molecule with regard to the centres of symmetry are approximately the same as those of the corresponding atoms of tartaric acid in the racemic acid structure.

According to Parry one of the important linkages in the racemic acid structure is a square system of hydrogen bonds between hydroxyl groups on four molecules, thus forming columns parallel to the, say, c' axis ($c' = c$ for racemic acid). Each hydroxyl group is supposed to take part in two bonds, one with a hydroxyl group of an antipode molecule and the other with a hydroxyl group of a molecule of the same configuration related by translation in the direction of c'.

Analogous squares are formed in the mesotartaric acid structures (see Figs. 8 and 10; in both Figures c' corresponds to the projection axis). From the high values of the valence angles and our findings with regard to the hydrogen bond formation it may be concluded that these *hydroxyl squares* are of secondary importance for the coherence of the structures compared with the links to be described next.

In the structure of racemic acid one carboxyl group of the molecule is directly linked with a carboxyl group of a centrosymmetrically related molecule, and the other carboxyl group is indirectly connected with a counterpart through water molecules. The first type of linkage (*carboxylic acid dimers*) is found at one side of the molecule in the anhydrous form (Fig. 10), the second type (*hydrated links*) at one side of the molecule in the structure of the triclinic hydrate (Fig. 8). In the monoclinic hydrate (Fig. 9) one side of the molecule takes part in a carboxylic acid dimer configuration, but the linkage through water molecules at the other side of the molecule is a less common mutation of the hydrated links found in other cases. Here a tetrahedral arrangement of close neighbours around the water oxygen atom O(7) is achieved by mutual hydrogen bonding of water oxygen atoms related by the twofold screw axis.

Evidently the geometry of the mesotartaric acid molecule does not permit an ideal three-dimensional arrangement with both types of intermolecular linkages present.

References

BOOTSMA, G. A. & SCHOONE, J. C. (1964). *Acta Cryst.* 17, 462.

BOOTSMA, G. A. (1964). Thesis, Utrecht.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). USAEC Report ORNL TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

COCHRAN, W. & DOUGLAS, A. S. (1957). *Proc. Roy. Soc.* A, 243, 281.

KROON, J., PEERDEMAN, A. F. & BIJVOET, J. M. (1965). *Acta Cryst.* 19, 293.

LIDE, D. R. (1962). *Tetrahedron*, 17, 125.

LONGCHAMBON, M. L. (1926). *C. R. Acad. Sci. Paris*, 182, 473.

PARRY, G. S. (1951). *Acta Cryst.* 4, 131.

SCHNEIDER, W. (1928). *Z. Kristallogr.* 69, 49.

SCHUIJFF, A. & HULSCHER, J. B. (1965). *Rev. Sci. Instrum.* 36, 957.

VAND, V. & PEPINSKY, R. (1956). *Z. Kristallogr.* 107, 3.

VRIES, A. DE (1965). *Acta Cryst.* 18, 473.

WOOLFSON, M. M. (1961). *Direct Methods in Crystallography*. Oxford: Clarendon Press.

A Neutron Diffraction Study of the Crystal Structure of Lithium Hydrazinium Sulphate

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A single-crystal neutron-diffraction investigation of lithium hydrazinium sulphate has been made in which the intensities of 215 reflexions in all the three prism zones were measured. The structure was refined by Fourier and least-squares techniques. The heavy-atom positions obtained agree very well with values from the X-ray determination. The hydrogen atoms of the $NH_2-NH_3^+$ ion are arranged tetrahedrally about the nitrogen atoms and the configuration was found to be staggered. The NH_2 groups of the ions are linked into infinite chains by hydrogen bonds pointing in the negative c direction. The hydrogen atoms of the NH_3 group are static and do not rotate along the N–N axis.

The interesting electrical properties of room temperature ferroelectric lithium hydrazinium sulphate ($LiN_2H_5SO_4$) have been the subject of a great deal of investigation. The proton and ^7Li nuclear magnetic resonance signals have been investigated in detail over a wide temperature range, $-180°C$ to $+210°C$, by Cuthbert & Petch (1963). From these experiments they concluded that (1) at the temperature region about

