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Hydrogen Bond Studies

8. The Crystal Structure of Dihydrazinium Sulphate $(N_2H_5)_2SO_4$

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The crystal structure of dihydrazinium sulphate, $(N_2H_5)_2SO_4$, has been determined from three-dimensional single crystal X-ray data. The crystals are monoclinic, space group $P2_1/c$, with four molecules in a unit cell with the dimensions: $a = 5.157$, $b = 11.064$, $c = 10.971$ Å, $\beta = 100.04°$. The sulphate ion shows only a small departure from regular tetrahedral geometry and the S–O distances are 1.46 – 1.47 Å. The N–N distances in the two independent $N_2H_5^+$ ions are 1.43 and 1.44 Å, respectively. The hydrazinium ions are hydrogen-bonded to the oxygen atoms of the sulphate ions and are probably also interlinked by weak bonds into groups of four hydrazinium ions. A possible assignment of the hydrogen atoms to these bonds is given. This assignment is partly confirmed by the "hydrogen peaks" appearing in the difference Fourier maps.

Three sulphates of hydrazine are known and have the following compositions: $N_2H_4 \cdot H_2SO_4$, $2N_2H_4 \cdot H_2SO_4$, and $N_2H_4 \cdot 2H_2SO_4$. The crystal structure of the first of these salts was determined by Nitta, Sakurai and Tomiie,[1] who concluded that this compound should be formulated as $N_2H_6SO_4$, *i.e.* as a hydrazinium (2+) salt. Pratt and Richards [2] came to the same conclusion, when studying the proton magnetic resonance spectra of this salt. However, Bock [3] has discussed the existence of $N_2H_6^{2+}$ ions and has pointed out that this compound of hydrazine might be formulated as $N_2H_5 \cdot HSO_4$. The present investigation concerns the determination of the crystal structure of $2N_2H_4 \cdot H_2SO_4$ from single crystal X-ray data. As will be shown below, the compound is correctly formulated as a hydrazinium (1+) salt, $(N_2H_5)_2SO_4$. The same conclusion was reached by Pratt and Richards [2] as a result of a proton magnetic resonance study. The third sulphate of hydrazine, $N_2H_4 \cdot 2H_2SO_4$, should probably be formulated as $N_2H_6(HSO_4)_2$, but its structure has not been determined.

EXPERIMENTAL

Dihydrazinium sulphate was prepared from hydrazine monohydrate (*purum*) by the addition of sulphuric acid (*purum*) to give a pH between 4 and 5. The crystals were recrystallized from dilute alcohol and dried in air after filtering. According to Christensen and Gilbert [4] this method of preparation yields the monohydrate, but analysis of the sample showed it to be anhydrous (analysed by titration using the bromate method at the Central Analytical Laboratory, Institute of Chemistry, University of Uppsala). The sample contained 39.4 % N_2H_4; calculated for $(N_2H_5)_2SO_4$: 39.6 % N_2H_4 and for $(N_2H_5)_2SO_4 \cdot H_2O$: 35.5 % N_2H_4.

Dihydrazinium sulphate is very soluble in water and dilute alcohol. When the sample was filtered, some concentrated mother liquor solidified on the crystals, so that these could not be used for single crystal studies. In order to obtain suitable single crystals it was necessary to treat the crystals with dilute alcohol before mounting to dissolve away the crystallized mother liquor and also the edges of the crystals. After a number of attempts it was possible to obtain single crystals in both cylindrical and spherical form. The crystals were mounted on glass fibres.

Two crystals were used for the single crystal studies. Crystal 1 had a cylindrical form (diameter 0.13 mm, length 0.66 mm) with the crystallographic a-axis coincident with the cylinder axis. With the crystal rotating about this axis, equi-inclination Weissenberg photographs of zones with $0 \leq h \leq 4$, were recorded using Cu$K\alpha$ radiation and the multiple-film technique (five films). In order to correlate the intersecting layers, a second crystal (spherical form, diameter 0.26 mm) was mounted and rotated about the b-axis. The zones $0 \leq k \leq 6$ were recorded in a similar way. These reflexions were used for scaling purposes only. The relative intensities were estimated visually by comparison with a calibrated scale. The intensity range was 1 to 3500. The number of independent reflexions recorded from crystal 1 was 1162, but 184 of these were too weak to be measured. These were not included in the refinements, which are thus based on 978 measured reflexions from crystal 1. The number of reflexions measured from crystal 2 was 759.

The data were corrected for the Lorentz and polarization effects and also for absorption on an IBM 7090 computer using the programme ERLPA written by Van den Hende.[5] The absorption coefficient μ for Cu$K\alpha$ radiation is 43.3 cm^{-1}. The resulting $\mu R/\cos \beta$ for crystal 1 is between 0.28 (layer 0) and 0.35 (layer 4). The value of μR for crystal 2 is equal to 0.56.

The correlation of the intersecting layers was made on the computer FACIT using the programme BAS written by P. E. Werner, University of Stockholm. This programme is based on a least squares method devised by Rollett and Sparks.[6] The number of common reflexions observed on both sets of films was 585. However, some of the weakest reflexions were given zero weight, which reduced the number of reflexions for the scaling to about 530. The weights used for these were $w = 1/F_1^2F_2^2$, where F_1 and F_2 are the absolute values of the observed structure factors from crystals 1 and 2, respectively.

In a note concerning the relative scaling of X-ray photographs, Hamilton, Rollett and Sparks [22] reported that the method for the calculation of interlayer scale factors presented earlier by Rollett and Sparks [6] has its limitations and can lead to some peculiar results. This note appeared at a time when all refinements of the present structure were finished. However, the results from the programme BAS seem to be acceptable in the present case, as the five interlayer scale factors of the data from crystal 1 obtained by a least squares refinement with the programme SFLS (see below) deviated by less than about ± 7 % from those obtained by BAS. In this refinement the coordinates and isotropic thermal parameters of all the atoms, except the hydrogens, were also varied. Although the differences seem to be rather large, further refinements of the structure with the interlayer scale factors determined by other methods were not considered to be necessary. In addition, differences in the scale factors, obtained by the methods described above, might depend upon anisotropy in the atomic vibrations.

The density of dihydrazinium sulphate was determined by weighing the specimen in air and in m-xylene, as described in the *International Tables* [7] (Vol III, p. 18). The value of the density obtained was 1.75 g cm^{-3}.

In order to obtain information about possible phase transformations, some powder photographs (Debye-Scherrer type) were taken in a Weissenberg camera, equipped with a low-temperature apparatus. Exposures were made at room-temperature and at −184°C. The photographs obtained indicated no phase changes; only a slightly smaller unit cell was observed at −184°C.

UNIT CELL AND SPACE GROUP

The data showed that the diffraction symmetry was that of the monoclinic Laue group $2/m$. Systematic absences were: $(h0l)$ for $l \neq 2n$ and $(0k0)$ for $k \neq 2n$. Assuming that the absences correspond to space group extinctions these results suggest the space group $P2_1/c$ (C_{2h}^5). The subsequent refinement of the structure in this space group gave good agreement with the observed data, thus confirming the choice. The general 4-fold equivalent positions in $P2_1/c$ are as follows:[8]

$$(x,y,z);\ (\bar{x},\bar{y},\bar{z});\ (\bar{x},\ \tfrac{1}{2}+y,\ \tfrac{1}{2}-z);\ (x,\ \tfrac{1}{2}-y,\ \tfrac{1}{2}+z)$$

The unit cell parameters as determined from quartz-calibrated zero-layer Weissenberg photographs are:

$a = 5.157 \pm 0.002$, $b = 11.064 \pm 0.002$, $c = 10.971 \pm 0.007$ Å
$\beta = 100.04 \pm 0.04°$
($a = 4.913$ Å for α-quartz; λ Cu$K\alpha_1 = 1.54051$ Å, λ Cu$K\alpha_2 = 1.54433$ Å).

The uncertainties in the cell dimensions given above are estimated standard deviations.

The density, calculated on the basis of a unit cell containing four molecules of $(N_2H_5)_2SO_4$, is 1.75 g cm^{-3}. The observed density was 1.75 g cm^{-3} (see above).

DETERMINATION OF THE ATOMIC COORDINATES

The positions of the sulphur atom and the four independent oxygen atoms were determined from a three-dimensional Patterson synthesis. The coordinates of the four independent nitrogen atoms were then obtained from a three-dimensional F_o-synthesis, based on the known sulphur and oxygen positions. All these atoms are in the general 4-fold positions of the space group $P2_1/c$.

The preliminary atomic coordinates were first improved in a series of three-dimensional electron density calculations. Only the reflexions obtained from crystal 1 were used in all refinements; reflexions too weak to be measured were given zero weight in all calculations. The Fourier calculations were made on the computer FACIT EDB using programmes (designated STRIX and PROFFS) written by Liminga and Olovsson.[9]

The atomic coordinates, individual temperature factors (both isotropic and subsequently anisotropic) and an over-all scale factor were then further refined by the method of least squares. The interlayer scale factors used were those obtained by the programme BAS as described earlier. The first series of least squares calculations were performed on FACIT EDB using a programme (designation SFLS) written by Brändén and Åsbrink. The main

features of this programme have been reported earlier.[10] A block-diagonal approximation is used in this programme to minimize the function $\sum w (|F_o| - |F_c|)^2$. The weights, w, were calculated according to an equation suggested by Cruickshank *et al.*[11] as follows: $w = 1/(a + |F_o| + c|F_o|^2)$. The final values used for the parameters a and c were 5.0 and 0.075, respectively. After about ten cycles of least squares refinements the "discrepancy index" $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ was 0.116 (unobserved reflexions omitted in calculating all R-values). In the last cycle the shifts of all parameters were less than about one tenth of their estimated standard deviations.

At this stage of the refinement a three-dimensional difference Fourier synthesis with $(F_o - F_c)$ as coefficients was calculated. Possible hydrogen positions were now determined; the location of the hydrogen atoms was based on arguments as described below. When these predicted hydrogen positions were compared with the difference Fourier maps, peaks could be found for all the positions. Apart from these "hydrogen peaks" a number of other peaks appeared, particularly around the sulphur and oxygen atoms, but these could be interpreted as arising from diffraction effects or from the anisotropic motion of these atoms. In some cases, however, the location of the hydrogen atoms is uncertain, as is mentioned below.

Some cycles of least squares calculations were now performed, with the hydrogen atoms included but keeping their positions constant. The R_1-value decreased from 0.116 to 0.109. The total shifts in the atomic coordinates were about one standard deviation as a maximum. When the observed and calculated structure factors were compared at this stage it was found that some low angle reflexions with high intensities systematically showed values of F_o much smaller than F_c, possibly due to secondary extinction effects. These 9 reflexions were now excluded from the data. After some cycles of refinement, now based on 969 observed reflexions, the R_1-value decreased from 0.109 to 0.104. The shifts in the atomic parameters were small; only the standard deviations showed some improvement.

