N(2)–H bonds. Previous work (Sequeira, Berkebile & Hamilton, 1968, for example) shows that such corrections for librating groups makes the bonds too long; the assumption of the riding motion model is not really adequate in these cases when large amplitudes are involved. Small differences in the N–H bond lengths are expected, since

this bond length is influenced by the strength of the hydrogen bonds in which it participates; the large uncertainties in the thermal motion corrections renders any more detailed discussion of N–H bond length differences fruitless.

Table 9. Principal axes of thermal ellipsoids for the hydrogen atoms and angles which these make with the N–H bond

The units for the amplitudes are 10^{-3} \AA .

	Amplitude	Direction
H(1)	124 (11)	23 (5)°
	200 (7)	69 (8)
	209 (8)	82 (13)
H(2)	135 (9)	24 (5)
	198 (7)	92 (23)
	205 (8)	114 (6)
H(3)	121 (10)	167 (4)
	208 (7)	77 (5)
	226 (8)	93 (5)
H(4)	129 (13)	159 (4)
	225 (10)	107 (5)
	444 (16)	102 (2)
H(5)	141 (13)	139 (4)
	251 (10)	120 (4)
	405 (15)	64 (3)
H(6)	152 (16)	150 (6)
	268 (14)	120 (6)
	524 (21)	90 (3)

The thermal parameters of the hydrogen atoms can also be related to the hydrogen bonding situation around the hydrazinium ion (Fig. 2). The hydrogen atoms attached to N(1) are each involved in one hydrogen bond; these bonds are close to being linear, and the $O \cdots H$ distances are rather short. The hydrogen bonding is more complicated for the hydrogen atoms attached to N(2); H(4) is involved in three hydrogen bonds and H(5) and H(6) in two each. Such bonds have been called trifurcated and bifurcated. The $O \cdots H$ distances are rather long for the bi- and trifurcated bonds, so it appears that the N(1)H₃ end is more strongly bonded to the neighboring sulfate groups than the N(2)H₃ end. This is reflected in the larger amplitudes of

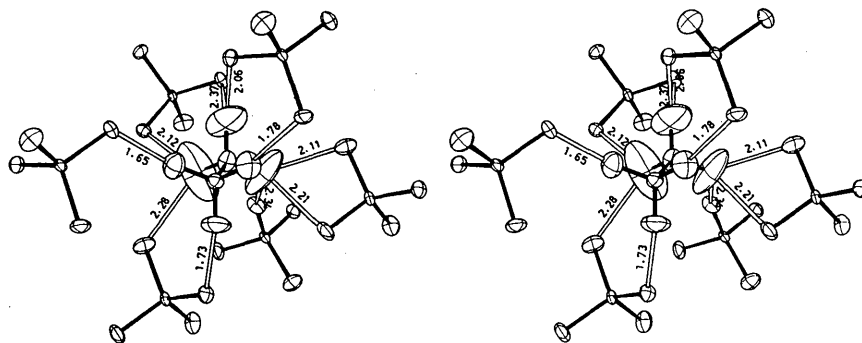


Fig. 2. Stereoscopic illustration of the bonding situation around a hydrazinium ion. All parameters are taken from the neutron study; thermal ellipsoids are scaled to include 50% probability.

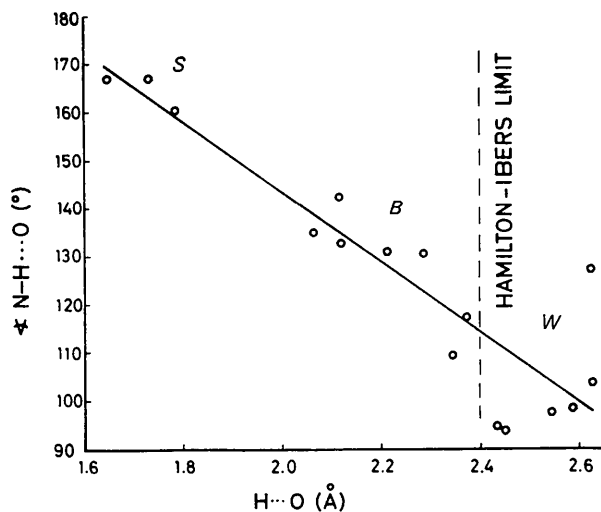


Fig. 3. Hydrogen bond angle-distance correlation in hydrazinium sulfate. *S* - single hydrogen bonds; *B* - bifurcated or trifurcated hydrogen bonds; *W* - weak hydrogen bonds or van der Waals contacts.

thermal motion. An explanation of the large thermal parameters of the hydrogen atoms attached to N(2) in terms of static disorder seems less likely.

The sulfate ion

For the following discussion, we prefer to use the more precise bond lengths from the X-ray study. The neutron values do not, however, differ significantly from the X-ray values.

The geometry of the sulfate ion shows a small but significant departure from a regular tetrahedron as indicated by some variation in the S-O bond lengths and also by the departure of the O-S-O bond angles from the tetrahedral value. This departure can be related to the hydrogen bonding situation around the sulfate group (see Fig. 4). The longest S-O distance,

1.491 Å, involves O(1) which acts as an acceptor for three rather short hydrogen bonds (1.73, 2.06 and 2.12 Å). The next longest S-O distance, 1.483 Å, is to O(2) which also accepts three hydrogen bonds (1.65, 2.21 and 2.37 Å); the longest of these is probably rather weak. The S-O distance to O(3) and O(4) is in both cases 1.468 Å; each of these oxygen atoms acts as an acceptor for two hydrogen bonds.