−180°C the hydrazinium ion $NH_2–NH_3^+$, is effectively in a rigid state inside the crystal and (2) in the temperature region −130° to +50°C the hydrogen atoms of the NH_3 group rotate around the N–N axis. Vanderkooy, Cuthbert & Petch (1964) found the d.c. conductivity to be markedly anisotropic with the direction of easiest conduction along the ferroelectric c axis. This large value was explained by them as due to transfer of protons along the hydrogen bonds from one nitrogen to the next of the NH_2 groups in the chain N–H···N–H···N–H··· which exists along the c axis in the structure. Using λ 2536 resonance radiation of mercury as exciter Raman scattering in single crystals was studied by Krishnan & Krishnan (1965). From the nature of the spectrum corresponding to N–H stretch-

ing vibrations, it was suggested that the hydrogen atoms in the NH_3 group may be rotating in the crystal. The crystal structure has been studied by means of 3-D data from X-ray diffraction techniques by Brown (1964) Van den Hende & Boutin (1964). Although the coordinates of hydrogen atoms could not be determined, Brown suggested that the hydrogen atoms of the NH_3 group may rotate around the N–N axis. Van den Hende & Boutin from their electron density maps postulated half-hydrogen positions around nitrogen.

The present investigation was initiated in order to locate accurately the hydrogen atoms in the molecule and also to compare the coordinates of other atoms obtained by neutron diffraction with those determined by the use of X-rays.

Table 1. *Atomic parameters and temperature factors*

		Brown	Van den Hende & Boutin	This work	Standard deviation	Temperature factor
S	x	0·1579	0·1589	0·159	0·001	$1·18 \pm 0·13$
	y	0·1286	0·1290	0·126	0·001	
	z	0·250	0·250	0·250	0·002	
O(1)	x	0·191	0·1870	0·193	0·001	
	y	0·106	0·1068	0·106	0·002	$1·74 \pm 0·16$
	z	0·519	0·5434	0·533	0·002	
O(2)	x	0·010	0·0132	0·012	0·001	
	y	0·154	0·1511	0·153	0·002	$1·41 \pm 0·14$
	z	0·220	0·2296	0·229	0·001	
O(3)	x	0·230	0·2335	0·230	0·001	
	y	0·259	0·2558	0·259	0·001	$1·78 \pm 0·16$
	z	0·149	0·1626	0·151	0·002	
O(4)	x	0·302	0·3048	0·304	0·001	
	y	0·497	0·4904	0·498	0·001	$1·52 \pm 0·13$
	z	0·596	0·6016	0·600	0·002	
N(1)	x	0·022	0·0285	0·024	0·001	
	y	0·418	0·4193	0·414	0·001	$2·22 \pm 0·13$
	z	0·746	0·7405	0·743	0·002	
N(2)	x	0·440	0·4460	0·440	0·001	
	y	0·217	0·2137	0·213	0·001	$1·61 \pm 0·13$
	z	0·742	0·7346	0·739	0·002	
Li	x	0·332	0·339	0·336	0·003	
	y	0·437	0·433	0·422	0·003	$1·20 \pm 0·12$
	z	0·253	0·271	0·256	0·003	
H(1)	x	—	—	0·118	0·003	
	y	—	—	0·381	0·004	$3·56 \pm 0·33$
	z	—	—	0·796	0·003	
H(2)	x	—	—	0·036	0·004	
	y	—	—	0·467	0·004	$5·15 \pm 0·34$
	z	—	—	0·571	0·004	
H(3)	x	—	—	0·345	0·003	
	y	—	—	0·189	0·003	$3·11 \pm 0·31$
	z	—	—	0·677	0·003	
H(4)	x	—	—	0·428	0·004	
	y	—	—	0·247	0·005	$6·37 \pm 0·52$
	z	—	—	0·924	0·004	
H(5)	x	—	—	0·469	0·002	
	y	—	—	0·292	0·004	$2·89 \pm 0·24$
	z	—	—	0·601	0·003	

Unit cell and space-group

The space group of lithium hydrazinium sulphate has been shown to be $Pna2$ (C_{2v}^9). The unit cell contains four molecules; all atoms are in fourfold general positions. The lattice constants are $a=9.913$, $b=8.969$, $c=5.178$ Å agreeing well with earlier X-ray data.

Experimental procedure

Crystals of lithium hydrazinium sulphate were grown from an aqueous solution of reagent grade Li_2CO_3 and $N_2H_6SO_4$ by slow evaporation. For each of the three zones, a crystal was cut and ground into a cylinder about 1 mm in diameter and approximately 5 mm in length so that the axis of the cylinder corresponded to the zone axis. Complete neutron diffraction data were collected for the $(hk0)$, $(h0l)$ and $(0kl)$ zones up to $\sin\theta/\lambda=0.70$, the neutron wavelength being 1.029 Å. The intensity of the incident monochromatic neutron beam was found to be 2×10^5 neutrons.cm^{-2}.sec^{-1}. The intensities of 215 independent reflexions were measured and a set of observed structure factors with weights for each reflexion was obtained as described in an earlier paper (Padmanabhan, Mehdi Ali & Srikanta, 1965). The linear absorption coefficient was found to be 2.9 cm^{-1}. There was no evidence for extinction effects in the crystal.