A series of least squares calculations was now performed on an IBM 7090 computer with a full matrix programme, a local modification of OR FLS, written by Busing *et al.*[12] The same weighting scheme as above was used. The coordinates and individual temperature factors for all but the hydrogen atoms were refined together with an over-all scale factor; the total number of varied parameters was thus 37. These calculations started from the parameter values obtained by the program SFLS described above. The "discrepancy indices" after 3 cycles were:

$$R_1 \text{ (as defined above)} = 0.104$$
$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{\frac{1}{2}} = 0.140$$

Some shifts in the parameters resulted, especially in the B-values; in some cases these were about twice the standard deviations.

Finally, three cycles of least squares calculations were run with anisotropic temperature factors for the sulphur, oxygen, and nitrogen atoms. The total number of parameters varied was now 82. The hydrogen atom parameters were not refined. In the last cycle the shifts in coordinate or thermal parameter

values were less than one tenth of the standard deviation for the parameter in question. The R_1 and R_2 values were now 0.085 and 0.111, respectively.

The atomic coordinates and thermal parameters together with their standard deviations after the final anisotropic least squares refinement are listed in Tables 1 and 2. The observed and calculated structure factors are listed in Table 6. Distances and angles together with their standard deviations, given in Tables 3—5, were calculated using the programme OR FFE written by Busing *et al.*[13] The standard errors of the distances and angles were computed from the errors for the atomic coordinates in the form of a variance-covariance matrix. This was obtained in the final least squares cycle using OR FLS. The errors for the cell dimensions were also included in these calculations.

The atomic scattering factors used in the above calculations were those for neutral S, O, N, and H, respectively, given in the *International Tables* [7] (Vol. III, p. 202).

Table 1. Atomic coordinates in $(N_2H_5)_2SO_4$.

Atom		x	y	z
S		0.1285 ± 0.0003	0.1583 ± 0.0001	0.2884 ± 0.0001
O(1)		0.4173 ± 0.0009	0.1530 ± 0.0004	0.3084 ± 0.0004
O(2)		0.0268 ± 0.0009	0.1456 ± 0.0004	0.1550 ± 0.0004
O(3)		0.0424 ± 0.0008	0.2754 ± 0.0003	0.3315 ± 0.0004
O(4)		0.0225 ± 0.0008	0.0613 ± 0.0004	0.3558 ± 0.0004
N(1)		0.3880 ± 0.0009	0.4668 ± 0.0004	0.3379 ± 0.0004
N(2)		0.2633 ± 0.0010	0.8486 ± 0.0004	0.4532 ± 0.0004
N(3)		0.3622 ± 0.0009	0.9302 ± 0.0004	0.0917 ± 0.0004
N(4)		0.4879 ± 0.0012	0.8291 ± 0.0005	0.3959 ± 0.0005
Hydrogen atoms:				
Bonded to N(1):	H(1)	0.258	0.395	0.335
	H(2)	0.315	0.540	0.379
	H(3)	0.410	0.488	0.249
N(3):	H(4)	0.25	0.00	0.11
	H(5)	0.30	0.85	0.13
N(2):	H(6)	0.174	0.927	0.417
	H(7)	0.323	0.858	0.547
	H(8)	0.134	0.777	0.433
N(4):	H(9)	0.43	0.77	0.33
	H(10)	0.64	0.79	0.46

DISCUSSION OF THE STRUCTURE

The structure is shown in projection in Fig. 1. The significant bond distances and angles with their standard deviations are given in Tables 3 — 5 and in Figs. 2—6. These distances and angles are based on the parameters listed in Table 1, obtained from the anisotropic least squares refinement (no correction for thermal motion).

Table 2. Anisotropic thermal parameters and their standard deviations (each multiplied by 10^4) in $(N_2H_5)_2SO_4$. The definition of the temperature factor is: $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	103 ± 8	31 ± 1	41 ± 1	5 ± 1	6 ± 2	−2 ± 1
O(1)	193 ± 22	69 ± 4	56 ± 3	14 ± 5	8 ± 6	−6 ± 3
O(2)	257 ± 23	66 ± 4	55 ± 4	6 ± 6	−14 ± 6	2 ± 3
O(3)	236 ± 21	45 ± 3	114 ± 5	5 ± 6	55 ± 7	−20 ± 3
O(4)	207 ± 20	58 ± 3	76 ± 4	7 ± 6	38 ± 6	12 ± 3
N(1)	168 ± 21	46 ± 3	55 ± 4	9 ± 6	23 ± 6	6 ± 3
N(2)	213 ± 24	46 ± 3	50 ± 4	1 ± 6	18 ± 7	−1 ± 3
N(3)	167 ± 22	60 ± 4	54 ± 4	−25 ± 6	10 ± 6	−4 ± 3
N(4)	293 ± 30	87 ± 5	62 ± 4	17 ± 8	38 ± 8	2 ± 4
H *	564	123	125	0	46	0

* Isotropic temperature factor in anisotropic form. The isotropic temperature factor coefficient B used for all hydrogen atoms was 6 Å^2.

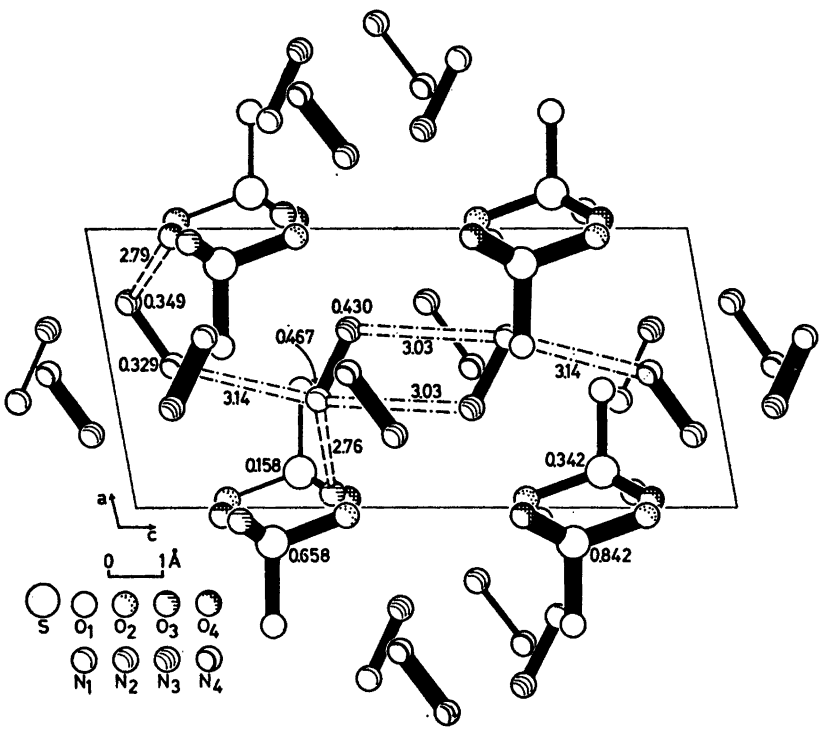

Fig. 1. The structure of $(N_2H_5)_2SO_4$ projected along the b-axis. The y-coordinate is given for some of the sulphur and nitrogen atoms. The shortest normal hydrogen bonds N(1) —O(3) and N(2)—O(4) are indicated and also the possible weak bonds between one group of four hydrazinium ions.

The structure can be described by referring to Fig. 1, which shows a view of the structure along the *b*-axis. The structure can be described as composed of compound layers of sulphate and hydrazinium ions, parallel to $(10\bar{2})$. The thickness of such a compound layer is about 2.5 Å and the interlayer distance is about 1.5 Å. The hydrazinium ions are nearly parallel to (010); the difference between the *y*-coordinates of two nitrogen atoms in a hydrazinium ion is smaller than 0.04. Hydrazinium ion I (comprising the nitrogen atoms N(1)—N(3)) makes an angle of about 20° with the $(10\bar{2})$ plane, while hydrazinium ion II (comprising the nitrogens N(2)—N(4)) makes approximately a right angle with this plane. The environment of hydrazinium ion I is complicated; the number of neighbours within 3.15 Å is ten, while hydrazinium ion II has six such neighbours. The hydrazinium ions are hydrogen-bonded to the sulphate ions and also weakly to each other to form a three-dimensional network.

Table 3. Interatomic distances and angles with their standard deviations within the sulphate ion in $(N_2H_5)_2SO_4$ (*cf.* Figs. 2 and 3).

Bond	Distance	Bond	Distance
S —O(1)	1.469 ± 0.005 Å	O(1) —O(2)	2.390 ± 0.006 Å
—O(2)	1.473 ± 0.004	—O(3)	2.409
—O(3)	1.473 ± 0.004	—O(4)	2.411
—O(4)	1.463 ± 0.004	O(2) —O(3)	2.401
		—O(4)	2.395
		O(3) —O(4)	2.388

Bonds	Angle
O(1) — S — O(2)	108.7 ± 0.3°
— O(3)	110.0 ± 0.2
— O(4)	110.7 ± 0.2
O(2) — S — O(3)	109.2 ± 0.3
— O(4)	109.4 ± 0.2
O(3) — S — O(4)	108.9 ± 0.3

THE SULPHATE ION

The sulphate ion forms an approximately regular tetrahedron (Table 3 and Figs. 2 and 3); the average value of the S—O bond distances is 1.469 Å with a deviation of 0.004 Å. The O—S—O bond angles show only small deviations from 109.5°, the value of the tetrahedral angle. The mean S—O bond length of 1.469 Å is in good agreement with the value of 1.473 Å found in $MgSO_4 \cdot 4H_2O$ (Baur [14]) and $MgSO_4 \cdot 6H_2O$ (Zalkin *et al.*[15]). When a correction was made for thermal motion assuming the oxygen atoms to ride on the sulphur atom, the average S—O bond length became 1.485 Å with a deviation of 0.007 Å. (This calculation was performed using the programme OR FFE[13].) The mean S—O bond length in $MgSO_4 \cdot 6H_2O$,[15] calculated in the same way, was 1.486 Å.

The environment of the four independent oxygen atoms is shown in Fig. 2. The number of closest nitrogen neighbours is three for O(1), O(2) and O(4),

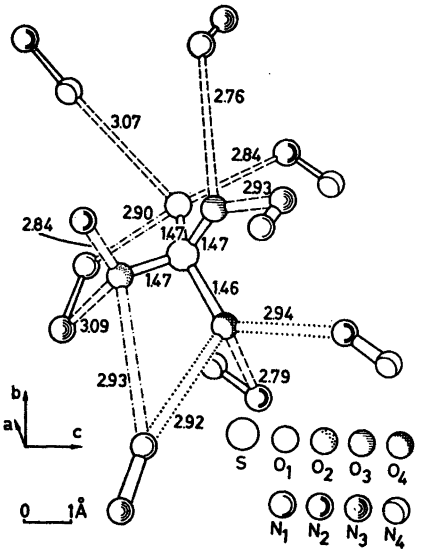

Fig. 2. Bond distances within the sulphate ion and to the nitrogen neighbours of the oxygen atoms. Dashed lines (- - -) indicate normal, or bent, hydrogen bonds, dashed and dotted lines (-·-·) bifurcated hydrogen bonds and dotted lines (· · ·) other types of contact.