The mean S-O bond length of 1.477(1) Å is slightly longer than the average of 1.473(1) Å from the mean values of five different sulfate hydrates (Baur, 1964). When a correction for thermal riding motion is applied, the mean value becomes 1.487 Å which is in good agreement with the values of 1.485 and 1.486 given by Baur for the three compounds where the assumptions for this correction were considered to be valid.

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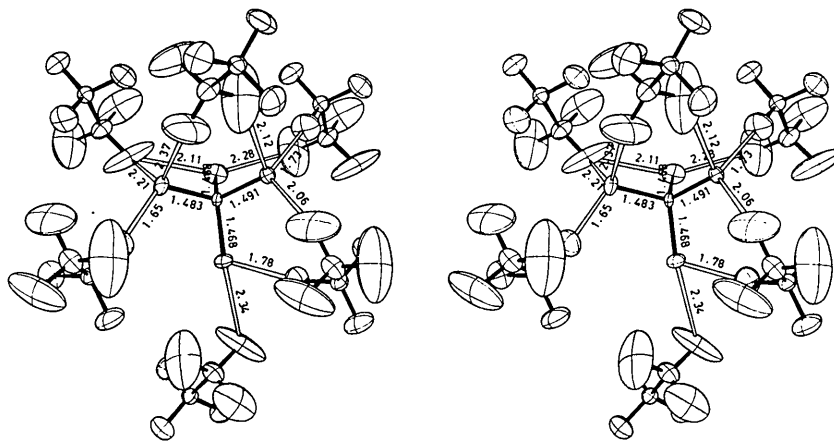


Fig. 4. Stereoscopic illustration of the bonding situation around a sulfate ion. The positional parameters for the sulfate ion are taken from the X-ray study; all other parameters are from the neutron study.

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Stereochemistry of Nucleic Acids and their Constituents. VI. The Crystal Structure and Conformation of Dihydrouracil: a Minor Base of Transfer-Ribonucleic Acid*

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Crystals of dihydrouracil are monoclinic, space group $P2_1/c$, $Z=4$, $a=4.210 \pm 0.001$, $b=5.816 \pm 0.001$, $c=19.777 \pm 0.003$ Å, $\beta=95.15 \pm 0.01^\circ$, $D_m=1.575$ g.cm⁻³, $D_x=1.577$ g.cm⁻³. The structure was solved by direct methods and refined by least squares to an R of 0.073, with 639 diffractometric intensities. The saturated ring displays a twist half-chair conformation with C(5) and C(6) displaced by 0.14 and 0.45 on either side of the dihydrouracil plane. The maximum torsion angle of 45.4° is about the saturated C(5)–C(6) bond. The molecule exists in the diketo form, and forms infinite zigzag hydrogen-bonded ribbons such that each base is hydrogen bonded to two adjacent bases related by centers of inversion. O(4) is not involved in hydrogen bonding, whereas O(2) is involved in two hydrogen bonds. The interplanar separation of the bases is 3.34 Å. The base stacking in dihydrouracil is typical of the ketopyrimidines.

Introduction

Transfer ribonucleic acid (*t*-RNA) is probably the smallest (about eighty nucleotides) of the naturally occurring nucleic acids. In addition to the common nucleotides, guanylic, adenylic, cytidylic and uridylic acids, *t*-RNA is composed of approximately 15–20 per cent of a unique class of minor nucleotides (Holley, Apgar, Everett, Madison, Marquisee, Merrill, Penswick & Zamir, 1965; Madison, Everett & Kung, 1966; Zachau, Dütting & Feldman, 1966; RajBhandary, Chang, Stuart, Faulkner, Hoskinson & Khorana, 1967). The majority of the minor nucleotides differ from the common forms only in the composition of the base, although sometimes 2'-*O*-methylated derivatives are also isolated. It is believed that the minor components influence significantly the secondary and tertiary structures of *t*-RNA. To determine the role of the minor components in *t*-RNA, the structural analyses of several minor constituents are presently being

carried out in our laboratory (Rao & Sundaralingam, 1969). In this article, we present the results of the crystal structure of the minor base dihydrouracil (DiHU), which is one of the more common minor bases and is located in the loops of the cloverleaf model for *t*-RNA proposed by Holley *et al.* (1965). A preliminary report on this work has already appeared (Rohrer & Sundaralingam, 1968). Dihydrouracil differs from the common base uracil in that the C(5)–C(6) bond is saturated.

Experimental

Dihydrouracil, purchased from Sigma Chemical Company, St. Louis, Missouri, was crystallized in dimethyl sulfoxide. The crystals showed preferred elongation in the *a*-axis direction and very pronounced cleavage parallel to the (001) plane, thus making selection of a suitable crystal difficult. More than 20 crystals were examined before one without partial cleavage was found. The crystal data for dihydrouracil are given in Table 1. Three-dimensional diffractometric intensities were collected up to $2\theta=134^\circ$, on a crystal mounted with the long direction parallel to the ϕ axis of the diffractometer, using the θ - 2θ scan mode and a scan speed of 1° per minute. Altogether 823 independent reflections were scanned, and 690 were con-

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