Treatment of data

Signs were given to the observed $hk0$ structure factors based on Brown's (1964) parameters. The resulting Fourier synthesis showed that the heavy atoms were identified correctly and also indicated without any ambiguity the positions of the two hydrogen atoms belonging to the NH_2 group of the N_2H_5 ion. In addition to this, as the nuclear density map indicated the contours of the three hydrogen atoms of the NH_3 group also it was thought that these hydrogen atoms might not be rotating around the N–N axis. To clear this doubt, structure factors were calculated for two models, viz. (1) with the hydrogen atoms of the NH_3 group rotating round the N–N axis (dynamic) and (2) with the hydrogen atoms not rotating (static). The nuclear scattering amplitudes used were 0.94, 0.32, 0.58, -0.18 and -0.38 (10^{-12} cm) for N, S, O, Li and H respectively.

For the dynamic model the contribution of the hydrogen atoms of the NH_3 group to the structure factors, as discussed by Bijvoet & Ketelaar (1932) and Zachariasen (1945), is $F=\sum_{j=1}^{N} f_j J_0(x_j)$, where $J_0(x_j)$ is the zero order Bessel function of argument x_j and $x_j=(4\pi a_j/\lambda)\sin\theta\sin\alpha$, a_j being the distance of the hydrogen atoms from the axis of rotation and α the angle between the plane containing the rotating atoms and the plane of reflexion. The summation is taken over all three of the hydrogen atoms. The equation for the F values as used in this $(hk0)$ projection is obtained from the general formula,

$$F_{hkl}=\exp\left\{-B(\sin^2\theta/\lambda^2)\right\}\left[\sum_j f_j \cdot \exp 2\pi i(hx_j+ky_j+lz_j)\right.$$

$$\left.+\sum_{j'} f_{j'} J_0(4\pi a_j/\lambda)\sin\theta\sin\alpha\right\},$$

where j refers to atoms in fixed positions and j' to the atoms involved in free rotation. With the above formula, structure factors were calculated for all the $hk0$ reflexions with $a_j=0.96$ Å and temperature factor (B_j) 2.0 Å^2 for the rotating hydrogen atoms (for the other atoms B values were the same as those used in the static model). The reliability index was found to be 0.23 and adjustments of a_j and B_j did not improve it. Hence the dynamic model was abandoned and structure factors were calculated for the static model. Using the coordinates for the hydrogen atoms obtained from the Fourier map, parameter refinement was carried out by least-squares treatment with the computer CDC-3600 using programs of Srikanta (1964) and Busing & Levy (1959). The weighted R index was 0.17 at the initial stage and converged to 0.10 after four cycles. The z coordinates of hydrogen atoms in the crystal were deduced from considerations of the bond distances projected on the (100) plane. Using these with the z coordinates for the other atoms obtained by X-ray methods, structure factors were computed for the non-centrosymmetric $(0kl)$ and $(h0l)$ zones. Because of the small number of reflexions recorded, complete refinement with anisotropic temperature factors was not carried out for these two zones although for the $(hk0)$ zone the R index with individual anisotropic temperature factors was reduced to 0.08. At the final stage of