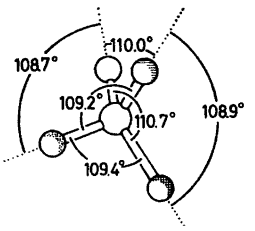

Fig. 3. Bond angles within the sulphate ion.

while O(3) has only two such neighbours. All S—O—N angles are in the range of 99° to 123° except one, namely S—O(3)—N(3), which is 151°. The values of the N—O—N angles lie in the range 86° to 108°, except for two which are 122° and 142°, respectively. The shortest oxygen-oxygen distance between different sulphate groups is 3.24 Å, namely between O(1) and O(4).

THE HYDRAZINIUM IONS

The N—N distances of 1.440 and 1.427 Å, respectively, in the two independent hydrazinium ions are in agreement with earlier values for this type of ion. The values, reported previously, are in the range of 1.43 to 1.46 Å. The N—N bond length found by Van den Hende and Boutin [16] in lithium hydrazinium sulphate was 1.447 Å; Brown [17] found this bond length in the same compound to be 1.46 Å. These two papers should be referred to for further references concerning structure determinations of other hydrazine compounds.

The following assumptions were made concerning the location of the hydrogen atoms: (*a*) The angles N—N—H and H—N—H are about 109°; (*b*) the N—H distances are about 1.03 Å. (Pratt and Richards [2] used these values for

their model of the $N_2H_5^+$ ion in a proton magnetic resonance study of $(N_2H_5)_2SO_4$, and concluded that they are probably close to the true values); (*c*) a nitrogen atom which belongs to the NH_3^+ end of an $N_2H_5^+$ ion may take part in three hydrogen bonds as the donor of hydrogen atoms, while a nitrogen atom belonging to the NH_2 group only can donate two hydrogen atoms but can accept one (or possibly more) to its lone pair of electrons; (*d*) the hydrogen bonds from the NH_3^+ end can be expected to be shorter than those from the NH_2 end. When these facts were taken into account it was possible to conclude that N(1) and N(2) must be part of the NH_3^+ groups of the hydrazinium ions. Details of the coordination of the hydrazinium ions and the hydrogen bonding system are described below.

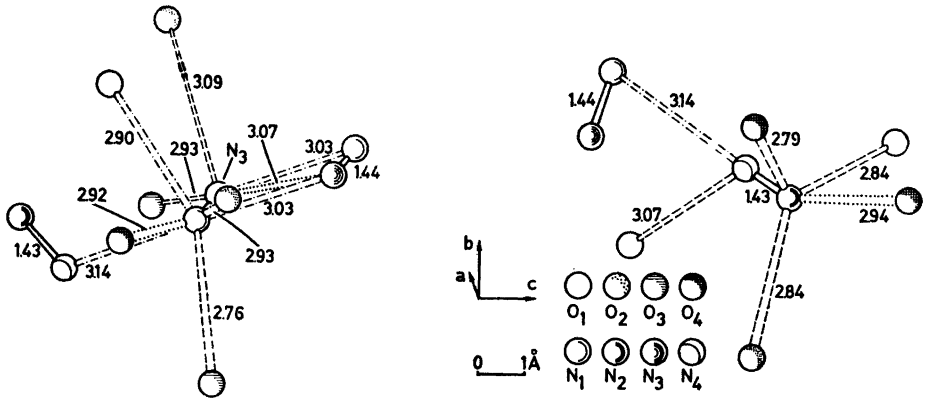

Fig. 4. Bond distances to the neighbours of hydrazinium ion I (left) and II. The notation of the bonds is the same as in Fig. 2.

Hydrazinium ion I. The distances and angles to the neighbours of this ion (composed of N(1)—N(3)) are listed in Table 4 and shown in Figs. 4 and 5. Thus, N(1) has four oxygen and two nitrogen neighbours within distances of 2.76 to 3.14 Å. One of these distances, N(1)—O(3), is significantly shorter than all others; (2.76 Å as compared with 2.90 Å or longer). The angle N(3)—N(1)—O(3) is 108°, which approaches the tetrahedral angle. It was assumed that this distance represented a normal hydrogen bond, N(1)—H····O(3). In the difference Fourier maps a resolved peak appeared on this connecting line. The hydrogen atom (numbered H(1) in Table 1) was placed on the line connecting N(1) to O(3), at a distance of 1.03 Å from N(1). When this position was fixed, it was possible to calculate the positions of the other two hydrogen atoms belonging to this NH_3^+ group following the assumptions given above. (The hydrogen positions were calculated using a program designated KOORDINAT, written by Lindgren and Lundgren, Uppsala for an IBM 1620 computer. This program calculates the position of any atom which is related to three other atoms in a specified way). It was found that the hydrogen atom H(2) is oriented in a direction between O(2) and N(3), the N(1)—O(2) and

Table 4. Bond distances and angles with their standard deviations within and around hydrazinium ion I in $(N_2H_5)_2SO_4$ (*cf.* Figs. 4 and 5).

Around N(1):		Around (N(3):	
Bond	Distance	Bond	Distance
N(1) — N(3)	1.440 ± 0.006 Å		
N(1) — H(1) ... O(3)	2.761 ± 0.006 Å	N(3) — H(4) ... O(2)	3.093 ± 0.007 Å
N(1) — H(3) ... O(1)	2.896 ± 0.006	N(3) — H(5) ... O(3)	2.935 ± 0.006
N(1) — H(3) ... N(4)	3.143 ± 0.007	N(3) ... H(2) — N(1)′	3.033 ± 0.006
N(1) — H(2) ... O(2)	2.925 ± 0.006	N(3) — O(2)′	3.187 ± 0.007
N(1) — H(2) ... N(3)′	3.033 ± 0.006	N(3) — N(3)′	3.074 ± 0.009
N(1) — O(4)	2.919 ± 0.006		
N(1) — other atoms >	3.45 Å	N(3) — other atoms >	3.35 Å

Bonds	Angle	Bonds	Angle
N(3) — N(1) — O(3)	108.1 ± 0.3°	N(1) — N(3) — O(2)	98.4 ± 0.3°
— O(1)	97.7 ± 0.3	— O(3)	128.6 ± 0.3
— N(4)	90.7 ± 0.3	— N(1)′	102.1 ± 0.3
— O(2)	140.0 ± 0.3	— O(2)′	154.4 ± 0.3
— N(3)′	77.9 ± 0.3	— N(3)′	74.8 ± 0.3
— O(4)	163.5 ± 0.3	O(3) — N(3) — O(2)	86.1 ± 0.2
O(3) — N(1) — O(1)	144.7 ± 0.2	— N(1)′	129.1 ± 0.2
— N(4)	80.2 ± 0.3	O(2) — N(3) — N(1)′	91.9 ± 0.3
— O(2)	92.7 ± 0.3		
— N(3)′	100.4 ± 0.3		
— O(4)	82.7 ± 0.2		
N(4) — N(1) — O(1)	75.7 ± 0.3		
— O(2)	127.1 ± 0.3		
— N(3)′	168.2 ± 0.3		
O(1) — N(1) — O(2)	81.9 ± 0.3		
— N(3)′	108.5 ± 0.3		
(O2) — N(1) — N(3)′	64.7 ± 0.3		

N(1)—N(3) distances being 2.93 and 3.03 Å, respectively. (The N(1)—N(3) distance of 3.03 Å is between ions related to each other by a centre of symmetry.) If these two distances correspond to any appreciable interaction with

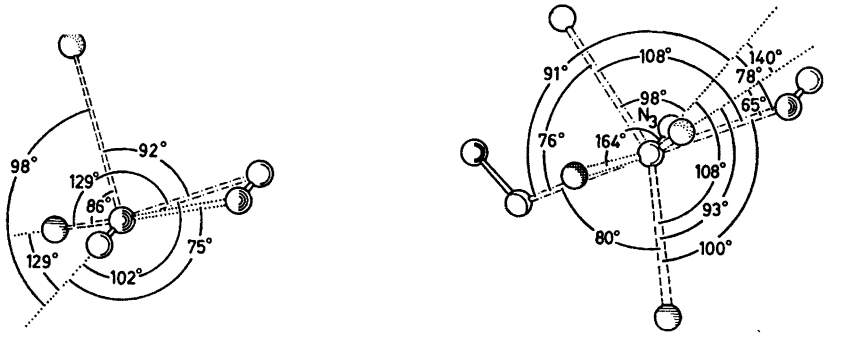

Fig. 5. Bond angles to the neighbours of hydrazinium ion I. The orientation and notation of the atoms and the bonds are the same as in Fig. 4.

H(2) they might be considered as representing a bifurcated hydrogen bond. The hydrogen atom H(3) may in the same way be thought to form a bifurcated hydrogen bond to O(1) and N(4); the N(1)—O(1) and N(1)—N(4) distances are 2.90 and 3.14 Å, respectively (Fig. 8).

In addition to the neighbours of N(1) mentioned above there is a further close oxygen neighbour, O(4); the N(1)—O(4) distance is 2.92 Å, and the angle N(3)—N(1)—O(4) is 164°. This oxygen atom lies close to the extension of the N—N axis and is thought to fit into a triangle of hydrogen atoms, which may together exert a weak attraction for this oxygen atom. A contact of this type also exists in the hydrazinium ion II (see below). Similar conditions have been found in other compounds, *e.g.* $LiN_2H_5SO_4$ (Brown[17]) with an N—O distance of 2.96 Å and an N—N—O angle of 165°. Another example is that of $N_2H_6SO_4$ (Nitta *et al.*[1]) where the same types of distance and angle were found with values of 2.82 Å and 165°, respectively.

The nitrogen atom N(3) which belongs to the hydrazinium ion I (the NH_2 end of this ion), has two oxygen and two nitrogen neighbours at distances within 2.93 to 3.09 Å. One of these, N(3)—N(1), (distance 3.03 Å) is assumed to represent part of a bifurcated hydrogen bond with N(1) as the donor of hydrogen atoms as described above. The other short nitrogen-nitrogen distance namely between N(3)-atoms related to each other by a centre of symmetry is 3.07 Å, implying that hydrogen bonding between these atoms is not possible. The N(3)—O(3) distance of 2.93 Å is short enough to represent a hydrogen bond, but this must be considerably bent as the angle N(1)—N(3)—O(3) is 129°, while the N(3)—O(2) distance of 3.09 is longer than expected for an hydrogen bond of this type. The hydrogen atom H(4) was placed near the line connecting N(3)—O(2) and the position of H(5) was calculated as described earlier, (Fig. 8). According to this distribution of the hydrogen atoms, the lone pair on N(3) is available near the line connecting N(3) to N(1), which seems to be reasonable. The angle *lone pair*-N—H is assumed to be about 109°. Some support for this arrangement was found in the difference Fourier maps, as peaks appeared at these two assumed hydrogen positions. However, the location of H(4) and H(5) is uncertain.