Table 2. *Observed and calculated structure amplitudes and calculated phases.*

h k l	F_o	F_c	α	h k l	F_o	F_c	α	h k l	F_o	F_c	α
2 0 0	0.74	0.49	180	5 5 0	3.10	2.99	0	0 0 4	6.87	7.04	283
4 0 0	8.22	8.33	0	5 6 0	5.68	5.54	180	0 0 6	4.82	5.08	120
6 0 0	2.13	2.03	0	5 7 0	4.77	4.69	0	0 1 1	2.31	2 25	98
8 0 0	2.92	3.02	180	5 8 0	0.77	0.75	180	0 1 3	4.91	5.30	223
10 0 0	1.95	2.13	0	5 9 0	1.36	1.14	0	0 1 5	4.10	4.22	284
0 2 0	0.18	0.10	0	510 0	1.01	0.93	180	0 1 7	1.71	1.57	159
0 4 0	1.67	1.48	180	6 1 0	3.29	3.30	180	0 2 2	4.16	4.18	0
0 6 0	2.33	2.15	180	6 2 0	4.70	4.54	0	0 2 4	3.81	3.49	123
0 8 0	4.27	4.32	0	6 3 0	3.70	3.67	180	0 2 6	1.08	1.08	246
010 0	2.68	2.19	0	6 4 0	5.71	5.58	180	0 3 1	3.87	3.75	317
012 0	1.42	1.52	0	6 5 0	0.49	0.31	0	0 3 3	3.02	3.39	26
1 1 0	1.05	1.06	0	6 6 0	1.14	1.12	0	0 3 5	0.84	0.91	219
1 2 0	3.82	3.92	180	6 7 0	4.21	4.18	0	0 3 7	1.70	1.87	319
1 3 0	0.89	0.80	0	6 8 0	2.23	2.75	0	0 4 2	2.32	2.16	143
1 4 0	1.64	1.49	180	6 9 0	0.15	0.06	190	0 4 4	4.12	4.59	182
1 5 0	1.04	0.78	180	610 0	0.22	0.17	180	0 4 6	3.16	3.42	339
1 6 0	2.46	2.78	0	7 1 0	0.55	0.93	180	0 5 1	3.94	4.16	16
1 7 0	8.67	8.80	0	7 2 0	1.49	1.63	180	0 5 3	6.80	7.03	183
1 8 0	1.81	1.64	0	7 3 0	5.90	5.68	180	0 5 5	4.50	4.47	284
1 9 0	2.58	2.47	180	7 4 0	2.98	2.81	0	0 6 2	2.5.	1.93	317
110 0	1.04	1.21	180	7 5 0	3.76	3.40	0	0 6 4	1.73	1.78	126
2 1 0	2.53	2.64	180	7 6 0	1.11	1.26	180	0 6 6	1.89	1.95	217
2 2 0	0.73	0.88	180	7 7 0	0.36	0.72	180	0 7 1	2.65	2.63	162
2 3 0	2.12	1.96	180	7 8 0	0.51	0.57	0	0 7 3	1.12	1.38	97
2 4 0	5.55	5.56	180	7 9 0	0.15	0.18	180	0 7 5	3.06	3.04	116
2 5 0	0.33	0.32	0	710 0	2.40	2.40	180	0 8 2	4.63	4.65	80
2 6 0	0.20	0.11	180	8 1 0	2.86	2.56	180	0 8 4	1.59	1.91	98
2 7 0	2.05	2.10	0	8 2 0	0.75	0.62	180	0 9 1	6.88	6.30	76
2 8 0	5.33	5.24	180	8 3 0	4.58	4.30	180	0 9 3	4.62	4.64	279
2 9 0	0.36	0.44	0	8 4 0	1.16	1.36	180	2 0 1	4.17	4.08	93
210 0	0.15	0.13	180	8 5 0	2.72	2.32	0	2 0 2	10.80	11.31	201
211 0	0.98	1.04	0	8 6 0	0.97	0.67	180	2 0 3	3.59	3.69	273
3 1 0	5.57	5.78	180	8 7 0	0.15	0.28	180	2 0 4	0.28	0.29	294
3 2 0	1.75	1.57	180	8 8 0	1.13	1.09	180	4 0 1	1.62	1.53	70
3 3 0	2.01	1.98	0	9 1 0	1.31	0.89	0	4 0 2	7.12	6.83	193
3 4 0	4.08	4.22	0	9 2 0	1.89	1.91	0	4 0 3	3.52	3.38	41
3 5 0	0.85	0.80	0	9 3 0	2.00	1.79	180	4 0 4	4.20	3.68	311
3 6 0	3.92	3.86	180	9 4 0	2.53	2.21	0	4 0 5	4.20	4.19	148
3 7 0	2.41	2.56	0	9 5 0	2.12	1.93	0	4 0 6	1.05	0.95	132
3 8 0	1.41	1.22	0	9 6 0	0.15	0.26	180	6 0 1	3.41	2.36	136
3 9 0	5.69	5.84	180	9 7 0	0.80	0.88	180	6 0 2	1.72	1.84	355
310 0	3.17	3.17	180	9 8 0	3.69	3.58	180	6 0 3	4.20	3.99	262
311 0	2.17	2.65	180	10 1 0	3.89	3.64	180	6 0 4	3.01	3.15	26
312 0	1.72	1.74	0	10 2 0	3.76	3.39	0	6 0 5	1.50	1.80	276
4 1 0	4.61	4.32	0	10 3 0	2.23	2.06	0	6 0 6	2.26	2.34	121
4 2 0	1.61	1.43	180	10 4 0	0.80	0.98	180	8 0 1	3.20	3.08	307
4 3 0	1.02	0.79	180	10 5 0	2.19	1.73	180	8 0 2	1.36	1.46	230
4 4 0	2.06	1.91	180	10 6 0	2.19	2.04	0	8 0 3	2.63	2.95	64
4 5 0	0.59	0.56	0	11 1 0	2.25	2.58	0	8 0 4	2.83	3.00	251
4 6 0	2.35	2.20	180	11 2 0	0.46	0.70	180	8 0 5	1.99	2.53	205
4 7 0	1.23	1.26	180	11 3 0	1.86	1.82	180	10 0 1	1.81	1.90	18
4 8 0	0.86	0.88	0	11 4 0	1.49	1.49	0	10 0 2	4.15	4.12	41
4 9 0	0.52	0.43	180	11 5 0	1.04	1.41	0	10 0 3	2.98	3.01	184
410 0	0.68	0.55	180	11 6 0	1.64	1.34	0	10 0 4	2.10	2.04	132
411 0	2.35	2.65	0	12 1 0	2.60	2.63	180	10 0 5	2.82	2.96	13
5 1 0	2.55	2.49	0	12 2 0	0.98	1.15	180	12 0 1	3.93	3.91	291
5 2 0	1.52	0.98	0	12 3 0	1.81	1.77	180	12 0 2	0.98	1.04	219
5 3 0	0.15	0.14	0	12 4 0	1.78	1.56	180	12 0 3	2.61	2.57	182
5 4 0	6.46	6.26	0	0 0 2	9.34	8.93	122				