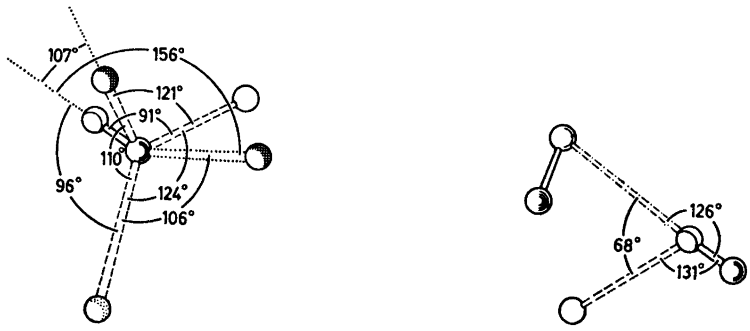

Fig. 6. Bond angles to the neighbours of hydrazinium ion II. The orientation and notation of the atoms and the bonds are the same as in Fig. 4.

Weak hydrogen bonds of the type $H_2N^+—H\cdots NH_2$ seem to exist between the hydrazinium ions with distances of 3.03 and 3.14 Å, respectively. The shorter of these is between ions related to each other by a centre of symmetry (See Figs. 1 and 7). As mentioned earlier, both of these bonds were considered to be part of bifurcated hydrogen bonds. By this arrangement the hydrazinium ions are bonded weakly to each other into groups with four ions in each (Fig. 7). The distances given above may be compared with those of 2.93 Å found in N_2H_5Br and 2.95 Å in N_2H_5Cl (Sakurai and Tomiie [18]) for the same type

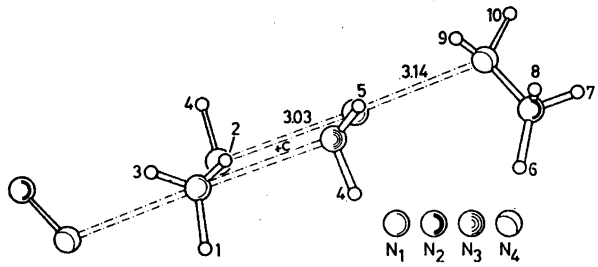

Fig. 7. One group of four hydrazinium ions, weakly bonded to each other. Small circles indicate hydrogen atoms. *C* denotes a centre of symmetry. The orientation of hydrazinium ion I is the same as in Fig. 4, but not that of ion II.

of hydrogen bond, *i.e.* between the same functional groups. Greater bond lengths are to be expected in the present case, since the hydrogen atoms involved in these bonds are shared by two acceptor atoms. In $LiN_2H_5SO_4$ [16,17] hydrogen bonds exist between $N_2H_5^+$ ions (distance 3.01 Å) but in this case they are between two NH_2 groups.

Hydrazinium ion II. The distances and angles to the neighbours of this ion, consisting of N(2)—N(4), are listed in Table 5 and shown in Figs. 4 and 6. Thus, N(2) has three nearest oxygen neighbours, O(1), O(2), and O(4), the N—O

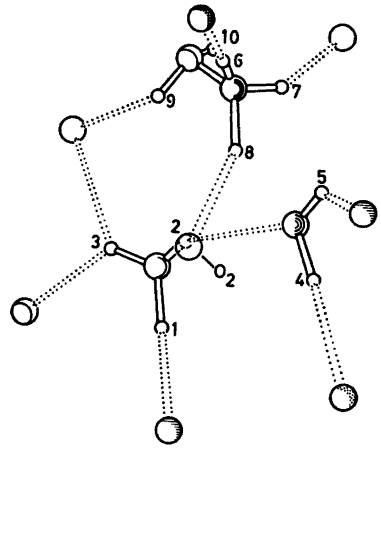

Fig. 8. The location of the hydrogen atoms is shown in this figure. Small circles indicate hydrogen atoms (numbered as in Table 1). The orientation and notation of the oxygen and nitrogen atoms are the same as in Fig. 4.

distances being 2.84, 2.84, and 2.79 Å, respectively. It was concluded that these distances represent hydrogen bonds. The assumption was made that the shortest of these bonds, N(2)—O(4), represents a normal hydrogen bond and this was supported by the observations that the angle N(4)—N(2)—O(4) is 107°, and that a well resolved peak appeared in the difference Fourier maps on the line joining N(2) to O(4). The hydrogen atom H(6) was then placed on this line and the positions of the other two hydrogen atoms belonging

Table 5. Bond distances and angles with standard deviations within and around hydrazinium ion II in $(N_2H_5)_2SO_4$ (*cf.* Figs. 4 and 6).

Around N(2):		Around N(4):	
Bond	Distance	Bond	Distance
N(2) — N(4)	1.427 ± 0.007 Å		
N(2) — H(7) ... O(1)	2.837 ± 0.006 Å	N(4) — H(9) ... O(1)	3.073 ± 0.007 Å
N(2) — H(8) ... O(2)	2.842 ± 0.006	N(4) ... H(3) — N(1)	3.143 ± 0.007
N(2) — H(6) ... O(4)	2.786 ± 0.006	N(4) — O(1)′	3.202 ± 0.007
N(2) — O(4)′	2.939 ± 0.006		
N(2) — other atoms	> 3.30 Å	N(4) — other atoms	> 3.30 Å
Bonds	Angle	Bonds	Angle
N(4) — N(2) — O(1)	91.2 ± 0.3°	N(2) — N(4) — O(1)	131.5 ± 0.4°
— O(2)	96.0 ± 0.3	— N(1)	125.6 ± 0.3
— O(4)	107.5 ± 0.3	— O(1)′	62.4 ± 0.4
— O(4)′	155.8 ± 0.4	O(1) — N(4) — N(1)	68.4 ± 0.2
O(4) — N(2) — O(1)	120.5 ± 0.2		
— O(2)	109.9 ± 0.2		
— O(4)′	75.0 ± 0.2		
O(1) — N(2) — O(2)	124.0 ± 0.2		
— O(4)′	68.1 ± 0.2		
O(2) — N(2) — O(4)′	105.9 ± 0.2		

to N(2) were calculated as earlier. Well resolved peaks also appeared in the difference Fourier maps at the positions where H(7) and H(8) were placed. These two hydrogen atoms are obviously situated off the lines connecting nitrogen with oxygen (Fig. 8). There is one further close oxygen neighbour of N(2), namely another O(4), at a distance of 2.94 Å; the angle N(4) — N(2) —O(4) is 156°. This oxygen atom is assumed to fit into a triangle of hydrogen atoms in the same way as is described for hydrazinium ion I.

The nitrogen atom N(4) of hydrazinium ion II (the NH_2 end of this ion) has only two neighbours within 3.15 Å, namely one oxygen and one nitrogen atom. The N(4) — N(1) distance of 3.14 Å was assumed to represent part of a bifurcated hydrogen bond with N(1) as the donor of hydrogen atoms, as mentioned earlier. The oxygen neighbour O(1) lies within 3.07 Å, which may correspond to a weak hydrogen bond. The angle N(2) — N(4) — O(1) is 131°. An attempt was made to assign hydrogen atoms to this nitrogen atom also, although the location of these is rather uncertain. In the difference Fourier maps a well resolved peak appeared at a probable hydrogen position, assuming the existence of a bent hydrogen bond between N(4) and O(1). The position of this hydrogen atom (H(9)) was taken from the difference

Table 6. Observed and calculated structure factors. Reflexions which were too weak to be measured are indicated with one asterisk. The $|F_o|$ values for these are given as $\frac{1}{2} F_{min}$. Two asterisks indicate reflexions which were excluded from the final refinements.

h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$
0	0	12	10.7	9.3	0	9	5	20.3	21.5	1	3	5	21.9	22.7	1	7	-9	11.4	10.8	2	0	2	23.9	23.0
0	0	10	7.9	8.0	0	9	4	17.7	18.3	1	3	4	3.6	4.0	1	7	-10	15.0	13.6	2	0	0	63.6	59.7
0	0	8	20.6	21.2	0	9	3	23.7	24.5	1	3	3	26.0	24.2	1	7	-11	10.0	10.0	2	0	-2	51.5	55.9
0	0	6	29.2	27.4	* 0	9	2	2.1	1.5	1	3	2	7.2	4.4	1	7	-12	3.6	3.6	2	0	-4	44.0	46.1
0	0	4	43.1	51.8	0	9	1	17.2	16.5	1	3	1	8.7	8.5	* 1	8	10	1.4	0.1	2	0	-6	10.5	9.5
**0	0	-2	52.7	74.9	* 0	10	9	1.3	0.3	1	3	0	8.1	5.9	1	8	9	15.4	13.7	2	0	-8	32.2	38.1
0	1	13	7.6	7.0	0	10	8	8.6	8.5	** 1	3	-1	78.2	102.8	* 1	8	8	1.9	1.4	2	0	-10	15.0	15.5
* 0	1	12	1.8	0.5	0	10	7	10.7	9.5	1	3	-2	43.2	46.0	1	8	7	19.1	19.2	2	0	-12	11.3	10.4
0	1	11	10.2	10.3	0	10	6	3.8	5.5	1	3	-3	55.2	61.1	1	8	6	4.2	3.7	2	1	12	9.1	8.6
0	1	10	5.1	4.4	0	10	5	5.7	6.1	1	3	-4	13.5	12.8	1	8	5	21.7	24.3	2	1	11	4.0	4.4
0	1	9	12.4	13.6	* 0	10	4	2.1	2.0	1	3	-5	3.3	3.5	* 1	8	4	2.1	1.5	2	1	10	10.8	9.1
0	1	8	22.1	21.6	0	10	3	14.5	14.0	1	3	-6	10.8	9.9	1	8	3	10.0	9.0	2	1	9	10.1	9.4
0	1	7	20.1	20.8	0	10	2	19.1	18.3	1	3	-7	40.2	43.3	1	8	2	5.7	6.7	2	1	8	8.3	8.2
0	1	6	30.1	32.8	0	10	1	17.9	18.3	1	3	-8	4.0	2.5	1	8	1	32.4	35.3	2	1	7	9.4	8.8
0	1	5	22.7	25.6	0	10	0	40.0	43.8	1	3	-9	23.2	25.9	1	8	0	3.9	3.3	2	1	6	18.9	19.4
**0	1	4	59.5	76.2	0	11	8	17.7	17.4	1	3	-10	7.9	8.6	1	8	-1	27.7	27.2	2	1	5	18.2	19.2
* 0	1	3	1.0	1.2	0	11	7	5.1	4.9	1	3	-11	18.6	18.9	* 1	8	-2	2.0	1.5	2	1	4	10.3	9.4
0	1	2	27.9	29.6	0	11	6	15.0	13.0	1	3	-12	6.1	5.4	1	8	-3	23.3	22.5	2	1	3	31.3	32.0
0	1	1	9.7	8.4	* 0	11	5	1.8	0.3	1	3	-13	10.0	9.3	1	8	-4	10.1	10.0	2	1	2	25.1	24.8
0	2	13	17.1	14.8	0	11	4	16.0	15.6	1	4	12	4.7	4.2	1	8	-5	10.3	10.2	2	1	1	28.5	29.5
0	2	12	10.4	9.3	0	11	3	8.9	8.3	1	4	11	13.4	12.0	1	8	-6	4.2	3.7	2	1	0	47.3	46.7
0	2	11	11.6	10.6	0	11	2	9.1	8.8	1	4	10	4.9	4.8	1	8	-7	9.4	8.4	2	1	-1	23.0	21.9
0	2	10	8.9	9.0	* 0	11	1	2.1	2.8	1	4	9	11.2	11.7	* 1	8	-8	2.0	0.0	2	1	-2	20.3	19.0
0	2	9	6.5	6.4	* 0	12	7	1.0	1.9	1	4	8	9.5	8.8	1	8	-9	14.2	12.2	2	1	-3	5.2	5.9
0	2	8	12.1	11.0	0	12	6	8.0	7.1	* 1	4	7	2.0	0.6	1	8	-10	4.6	4.6	* 2	1	-3	1.1	0.4
0	2	7	16.8	16.7	0	12	5	5.3	6.0	1	4	6	24.8	26.5	* 1	8	-11	1.3	0.5	2	1	-4	6.5	4.2
0	2	6	3.3	1.9	0	12	4	8.1	7.2	1	4	5	7.4	7.2	* 1	9	10	1.0	1.4	* 2	1	-5	1.4	0.4
0	2	5	23.5	23.5	0	12	3	11.6	10.3	* 1	4	4	1.6	1.2	* 1	9	9	1.4	2.4	2	1	-6	14.4	12.6
0	2	4	21.9	22.7	0	12	2	7.7	8.2	1	4	3	12.2	10.2	* 1	9	8	9.3	8.6	2	1	-7	5.4	5.4
**0	2	3	61.3	75.8	0	12	1	16.5	14.1	1	4	2	8.6	7.2	* 1	9	7	1.9	2.6	2	1	-8	9.3	8.4
**0	2	2	19.7	19.5	0	12	0	17.1	15.6	1	4	1	2.6	1.3	1	9	6	4.1	4.7	2	1	-9	4.1	2.8
**0	2	1	47.9	61.3	0	13	5	13.7	14.2	1	4	0	7.2	7.5	1	9	5	17.6	18.7	2	1	-10	5.9	5.6
0	2	0	26.5	28.8	0	13	4	3.5	3.8	1	4	-1	26.5	23.6	1	9	4	5.2	7.3	* 2	1	-11	2.0	1.0
0	3	13	8.6	7.4	0	13	3	7.1	7.4	1	4	-2	19.4	20.9	1	9	3	20.7	21.1	2	1	-12	12.3	11.0
* 0	3	12	1.7	0.9	* 0	13	2	1.5	1.4	1	4	-3	32.9	32.9	1	9	2	5.2	5.3	2	1	-13	8.6	7.5
* 0	3	11	2.0	3.4	0	13	1	5.3	5.1	1	4	-4	10.6	9.7	1	9	1	25.5	28.6	* 2	2	12	1.1	1.2
* 0	3	10	2.1	1.2	* 0	14	2	0.9	1.9	1	4	-5	43.6	50.2	1	9	0	13.2	12.6	2	2	11	5.9	6.1
0	3	9	20.2	19.9	0	14	1	8.5	9.3	1	4	-6	23.7	22.9	1	9	-1	15.0	14.1	2	2	10	8.8	7.5
0	3	8	9.0	9.5	0	14	0	9.4	9.9	1	4	-7	18.8	20.1	1	9	-2	19.5	20.6	2	2	9	6.5	6.5
0	3	7	40.4	46.2						1	4	-8	14.8	13.7	1	9	-3	10.3	10.6	* 2	2	8	2.1	1.6
0	3	6	5.9	5.3	1	0	12	13.8	12.4	1	4	-9	4.2	4.2	1	9	-4	4.2	3.6	2	2	7	25.8	29.3
0	3	5	28.5	29.4	* 1	0	10	2.1	0.1	1	4	-10	10.2	9.9	1	9	-5	5.2	5.7	2	2	6	11.6	11.4
* 0	3	4	1.4	0.1	1	0	9	2.9	1.4	1	4	-11	7.8	7.7	1	9	-6	9.4	8.4	2	2	5	28.1	29.4
0	3	3	18.3	18.9	1	0	8	51.2	61.7	1	4	-12	4.7	3.6	1	9	-7	7.5	8.6	2	2	4	27.8	27.8
0	3	2	30.5	31.0	1	0	6	33.4	36.9	1	4	-13	4.9	5.5	1	9	-8	13.7	12.7	2	2	3	15.5	14.9
0	3	1	42.9	50.8	1	0	4	3.2	2.2	1	5	12	8.2	7.7	1	9	-9	10.1	9.1	2	2	2	2.9	1.1
0	4	13	4.6	4.8	** 1	0	-2	78.7	92.7	* 1	5	11	1.6	0.1	1	9	-10	10.1	9.9	2	2	1	33.2	27.6
0	4	12	15.8	12.9	1	0	-4	39.6	46.0	1	5	10	9.9	8.5	1	10	9	4.9	6.3	2	2	0	19.3	14.4
0	4	11	9.2	8.0	1	0	-6	13.2	11.9	* 1	5	9	2.1	1.2	1	10	8	2.8	3.6	2	2	-1	29.3	21.4
0	4	10	11.6	10.4	1	0	-8	4.7	3.7	1	5	8	19.7	22.6	* 1	10	7	1.7	1.9	2	2	-2	20.1	18.2
0	4	9	17.3	18.4	1	0	-10	16.9	17.9	* 1	5	7	2.1	2.3	1	10	6	18.0	16.9	2	2	-4	17.6	17.8
0	4	8	9.2	9.7	1	0	-12	5.3	5.1	1	5	6	23.0	22.5	1	10	5	3.9	4.8	2	2	-6	16.4	15.6
0	4	7	4.7	5.1	1	0	-14	16.7	18.6	1	5	5	14.6	14.5	1	10	4	7.1	8.0	2	2	-6	12.6	10.3
0	4	6	7.1	7.0	* 1	1	13	1.1	1.6	1	5	4	7.3	7.3	1	10	3	10.7	11.5	2	2	-7	4.7	2.4
0	4	5	9.0	8.4	* 1	1	12	5.6	4.9	* 1	5	3	1.6	1.6	* 1	10	2	2.1	0.1	2	2	-8	5.5	5.8
0	4	4	15.3	13.4	1	1	11	3.8	3.6	1	5	2	17.6	17.8	1	10	1	6.7	6.6	2	2	-9	22.0	22.8
0	4	3	33.5	36.6	* 1	1	10	2.1	0.0	1	5	1	13.9	12.7	1	10	0	13.4	13.5	2	2	-10	4.1	3.7
0	4	2	14.5	13.8	1	1	9	4.2	3.1	1	5	0	18.8	17.7	1	10	-1	18.0	20.4	2	2	-11	19.2	19.2
0	4	1	31.4	32.1	1	1	8	10.4	10.0	1	5	-1	13.9	12.7	1	10	-2	20.7	21.1	2	2	-12	8.5	7.0
0	4	0	47.1	55.8	1	1	7	4.6	4.0	1	5	-2	42.5	44.1	1	10	-3	7.9	9.0	2	2	-13	2.7	2.6
* 0	5	13	0.8	1.3	1	1	6	4.2	4.4	1	5	-3	19.7	17.9	1	10	-4	11.1	11.0	* 2	3	12	1.0	0.8
0	5	12	3.5	3.1	1	1	5	18.4	17.4	1	5	-4	29.3	27.4	1	10	-5	5.8	5.9	2	3	11	19.0	18.6
* 0	5	11	1.8	0.3	1	1	4	15.2	17.0	1	5	-5	4.3	3.9	1	10	-6	13.5	13.8	* 2	3	10	1.8	1.7
0	5	10	14.4	13.2	1	1	3	8.0	8.3	1	5	-6	10.7	8.4	1	10	-7	8.9	8.0	* 2	3	9	2.0	2.7
0	5	9	10.3	11.8	** 1	1	2	60.0	79.4	1	5	-7	4.0	2.9	1	10	-8	7.9	8.5	* 2	3	8	2.1	1.4
0	5	8	32.9	35.9	1	1	1	41.8	46.4	1	5	-8	31.1	33.2	* 1	10	-9	1.3	0.5	2	3	7	13.6	13.2
0	5	7	14.5	15.0	1	1	0	24.7	26.8	* 1	5	-9	2.1	2.0	1	10	8	3.2	3.7	2	3	6	12.3	11.4
0	5	6	38.2	42.1	1	1	-1	15.1	15.1	1	5	-10	28.9	27.9	* 1	11	7	1.3	0.1	2	3	5	12.9	11.5
0	5	5	5.0	5.8	1	1	-2	35.5	38.1	1	5	-11	9.4	8.0	1	11	6	5.9	5.0	2	3	4	8.0	6.8
0	5	4	26.9	27.8	1	1	-3	27.6	28.6	1	5	-12	4.4	4.6	* 1	11	5	1.8	0.6	2	3	3	14.8	14.1
0	5	3	10.5	8.8	* 1	1	-4	1.2	0.6	1	5	-13	4.9	4.2	1	11	4	16.8	16.2	2	3	2	11.1	8.3
0	5	2	44.7	45.9	1	1	-5	18.0	18.6	* 1	6	11	1.5	0.9	* 1	11	3	2.0	3.8	2	3	1	8.0	4.2
0	5	1	4.8	4.7	1	1	-6	20.9	21.4	1	6	10	13.1	11.2	1	11	2	23.1	23.1	2	3	0	9.1	7.3
0	6	12	14.1	14.4	* 1	1	-7	1.7	0.5	* 1	6	9	2.0	2.9	* 1	11	1	2.1	1.7	2	3	-1	26.7	27.1
* 0	6	11	1.6	0.4	1	1	-8	19.7	20.7	1	6	8	18.2	17.4	* 1	11	0	7.7	7.4	2	3	-2	14.5	12.9
0	6	10	11.4	10.7	1	1	-9	14.3	13.9	1	6	7	4.2	4.0	* 1	11	-1	2.1	0.9	2	3	-3	22.8	23.4
0	6	9	9.2	9.4	1	1	-10	20.7	22.6	1	6	6	15.9	15.7	* 1	11	-2	10.3	9.4	2	3	-4	8.0	5.4
0	6	8	12.3	13.2	1	1	-11	14.9	14.2	1	6	5	8.8	9.3	* 1	11	-3	2.0	2.7	2	3	-5	29.3	29.7
0	6	7	8.3	9.2	1	1	-12	7.4	7.3	1	6	4	8.4	8.7	* 1	11	-4	2.0	0.3	2	3	-6	19.2	19.4
0	6	6	2.0	0.9	1	1	-13	11.0	9.9	1	6	3	7.9	7.5	1	11	-5	6.4	6.1	* 2	3	-7	1.9	1.0
0	6	5	11.9	13.5	1	1	-14	4.9	6.1	1	6	2	11.2	10.9	1	11	-6	6.4	6.3	2	3	-8	4.0	4.0
0	6	4	21.2	21.4	1	2	13	5.6	6.1	1	6	1	5.7	4.9	* 1	11	-7	1.5	2.4	2	3	-9	20.2	21.5
0	6	3	10.1	9.0	* 1	2	12	1.6	2.5	1	6	0	5.1	4.2	1	11	-8	7.1	7.0	2	3	-10	10.1	9.7
0	6	2	28.6	28.8	* 1	2	11	1.9	1.7	* 1	6	-1	1.6	1.7	1	12	6	8.7	10.1	2	3	-11	4.7	5.2
0	6	1	36.1	39.0	1	2	10	4.1	3.8	1	6	-2	30.0	29.4	1	12	5	2.8	2.9	2	3	-12	4.7	4.3
0	6	0	46.1	50.6	1	2	9	16.7	16.9	1	6	-3	25.2	25.9	* 1	12	4	1.6	0.3	2	3	-13	9.9	9.5
0	7	12	3.7	3.7	1	2	8	18.8	19.7	1	6	-4	28.2	27.1	1	12	3	7.1	7.0	* 2	4	11	1.4	1.9
* 0	7	11	1.4	1.8	1	2	7	12.2	12.1	1	6	-5	17.8	15.8	1	12	2	5.6	4.9	2	4	10	11.0	10.1
* 0	7	10	1.8	3.4	1	2	6	20.9	21.6	1	6	-6	31.4	33.1	1	12	1	5.7	4.8	2	4	9	17.0	17.3
0	7	9	11.4	11.1	1	2	5	28.8	29.0	* 1	6	-7	2.1	1.8	1	12	0	5.2	5.2	2	4	8	47.3	46.7
0	7	8	5.9	6.8	1	2	4	6.3	5.0	* 1	6	-8	11.6	10.9	1	12	-1	7.8	6.7	2	4	7	26.8	32.2
0	7	7	27.8	33.3	1	2	3	44.1	49.6	* 1	6	-9	2.1	0.2	1	12	-2	12.5	10.5	2	4	6	11.6	12.3
0	7	6	15.3	16.2	1	2	2	10.4	9.4	* 1	6	-10	2.0	0.4	1	12	-3	11.0	9.5	2	4	5	8.4	7.9
0	7	5	21.9	22.1	** 1	2	1	53.4	64.8	1	6	-11	3.4	1.6	1	12	-4	12.9	11.3	2	4	4	16.8	16.2
0	7	4	25.5	26.8	1	2	0	30.1	30.5	1	6	-12	4.6	5.1	1	12	-5	6.5	6.7	2	4	3	14.8	12.8
0	7	3	9.7	9.4	** 1	2	-1	49.2	58.0	1	7	11	2.9	3.0	1	12	-6	10.4	9.2	2	4	2	3.6	2.9
0	7	2	10.1	9.6	1	2	-2	33.5	37.0	1	7	10	3.2	3.0	1	12	-7	6.6	7.4	2	4	1	19.0	17.1
0	7	1	17.8	17.9	1	2	-3	10.8	12.1	1	7	9	3.7	4.2	* 1	13	4	1.1	1.1	2	4	0	1.9	2.2
0	8	11	10.0	10.6	* 1	2	-4	1.3	1.1	1	7	8	19.1	19.4	* 1	13	3	1.3	2.5	2	4	-1	12.3	9.0
0	8	10	4.3	4.7	1	2	-5	3.9	3.8	* 1	7	7	2.1	2.1	* 1	13	2	1.4	2.6	2	4	-2	13.1	11.4
0	8	9	14.2	13.6	1	2	-6	5.5	5.0	* 1	7	6	2.1	1.1	1	13	1	13.3	12.8	2	4	-3	3.5	3.0
* 0	8	8	2.0	3.2	1	2	-7	29.3	31.9	1	7	5	20.7	22.7	1	13	0	4.2	5.2	* 2	4	-4	1.5	0.3
0	8	7	7.2	6.9	1	2	-8	5.0	4.0	* 1	7	4	2.0	1.8	1	13	-1	16.7	14.7	2	4	-5	15.0	13.6
0	8	6	6.6	7.2	1	2	-9	21.3	23.7	1	7	3	10.2	8.5	* 1	13	-2	1.5	1.9	2	4	-6	13.8	11.1
0	8	5	5.1	3.9	1	2	-10	4.2	3.5	1	7	2	20.7	20.5	1	13	-3	5.8	5.1	2	4	-7	16.9	16.5
0	8	4	7.9	7.4	1	2	-11	5.8	5.7	1	7	1	8.9	8.2	1	13	-4	3.5	3.0	2	4	-8	18.7	19.1
0	8	3	26.9	28.2	* 1	2	-12	1.8	1.0	1	7	0	16.8	16.0	1	13	-5	2.0	1.6	2	4	-9	20.3	20.4
* 0	8	2	1.9	0.8	1	2	-13	6.8	5.5	1	7	-1	34.5	34.5	1	14	0	5.5	7.5	2	4	-10	5.7	4.1
0	8	1	39.2	39.2	* 1	3	12	1.5	1.3	1	7	-2	17.7	15.7	1	14	-1	4.6	4.8	2	4	-11	5.9	5.6
0	8	0	12.0	12.2	* 1	3	11	1.8	0.1	1	7	-3	19.9	18.2						2	4	-12	6.7	5.6
* 0	9	10	1.3	1.4	1	3	10	10.4	9.0	1	7	-4	8.7	8.0	2	0	12	2.9	2.3	* 2	4	-13	1.1	1.6
0	9	9	9.5	8.5	1	3	9	11.2	11.5	1	7	-5	12.1	10.2	2	0	10	13.3	12.5	* 2	5	11	1.2	2.6
0	9	8	6.3	6.8	* 1	3	8	2.1	2.3	1	7	-6	8.8	8.0	2	0	8	24.1	24.9	2	5	10	3.2	3.6
0	9	7	14.2	13.8	1	3	7	12.5	10.6	1	7	-7	26.4	26.4	2	0	6	36.8	41.3	* 2	5	9	1.9	0.5
0	9	6	11.3	9.8	1	3	6	12.6	11.9	1	7	-8	18.4	17.0	2	0	4	32.9	37.5	* 2	5	8	2.0	2.0