refinement the weighted reliability indices of the three zones are $R_{hk0}=0.10$, $R_{h0l}=0.10$, $R_{0kl}=0.09$.

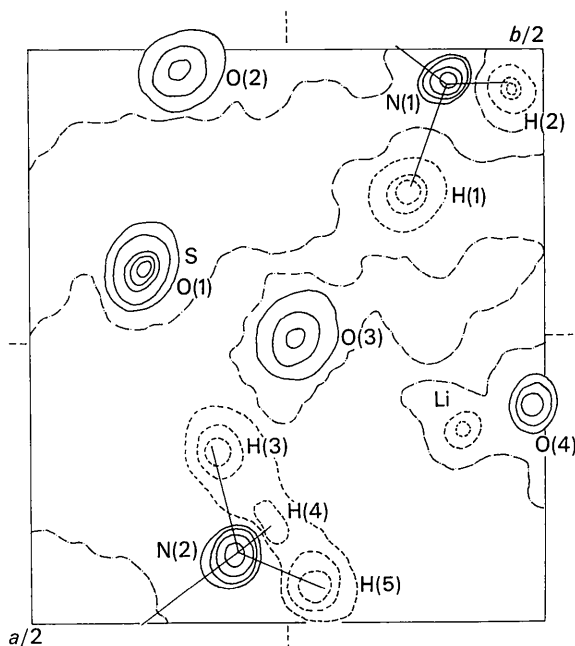The values of the parameters and their standard deviations are compared with those obtained by X-ray

Fig. 1. Nuclear scattering density projection along the c direction. Zero contour and negative contours shown by dashed lines. Contour level arbitrary.

methods in Table 1. The positional parameters were found from the average of each pair of least-squares values obtained from the three zones. The values of the observed structure factors and those calculated from the final least-squares parameters are shown in Table 2.

Discussion

The final nuclear density function $\varrho(xy)$ is shown in Fig. 1, and in Fig. 2 the schematic view of the unit cell is shown as viewed along the c axis. As indicated from X-ray studies, the sulphur and lithium atoms are both surrounded by tetrahedra of oxygen atoms. These tetrahedra share the corner oxygen atoms to form a three-dimensional network. Each oxygen atom is bonded to one lithium atom and one sulphur atom so that every LiO_4 tetrahedron is surrounded by four SO_4 tetrahedra and *vice versa*. Interatomic distances (thermal motions are not considered) and bond angles calculated from the parameters listed in Table 1 are given in Table 3. (Estimated error in neglecting thermal motion in bond distances is about 0.02 Å).

The sulphate ion

The SO_4 tetrahedron is slightly distorted. The distortion is not as much as that observed by Van den Hende & Boutin (1964). The average S–O distance of 1.48 Å agrees with the value of 1.49 Å given in the literature. No short distance indicating any double bond character as noted by Van den Hende & Boutin (1964) is found in the present study.

Table 3. *Interatomic distances and angles*

Environment of the sulphur atom

S–O(1)	1.51 ± 0.02 Å	O(1)–S–O(2)	$106.8 \pm 1.5°$
S–O(2)	1.48	O(1)–S–O(3)	110.5
S–O(3)	1.46	O(1)–S–O(4)	110.7
S–O(4)	1.46	O(2)–S–O(3)	109.8
Mean S–O		O(2)–S–O(4)	109.1
distance	1.48 Å	O(3)–S–O(4)	109.6
		Mean O–S–O	
		angle	109.4°

Hydrazinium ion

N(1)–N(2)	1.42 ± 0.02 Å	N(2)–N(1)–H(1)	$106.4 \pm 2.0°$
N(1)–H(1)	1.02	N(2)–N(1)–H(2)	116.0
N(1)–H(2)	1.02	N(1)–N(2)–H(3)	112.4
N(2)–H(3)	1.03	N(1)–N(2)–H(4)	107.4
N(2)–H(4)	1.01	N(1)–N(2)–H(5)	112.8
N(2)–H(5)	1.04	H(3)–N(2)–H(4)	104.3
H(1)–H(2)	1.61	H(3)–N(2)–H(5)	101.1
H(3)–H(4)	1.61	H(4)–N(2)–H(5)	117.8
H(3)–H(5)	1.60	H(1)–N(1)–H(2)	104.9
H(4)–H(5)	1.76		
N(1)–O(4)	2.96	N(2)–N(1)–H(1)	106.0
N(1)–N(1')	3.04	N(2)–N(1)–H(2)	116.1
H(1)–O(4)	2.30	N(2)–N(1)–H(2')	110.1
H(2)–N(1')	2.06	N(1)–H(1)–O(4)	120.2
H(3)–O(1)	1.84	N(1)–H(2)–N(1')	116.9
H(4)–O(2')	2.02	N(2)–H(3)–O(1)	146.0
H(5)–O(2)	2.29	N(2)–H(4)–O(2')	152.1
		N(2)–H(5)–O(2)	122.9

The dihedral angle between the planes containing atoms N(1), N(2), H(1) and N(1), N(2), H(4) is 66°.

The hydrazinium ion

The interesting feature in the structure of $LiN_2H_5SO_4$ is the existence of the infinite chains of hydrogen bonds in the direction of the c axis. The Fourier maps as well as structure factor agreements indicate that the hydrogen atoms of the NH_2 group of the N_2H_5 ion are ordered inside the crystal and the NH_2 group is linked by one hydrogen bond to the oxygen of the SO_4 ion and by the other to the adjacent NH_2 group. As illustrated in Fig. 3, two possible configurations of the chain are possible. The present study shows that the hydrogen bond $N(1)-H\cdots N(1)$ is pointing downward, *i.e.* in the negative c direction.

Although Cuthbert & Petch (1963) have reported that the hydrogen atoms of the NH_3 group rotate round the $N(1)-N(2)$ axis, the Fourier syntheses as well as structure factor calculations do not support that conclusion and they indicate the static model. Structure factors were calculated assuming hindered rotation, but the agreement between F_o and F_c was not good.

By means of the rotating crystal spectrometer (Venkataraman, Satya Murthy, Usha Deniz, Dasanacharya & Iyengar, 1965) an inelastic spectrum giving the energy distribution of cold neutrons scattered from the powdered specimen was taken at room temperature with the counter fixed at an angle of 80°. The observed spectrum was compared with those of NH_4I, NH_4ClO_4 (Janik, 1965) in which the NH_4 ions execute free rotation. The spectrum observed for $LiN_2H_5SO_4$ showed a sharp peak (Fig. 4) whereas in the other two cases, where rotating groups exist, one obtains a broad distribution of scattered neutrons without any appearance
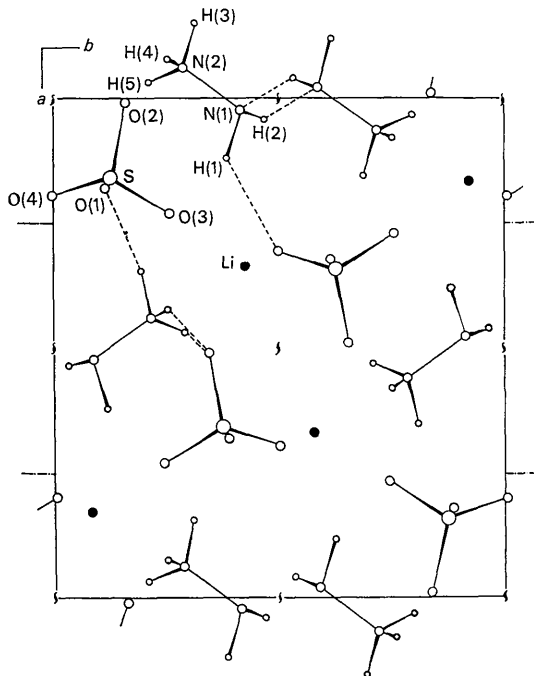
of a sharp peak in the region corresponding to 300–400 cm^{-1} (35–40 meV), thus supporting the view that there are no rotating groups in lithium hydrazinium sulphate.