h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$
2	5	7	2.9	3.6	2	10	-2	11.6	10.8	3	3	-10	3.2	3.3	3	9	-1	20.6	23.0	4	4	6	2.0	2.3
2	5	6	14.8	15.8	2	10	-3	5.7	5.7	3	3	-11	4.6	4.2	3	9	-2	14.2	14.6	4	4	5	2.1	2.2
* 2	5	5	1.9	1.3	* 2	10	-4	2.0	0.8	3	3	-12	3.4	3.4	3	9	-3	15.0	15.0	* 4	4	4	1.4	1.8
* 2	5	4	1.8	0.7	2	10	-5	4.7	5.2	3	3	-13	2.9	4.1	3	9	-4	2.3	2.6	4	4	3	10.2	10.2
2	5	3	6.9	5.5	2	10	-6	4.5	4.2	* 3	4	9	1.3	2.5	3	9	-5	3.2	2.9	4	4	2	9.0	8.8
2	5	2	3.2	2.6	* 2	10	-7	1.7	1.5	3	4	8	13.0	11.3	* 3	9	-6	1.5	0.4	4	4	1	23.0	23.9
2	5	1	9.3	7.0	2	10	-8	17.0	16.4	3	4	7	7.3	5.9	3	9	-7	14.8	13.2	4	4	0	10.2	8.4
2	5	0	23.1	20.8	2	10	-9	6.5	6.9	3	4	6	13.7	12.7	* 3	9	-8	1.2	0.5	4	4	-1	37.3	45.2
2	5	-1	12.6	11.2	2	11	6	4.3	4.5	3	4	5	21.6	21.5	3	9	-9	5.2	4.9	4	4	-2	26.7	28.2
2	5	-2	45.6	49.8	2	11	5	1.5	1.7	3	4	4	18.0	17.9	* 3	9	-10	0.4	2.3	4	4	-3	15.6	14.4
2	5	-3	11.1	8.6	* 2	11	4	1.6	2.3	3	4	3	24.1	24.6	3	10	6	9.8	11.5	4	4	-4	21.6	23.2
2	5	-4	36.1	36.4	2	11	3	3.5	3.8	3	4	2	9.5	8.4	3	10	5	11.9	11.8	4	4	-5	8.7	7.5
2	5	-5	14.3	11.6	2	11	2	13.8	13.8	3	4	1	16.4	15.7	3	10	4	22.6	24.0	4	4	-6	5.9	4.3
2	5	-6	22.8	23.0	2	11	1	3.8	3.7	3	4	0	18.4	15.8	3	10	3	16.0	15.3	4	4	-7	3.0	2.7
* 2	5	-7	2.0	1.1	2	11	0	22.0	23.4	3	4	-1	12.6	12.1	3	10	2	15.7	14.4	4	4	-8	7.3	6.0
2	5	-8	11.7	10.1	2	11	-1	6.0	6.6	3	4	-2	24.5	23.5	3	10	1	10.1	9.2	4	4	-9	12.9	11.8
2	5	-9	8.3	7.9	2	11	-2	13.1	11.9	3	4	-3	19.0	16.6	3	10	0	3.1	3.0	4	4	-10	15.2	15.1
2	5	-10	3.9	4.2	* 2	11	-3	1.9	2.6	3	4	-4	7.6	6.4	3	10	-1	5.4	5.2	4	4	-11	7.2	7.8
* 2	5	-11	1.8	0.8	2	11	-4	6.2	6.0	3	4	-5	21.7	21.4	3	10	-2	3.8	3.1	4	5	8	3.1	4.6
* 2	5	-12	8.6	8.2	* 2	11	-5	1.7	1.1	3	4	6	12.3	12.3	3	10	-3	6.5	5.7	4	5	7	5.7	5.1
* 2	6	11	0.9	0.2	* 2	11	-6	1.6	0.8	3	4	-7	22.9	25.0	3	10	-4	4.2	4.3	4	5	6	16.1	15.4
2	6	10	16.3	17.1	* 2	11	-7	1.4	0.9	3	4	-8	22.0	23.0	* 3	10	-5	1.4	1.9	4	5	5	2.0	1.5
2	6	9	8.6	7.6	* 2	11	-8	1.1	0.7	3	4	-9	2.3	2.0	3	10	-6	2.6	2.2	4	5	4	20.1	21.5
2	6	8	14.1	14.4	2	12	5	6.9	7.4	3	4	-10	15.1	14.5	* 3	10	-7	1.2	0.4	4	5	3	3.0	2.7
2	6	7	17.1	18.4	2	12	4	9.7	10.4	3	4	-11	10.1	9.9	3	10	-8	9.7	11.3	4	5	2	22.2	24.9
2	6	6	17.5	18.8	2	12	3	4.9	4.4	* 3	4	-12	1.1	1.9	3	11	5	1.7	2.6	4	5	1	9.6	8.5
2	6	5	2.9	3.1	2	12	2	8.4	8.4	3	5	9	3.5	3.4	3	11	4	4.8	4.7	4	5	0	10.9	8.8
2	6	4	18.6	18.8	2	12	1	7.5	6.7	3	5	8	13.1	12.9	* 3	11	3	1.1	1.1	4	5	-1	5.5	4.2
2	6	3	5.9	4.8	* 2	12	0	1.6	1.4	* 3	5	7	1.6	0.5	3	11	2	6.8	6.0	4	5	-2	16.6	16.0
2	6	2	15.4	14.2	2	12	-1	2.3	2.6	3	5	6	8.5	6.9	3	11	1	2.6	2.4	4	5	-3	5.6	4.5
2	6	1	11.5	11.0	2	12	-2	6.9	7.3	* 3	5	5	1.6	0.2	3	11	0	14.9	13.8	4	5	-4	18.0	17.8
* 2	6	0	1.6	1.2	2	12	-3	5.4	4.7	3	5	4	10.3	8.7	* 3	11	-1	1.3	0.9	4	5	-5	8.9	7.4
2	6	-1	13.7	13.0	2	12	-4	8.1	7.5	3	5	3	4.4	4.4	3	11	-2	13.2	11.2	4	5	-6	22.9	25.5
2	6	-2	6.8	5.6	2	12	-5	6.9	6.4	3	5	2	18.5	18.8	3	11	-3	7.9	7.1	4	5	-7	7.3	7.4
2	6	-3	8.6	7.1	2	12	-6	9.6	10.4	3	5	1	11.9	10.1	3	11	-4	20.4	20.1	4	5	-8	14.1	13.8
2	6	-4	11.3	9.9	2	13	3	10.5	9.8	3	5	0	28.4	26.7	3	11	-5	3.3	3.6	4	5	-9	5.4	5.1
2	6	-5	2.7	1.8	* 2	13	2	1.0	0.8	* 3	5	-1	1.3	0.4	3	11	-6	13.1	14.1	4	5	-10	11.3	12.1
2	6	-6	25.3	25.0	2	13	1	2.9	3.7	3	5	-2	38.6	43.0	* 3	11	-7	0.8	0.1	* 4	5	-11	0.8	1.9
2	6	-7	4.1	3.1	* 2	13	0	1.2	0.9	3	5	-3	18.6	19.8	3	12	2	8.4	9.8	* 4	6	7	1.0	2.0
2	6	-8	17.7	18.5	2	13	-1	11.2	10.5	3	5	-4	40.1	43.7	3	12	1	9.5	10.0	4	6	6	6.1	5.1
2	6	-9	9.0	7.3	2	13	-2	7.2	7.0	3	5	-5	14.1	14.5	3	12	0	12.5	11.8	* 4	6	5	1.3	2.0
2	6	-10	5.9	5.9	2	13	-3	10.7	11.1	3	5	-6	19.1	19.6	* 3	12	-1	1.0	0.5	4	6	4	2.9	2.3
* 2	6	-11	1.6	2.8	2	13	-4	5.2	5.8	3	5	-7	3.3	3.5	3	12	-2	9.6	9.1	4	6	3	3.0	3.5
2	6	-12	8.9	8.0						3	5	-8	11.1	10.7	* 3	12	-3	1.0	0.4	4	6	2	15.5	15.9
2	7	10	6.9	7.5	3	0	6	29.7	31.0	* 3	5	-9	1.6	0.4	3	12	-4	2.2	2.2	4	6	1	7.9	7.5
* 2	7	9	1.6	2.7	3	0	4	59.9	70.7	3	5	-10	7.6	6.8						4	6	0	14.5	14.9
2	7	8	5.2	4.9	3	0	2	34.2	35.6	3	5	-11	4.1	3.0	4	0	6	3.6	3.0	4	6	-1	17.7	17.5
2	7	7	8.9	7.4	3	0	0	15.6	18.2	3	5	-12	4.1	4.9	4	0	4	12.8	11.7	4	6	-2	30.7	38.1
2	7	6	11.3	11.8	3	0	-2	14.8	17.4	* 3	6	9	1.1	1.8	4	0	2	22.0	20.3	4	6	-3	4.7	3.6
2	7	5	7.2	7.7	3	0	-4	20.9	19.4	3	6	8	14.6	13.7	4	0	0	16.2	15.3	4	6	-4	22.1	24.9
2	7	4	12.9	12.3	3	0	-6	10.1	8.6	3	6	7	7.4	6.9	4	0	-2	29.4	32.9	* 4	6	-5	1.4	0.1
2	7	3	8.0	7.0	3	0	-8	13.9	12.0	3	6	6	20.0	18.9	4	0	-4	23.5	26.2	4	6	-6	7.0	7.0
2	7	2	6.7	5.6	3	0	-10	23.2	23.9	3	6	5	16.2	16.0	4	0	-6	11.9	11.2	4	6	-7	5.0	4.6
2	7	1	14.0	11.7	3	0	-12	14.0	14.3	3	6	4	17.9	17.1	4	0	-8	5.2	4.1	4	6	-8	8.2	6.7
2	7	0	9.1	7.2	3	1	8	17.6	17.0	3	6	3	13.4	13.5	4	0	-10	20.0	20.6	4	6	-9	3.0	2.5
2	7	-1	32.1	33.0	3	1	7	8.2	7.5	3	6	2	21.6	21.4	4	0	-12	8.2	10.3	4	6	-10	7.0	7.5
2	7	-2	11.2	10.0	3	1	6	24.8	28.8	3	6	1	7.2	5.9	4	1	7	11.5	9.6	4	7	7	7.6	10.6
2	7	-3	9.4	7.0	3	1	5	6.5	5.5	3	6	0	27.1	29.6	4	1	6	20.5	21.4	4	7	6	7.8	8.4
2	7	-4	11.1	9.9	3	1	4	10.9	8.9	3	6	-1	11.2	10.5	4	1	5	19.5	21.3	4	7	5	12.3	11.7
* 2	7	-5	2.0	0.3	3	1	3	9.7	7.0	3	6	-2	9.0	7.9	4	1	4	19.5	19.6	4	7	4	12.8	10.9
2	7	-6	6.5	5.5	3	1	2	31.5	28.7	3	6	-3	7.5	7.0	4	1	3	12.3	10.8	4	7	3	19.4	19.0
2	7	-7	4.1	3.3	3	1	1	5.7	4.0	3	6	-4	17.3	17.0	4	1	2	24.2	21.3	4	7	2	19.7	15.7
2	7	-8	5.0	4.3	3	1	0	44.9	51.7	3	6	-5	7.6	6.9	4	1	1	14.9	13.5	4	7	1	7.3	7.1
2	7	-9	13.3	12.3	3	1	-1	28.0	32.1	3	6	-6	8.1	6.6	4	1	0	4.4	3.1	4	7	0	6.7	5.9
* 2	7	-10	9.1	7.8	3	1	-2	15.3	18.6	* 3	6	-7	1.6	1.9	4	1	-1	8.1	9.5	4	7	-1	6.7	6.1
* 2	7	-11	1.4	1.1	3	1	-3	25.0	24.5	3	6	-8	18.8	20.5	4	1	-2	23.0	23.3	4	7	-2	10.4	10.1
2	7	-12	11.1	11.0	3	1	-4	23.6	23.3	3	6	-9	3.8	3.8	4	1	-3	4.2	4.4	4	7	-3	16.6	17.8
2	8	9	6.5	7.3	* 3	1	-5	1.2	2.9	3	6	-10	16.6	16.4	4	1	-4	3.0	0.6	4	7	-4	10.8	10.5
* 2	8	8	1.7	1.6	3	1	-6	9.1	8.0	3	6	-11	4.8	4.8	4	1	-5	16.7	16.3	4	7	-5	8.9	9.2
2	8	7	25.3	24.6	3	1	-7	18.8	18.8	3	6	-12	2.7	4.1	4	1	-6	15.1	15.1	4	7	-6	14.3	13.4
* 2	8	6	2.0	0.7	3	1	-8	7.9	7.3	3	7	9	8.5	11.4	4	1	-7	14.2	14.6	4	7	-7	7.7	6.7
2	8	5	17.0	18.7	* 3	1	-9	1.6	1.2	3	7	8	11.5	11.0	4	1	-8	19.5	21.8	4	7	-8	12.1	10.4
* 2	8	4	2.1	2.2	3	1	-10	6.6	6.4	3	7	7	6.5	7.1	4	1	-9	13.6	15.4	4	7	-9	12.9	13.3
2	8	3	16.5	17.9	3	1	-11	13.8	12.4	3	7	6	15.9	14.5	4	1	-10	13.7	12.9	4	7	-10	2.6	3.8
2	8	2	9.1	9.8	3	1	-12	3.2	2.8	3	7	5	13.3	15.2	4	1	-11	7.5	7.5	* 4	8	8	0.8	0.9
* 2	8	1	2.0	0.6	3	1	-13	2.4	2.9	3	7	4	3.3	4.4	4	1	-12	3.7	3.8	4	8	5	10.8	10.8
2	8	0	4.9	4.6	3	2	9	4.6	3.4	* 3	7	3	1.6	3.0	4	2	7	7.0	6.2	4	8	4	3.9	3.5
2	8	-1	24.0	23.0	3	2	8	12.8	11.2	3	7	2	12.8	11.7	* 4	2	6	1.4	0.7	4	8	3	10.7	8.2
2	8	-2	4.9	5.2	3	2	7	19.2	19.0	3	7	1	15.1	14.2	4	2	5	7.3	7.3	* 4	8	2	1.3	0.0
2	8	-3	17.6	17.0	3	2	6	13.8	12.7	3	7	0	19.4	18.7	4	2	4	10.2	9.3	4	8	1	15.1	14.1
2	8	-4	5.0	4.2	3	2	5	32.3	35.2	3	7	-1	21.5	21.6	4	2	3	11.6	10.7	4	8	0	3.6	3.1
2	8	-5	13.8	13.4	3	2	4	4.6	2.5	3	7	-2	11.2	9.6	4	2	2	12.9	11.0	4	8	-1	18.4	16.6
* 2	8	-6	2.1	2.1	3	2	3	26.9	26.5	3	7	-3	31.1	34.5	4	2	1	17.8	14.7	* 4	8	-2	1.4	0.4
* 2	8	-7	2.0	2.0	3	2	2	11.6	9.2	3	7	-4	14.4	13.4	4	2	0	4.2	3.2	* 4	8	-3	10.5	8.7
2	8	-8	7.7	6.4	3	2	1	5.7	6.0	3	7	-5	7.1	5.9	4	2	-1	21.2	22.5	* 4	8	-4	1.4	0.2
2	8	-9	13.2	11.0	3	2	0	25.8	22.8	3	7	-6	9.5	10.0	4	2	-2	9.3	8.4	4	8	-5	19.9	18.7
2	8	-10	1.5	0.7	3	2	-1	9.5	6.4	3	7	-7	5.2	4.3	4	2	-3	24.4	26.6	4	8	-6	4.2	4.0
2	8	-11	8.6	9.1	3	2	-2	1.7	0.7	* 3	7	-8	1.5	1.1	4	2	-4	13.1	11.4	4	8	-7	7.3	5.7
* 2	9	8	0.9	1.6	3	2	-3	13.4	12.2	* 3	7	-9	1.4	2.1	4	2	-5	29.8	32.8	* 4	8	8	1.0	0.2
* 2	9	7	1.4	0.6	3	2	-4	11.5	11.9	3	7	-10	2.5	2.9	* 4	2	-6	1.3	0.8	4	8	-9	6.3	7.9
2	9	7	7.0	6.8	* 3	2	-5	1.2	1.1	3	7	-11	1.8	1.2	4	2	-7	2.9	1.1	4	9	5	14.2	17.3
2	9	6	6.4	6.9	3	2	-6	2.8	2.6	3	8	8	1.9	2.1	4	2	-8	3.0	3.8	4	9	4	10.3	11.0
2	9	5	2.0	0.7	3	2	-7	27.0	29.1	3	8	7	12.6	12.6	4	2	-9	14.7	15.7	4	9	3	9.8	10.1
2	9	4	4.1	4.4	3	2	-8	10.3	10.4	* 3	8	6	1.4	0.7	* 4	2	-10	1.3	0.5	4	9	2	10.6	9.4
2	9	3	24.7	26.7	3	2	-9	20.8	22.6	3	8	5	24.8	25.3	4	2	-11	17.0	17.2	4	9	1	7.2	5.9
2	9	2	5.1	4.9	3	2	-10	7.3	7.3	3	8	4	4.6	4.7	4	2	-12	6.8	8.4	4	9	0	3.8	2.9
2	9	1	22.7	25.1	3	2	-11	14.5	14.8	3	8	3	19.0	21.1	4	3	7	10.0	9.5	4	9	-1	3.8	2.4
2	9	0	2.1	0.1	* 3	2	-12	1.3	0.5	3	8	2	3.3	4.1	4	3	6	5.4	4.7	4	9	-2	10.6	8.3
2	9	-1	14.4	14.1	* 3	2	-13	0.9	2.0	3	8	1	15.1	13.6	4	3	5	22.2	23.3	* 4	9	-3	1.3	1.8
2	9	-2	5.9	5.2	3	3	9	19.6	19.6	* 3	8	0	1.6	0.9	4	3	4	3.0	2.5	4	9	-4	11.6	10.4
2	9	-3	4.2	3.2	* 3	3	8	1.6	0.3	3	8	-1	2.4	2.2	4	3	3	31.4	35.1	4	9	-5	13.9	12.1
2	9	-4	12.5	14.0	3	3	7	14.5	13.6	* 3	8	-2	1.6	1.0	4	3	2	13.6	12.1	4	9	-6	8.9	9.7
* 2	9	-5	2.1	1.8	3	3	6	12.4	11.8	* 3	8	-3	7.5	6.7	4	3	1	19.3	18.1	4	9	-7	10.1	11.6
* 2	9	-6	2.0	2.8	3	3	5	22.1	21.3	* 3	8	-4	1.6	2.5	4	3	0	7.7	6.5	* 4	9	8	0.7	0.4
* 2	9	-7	1.9	0.5	3	3	4	7.6	6.4	* 3	8	-5	8.1	8.5	4	3	-1	5.8	4.7	4	10	3	6.6	8.3
* 2	9	-8	1.8	1.0	3	3	3	7.8	6.0	* 3	8	-6	1.6	1.1	4	3	-2	10.3	9.4	4	10	2	10.2	11.3
2	9	-9	3.7	3.8	3	3	2	15.6	11.7	* 3	8	-7	18.4	19.2	4	3	-3	26.2	30.9	4	10	1	9.3	9.5
* 2	9	-10	1.2	2.0	3	3	1	23.6	19.2	* 3	8	-8	1.4	0.8	4	3	-4	3.1	3.0	4	10	0	9.8	9.9
2	10	8	7.4	10.3	3	3	0	10.3	9.0	3	8	-9	10.9	10.3	4	3	-5	29.3	34.2	4	10	-1	5.5	4.7
2	10	7	9.4	9.0	3	3	-1	45.2	49.8	3	8	-10	2.5	2.9	4	3	-6	9.9	8.6	4	10	-2	15.8	17.6
2	10	6	17.5	16.3	3	3	-2	4.2	2.7	3	9	7	11.1	13.2	4	3	-7	15.4	14.7	4	10	-3	4.3	4.5
2	10	5	12.3	13.0	3	3	-3	47.1	55.6	3	9	6	7.2	6.1	4	3	-8	7.9	8.4	4	10	-4	12.8	13.0
2	10	4	16.2	14.1	3	3	-4	11.2	9.8	3	9	5	8.7	8.1	4	3	-9	14.2	13.6	4	10	-5	4.0	4.0
2	10	3	4.8	4.5	3	3	-5	7.6	5.8	3	9	4	3.6	3.1	* 4	3	-10	1.3	1.9	4	10	-6	4.2	3.8
2	10	2	4.0	3.0	3	3	-6	4.2	3.5	3	9	3	3.1	3.1	4	3	-11	6.2	6.5	* 4	11	0	2.0	2.1
2	10	1	5.0	5.1	3	3	-7	7.4	6.3	3	9	2	3.2	1.5	4	3	-12	2.9	3.8	* 4	11	-1	0.8	0.2
2	10	0	5.8	5.1	* 3	3	-8	1.6	1.7	3	9	1	15.4	14.4	4	4	8	3.3	3.3	* 4	11	-2	6.9	7.4
2	10	-1	5.0	4.3	* 3	3	-9	1.6	1.1	3	9	0	19.0	20.4	* 4	4	7	1.2	1.2	4	11	-3	0.6	1.0
																				4	11	-4	2.3	3.0