The N–N distance observed in the present study is 1.42 Å, whereas the N–N bond length for hydrazine is 1.46 Å in the crystalline state (Giguère & Schomaker, 1943) and in the case of hydrazonium ion 1.42 Å has been reported in the literature (Nitta, Sakurai & Tomiie, 1951). The hydrogen atoms of the NH_2 group are staggered with respect to the hydrogen atoms bonded to N(2). The dihedral angle between the planes containing atoms $N(1)N(2)H(1)$ and $N(1)N(2)H(4)$ is 66° and so the staggering appears to be nearly maximum. The average N–H distance for the NH_2 group is 1.02 Å and for the NH_3 group 1.03 Å. The hydrogen atoms surround their respective nitrogen atoms in a nearly tetrahedral arrangement. The nitrogen atom in the NH_3 group forms four σ bonds and so one expects the bond angles to be tetrahedral. In the case of the NH_2 group also the observed tetrahedral arrangement is explained as due to the nitrogen atom forming three σ
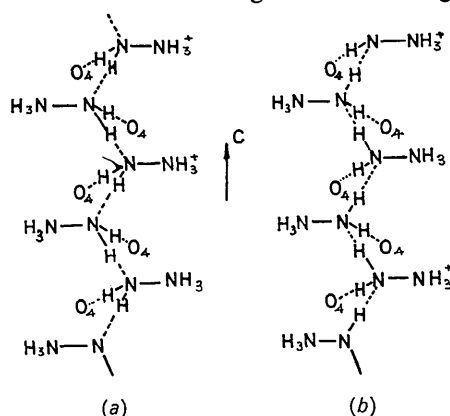

Fig. 3. The arrangement of the hydrogen bonded chain of hydrazinium ions running along the screw axis. (*a*) and (*b*) are the two possible configurations of the chain.
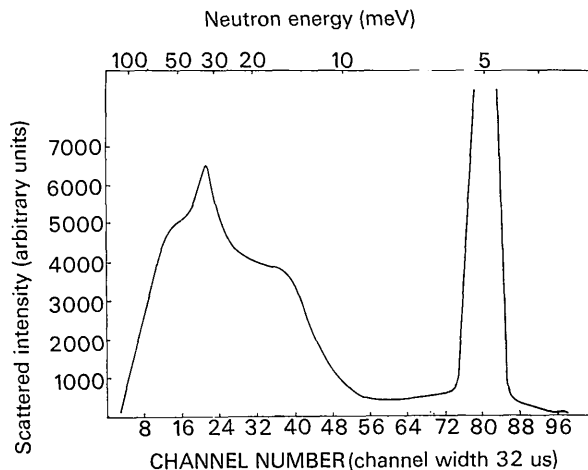

Fig. 2. The structure of $LiN_2H_5SO_4$ viewed along the c axis. Dashed lines represent hydrogen bonds.

Fig. 4. Time of flight distributions of neutrons scattered at an angle of 80° by polycrystalline $LiN_2H_5SO_4$, obtained by the rotating crystal spectrometer.

bonds and using its lone pair electrons to accept a hydrogen bond from the neighbouring hydrazinium ion. The N(1) atom thus takes part in three hydrogen bonds, twice as the donor and once as the acceptor of the hydrogen atom. The hydrogen atom H(1) is bonded to oxygen of the sulphate ion and the N(1)–H(1)$\cdots$O(4) hydrogen bond is bent with the N(1)–H(1) direction making an angle 44° whereas Cuthbert & Petch (1963) report 39°. The other hydrogen atom H(2) is bonded to nitrogen of the neighbouring NH$_2$ group and the N(1)–H(2) direction makes an angle of 18° with the N(1)–N(1) direction, which is more than the value of 4.5° reported by Cuthbert & Petch (1963). The hydrogen atoms of the NH$_3$ group are bonded to the nearest neighbouring acceptor oxygen atoms of the sulphate ion. The bonds are not collinear but bent, the angles being 123–152°.