Fourier maps. It then became possible to calculate the position of H(10), assuming that the lone pair of N(4) is engaged in a bifurcated hydrogen bond, as described earlier. The hydrogen atom H(10) does not seem to be used for hydrogen bonding (Fig. 8).

Comparison with other structures. In the present compound, $(N_2H_5)_2SO_4$, hydrogen bonds obviously exist between hydrazinium ions and sulphate ions. These bonds are of two types, namely $H_2N^+—H\cdots OSO_3^{2-}$ and $HN—H\cdots OSO_3^{2-}$. Hydrogen bonds of the first type have been studied earlier in the two compounds, $LiN_2H_5SO_4$[16,17] and $N_2H_6SO_4$.[1] In the first of these the NH_3^+ group has five oxygen atoms within possible hydrogen bond distances. The N—N—O angles are about 100° for three of these possible bonds, with distances of 2.91, 3.02, 2.82 Å, and about 120° and 165° for the rest, with distances of 2.99 and 2.96 Å. (The values referred to are taken from Brown's paper [17]). The environment of the $N_2H_6^{2+}$ ion in $N_2H_6SO_4$[1] is rather complicated; the total number of oxygen neighbours within 3.03 Å is twelve (six to each NH_3^+ group). According to the interpretation made by Nitta *et al.*[1] one of the NH_3^+ groups forms three normal hydrogen bonds to oxygen (2.73, 2.73, and 2.77 Å) while the other NH_3^+ group generates three bifurcated hydrogen bonds (2.82, 2.79, 2.99, 2.82, 2.80). (One oxygen atom is assumed to be involved in two bifurcated bonds.) In the present compound, $(N_2H_5)_2SO_4$, the number of neighbours within possible hydrogen bond distances around N(1) is six, *i.e.* larger than the number of hydrogen atoms available for bonding. Hence the situation is comparable with the examples given above. The environment of N(2) in $(N_2H_5)_2SO_4$ is more regular, however. This NH_3^+ group seems to be engaged in three relatively normal hydrogen bonds. The NH_2 groups in the present compound also show variation in both coordination and possible hydrogen bond distances of the $HN—H\cdots OSO_3^{2-}$ type; furthermore, these hydrogen bonds must be considerably bent, as was mentioned earlier. In $Li(N_2H_5)SO_4$,[17] one bond was assumed to be of the $HN—H\cdots OSO_3^{2-}$ type (length 2.98 Å, angle N—N—O 136°). The three compounds discussed above show large variations in hydrogen bond distances between the same functional groups. This might be due to packing effects, which may cause shortening or lengthening away from the expected hydrogen bond distances.

Proton magnetic resonance studies have been made on $Li(N_2H_5)SO_4$ by Cuthbert and Petch (private communication to Brown [17]) and on $(N_2H_5)_2SO_4$ and $N_2H_6SO_4$ by Deeley, Lewis and Richards.[19] In the case of $Li(N_2H_5)SO_4$, the spectra indicated that the NH_3^+ group rotates with the N—N bond as the axis of rotation. Deeley *et al.* interpreted their spectra, obtained at room temperature, in terms of possible motion of or within the hydrazinium ions, while spectra obtained at low temperatures indicated restriction of these motions. In all these cases, the NH_3^+ groups are hydrogen bonded to the sulphate oxygens. Since the bonds are rather short, especially in $N_2H_6SO_4$, it might be expected that the forces associated with the hydrogen bonds would be strong enough to considerably restrict rotation around the N—N bond. In the present instance, however, the NH_2 groups (especially $N(4)H_2$) seem to be engaged in only weak hydrogen bonding. These groups might then be more free to move. As was mentioned earlier, powder photographs of $(N_2H_5)_2SO_4$ taken at room-temperature and at −184°C did not show any phase change.

The differences in intensity, due to temperature effects, were remarkably small, indicating that the changes in the atomic vibrations are small in the relevant temperature range.

Dihedral angles within the $N_2H_5^+$ ions. The dihedral angle between the planes defined by N(3) — N(1) — H(2) and N(1) — N(3) — H(4) is found to be about 70° when that of the planes N(4) — N(2) — H(8) and N(2) — N(4) — H(9) is about 20° (see Fig. 7). This means that hydrazinium ion I has approximately the staggered configuration while the form of ion II is more nearly eclipsed. The $N_2H_6^{2+}$ ion has been found to have the staggered configuration in $N_2H_6F_2$ (Kronberg and Harker [20]) and $N_2H_6Cl_2$ (Donohue and Lipscomb [21]). The configuration of the $N_2H_5^+$ ion seems not to have been discussed in earlier papers.

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