We thank Mr G. Venkataraman for help in taking the inelastic spectrum.

References

BIJVOET, J. M. & KETELAAR, J. A. A. (1932). *J. Amer. Chem. Soc.* **54**, 625.

BROWN, I. D. (1964). *Acta Cryst.* **17**, 654.

BUSING, W. R. & LEVY, H. A. (1959). Oak Ridge National Laboratory, Central Files No. 59–4–37.

CUTHBERT, J. D. & PETCH, H. E. (1963). *Canad. J. Phys.* **41**, 1629.

GIGUÈRE, P. A. & SCHOMAKER, V. C. (1943). *J. Amer. Chem. Soc.* **65**, 2025.

JANIK, J. A. (1965). In *Inelasting Scattering of Neutrons in Solids and Liquids.* Vienna: I.A.E.A.

KRISHNAN, R. S. & KRISHNAN, K. (1965). *Proc. Indian Acad. Sci.* **61**, 122.

NITTA, J., SAKURAI, K. & TOMIIE, Y. (1951). *Acta Cryst.* **4**, 289.

PADMANABHAN, V. M., MEHDI ALI, S. & SRIKANTA, S. (1965). *Acta Cryst.* **18**, 567.

SRIKANTA, S. (1965). CDC-3600 Fortran crystallographic programs – AEET – 203.

VAN DEN HENDE, J. H. & BOUTIN, H. (1964). *Acta Cryst.* **17**, 660.

VANDERKOOY, J., CUTHBERT, J. D. & PETCH, H. E. (1964). *Canad. J. Phys.* **42**, 1871.

VENKATARAMAN, G., SATYA MURTHY, M. S., USHA DENIZ, K., DASANACHARYA, B. A. & IYENGAR, P. K. (1965). In *Inelastic Scattering of Neutrons in Solids and Liquids,* Vienna: I.A.E.A.

ZACHARIASEN, W. H. (1945). *Theory of X-ray Diffraction in Crystals,* New York: John Wiley.

The Crystal Structure of β-DL-Arabinose

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The crystal structure of β-DL-arabinose (C$_5$H$_{10}$O$_5$) has been determined from integrated photographic intensity data by the application of a sign-correlation procedure on an IBM 1620 computer. The structure was refined by anisotropic least squares to give a final R value of 0·076 for 1122 reflections. The space group is P2$_1$/c, with Z=4 and unit-cell dimensions a=5·925 (σ=0·004), b=7·820 (σ=0·003), c=13·354 (σ=0·006) Å and β=99·45° (σ=0·06). All the hydrogen atoms were located on difference syntheses, but were not refined. It is found that the bond C(1)–O(1)H is 1·392 Å and is significantly shorter than the mean value of 1·423 Å for the other C–OH bonds. There is no significant difference between the two ring C–O distances. These observations are consistent with those from other recent structure determinations of pyranose sugars. The D and L molecules are hydrogen-bonded in pairs across the centers of symmetry and throughout the crystal structure by centrosymmetrically related chains of hydrogen bonds, each of which links molecules of the same sense. All the oxygen atoms in the structure are involved in this hydrogen-bonding scheme.

Introduction

Both D- and L-arabinose are of biological origin. L-Arabinose occurs naturally as a free sugar and is widely distributed in the combined state in plant products, usually as a furanoside. D-Arabinose is found rarely but does occur in certain plants and in the polysaccharide of tubercle bacilli. The DL material has the trivial name 'pectinose', presumably because it can be obtained from the degradation of the polysaccharides in pectin substances.

When a DL mixture crystallizes, it may do so to form a racemic structure with a centric space group. This permits, at least in principle, a more straightforward solution to the phase problem and the attainment of a better accuracy by a factor of two in the atomic parameters (Cruickshank, 1950). We have taken advantage of this in DL-arabinose, and as far as we know, this is the first example of a centrosymmetric structure determination of a free DL sugar. The crystal structure of β-L-arabinose has been determined from a refinement of two projections by Hordvik (1961).