reste du stéroïde, comme en témoigne la Fig. 4 représentant deux projections orthogonales de l'ensemble cycle *D*-molécule d'eau, en prenant les atomes C(13)–C(14)–C(17) comme référence.

Cette orientation particulière est assurée par deux interactions de natures différentes, avec le cycle *D*:

- une liaison hydrogène avec l'atome d'oxygène de la fonction 17β ol (2,82$_9$ Å).
- un contact de van der Waals avec le groupement méthyl C(18) (3,64$_4$ Å).

Il est vraisemblable que ce comportement identique des stéroïdes 17β ol en présence d'eau au moment de la cristallisation, est en rapport étroit avec l'activité biologique importante constatée pour tous ces dérivés.

On sait en effet que:

- pour qu'il y ait fixation au niveau de la protéïne de transport, la fonction 17β-ol est indispensable aussi bien pour les androgènes que pour les oestrogènes.
- mais d'autre part, au niveau des récepteurs, le remplacement de la fonction 17β-ol par une fonction 17-one ou 17α-ol diminue considérablement l'activité des oestrogènes, et annule complètement celle des androgènes.

En supposant que les protéïnes réceptrices et de transport possèdent au niveau du site de fixation des radicaux polaires capables de jouer le même rôle que l'eau dans le milieu cristallin, il est vraisemblable:

- que le méthyl C(18) pourrait contribuer aussi activement que le 17β-ol à la fixation sur le récepteur.
- que les liaisons contractées par le 17β-ol et le méthyl 18 ayant une orientation constante par rapport au reste de la molécule, elles constituent un système capable d'orienter le stéroïde de façon particulière, au moment de la fixation du cycle *D* au récepteur.

Pour essayer de mettre en évidence cette dernière supposition, nous avons l'intention de cristalliser différents complexes: stéroïdes plus dérivés d'acides aminés ou molécules hydroxylées, afin de voir si une orientation particulière persiste dans ce cas.

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An X-ray Refinement of the Crystal Structure of Lithium Ammonium Tartrate Monohydrate

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The crystal structure of lithium ammonium tartrate monohydrate, which is ferroelectric below about 100°K, has been solved by the symbolic addition method and refined using three-dimensional X-ray intensity data collected on an automatic diffractometer at room temperature. The final *R* value is 0·042. The structures reported by Vernon & Pepinsky and by Sprenkels have been confirmed and the positions of the hydrogen atoms determined. One set of ammonium ions exhibits a large thermal motion of the hydrogen atoms. A three-dimensional network of hydrogen bonds has been proposed.

Introduction

Lithium ammonium tartrate monohydrate (abbreviated as LAT), $LiNH_4C_4H_4O_6.H_2O$, exhibits ferroelectric activity below about 100°K (Matthias & Hulm, 1951; Merz, 1951). Although the structure of LAT at room temperature has been analysed previously (Vernon & Pepinsky, 1953; Sprenkels, 1956), more detailed knowledge of the structure was desired to elucidate the nature of the ferroelectric phase transition (Shirane, Jona & Pepinsky, 1955; Jona & Shirane, 1962). In the present study the positions of the hydrogen atoms have been determined, along with the refinement of the non-hydrogen atoms, by using three-dimensional X-ray intensity data collected on an automatic diffractometer.

Experimental

Single crystals of LAT were grown by slow evaporation from an aqueous solution containing lithium tartrate and ammonium tartrate in equimolar ratio. They are colourless prisms elongated along the *c* axis. The space group, $P2_12_12$, reported previously (Vernon & Pepinsky, 1953; Sprenkels, 1956) was confirmed. The unit-cell parameters were obtained from a least-squares procedure by minimizing the quantity $\sum w(\sin^2 \theta_{\rm obs} - \sin^2 \theta_{\rm cal})^2$, using values of 2θ measured on a diffractometer, where the weight was made proportional to $1/\sin^2 2\theta$. The lattice constants thus obtained are listed in Table 1, along with those given by Vernon & Pepinsky (1953) and Sprenkels (1956).

Table 1. *Unit-cell parameters of LAT at room temperature*

a	*b*	*c*	Reference
7·884 (6) Å	14·565 (8) Å	6·409 (4) Å	Present work*
7·86	14·60	6·47	Vernon & Pepinsky (1953)
7·878	14·642	6·426	Sprenkels (1956)

* λ(Mo $K\alpha$) = 0·71069 Å was used. The e.s.d.'s given in parentheses are referred to the last figure.

Intensity data were collected on a Rigaku automatic four-circle diffractometer controlled by a FACOM 270–20 computer with Mo $K\alpha$ radiation monochromated by a LiF crystal, using the ω–2θ scan technique. The dimensions of the crystal used were about $0·3 \times 0·3 \times 0·3$ mm. The scanning speed was 0·5° per min and the scan range $\Delta 2\theta$ was varied according to the relation: $\Delta 2\theta = 2° + 0·8° \tan \theta$. The background was measured for 30 sec at the beginning and end of each scan. As a check of the stability on the crystal and the instruments, three standard reflexions were monitored every 30 reflexions, and no significant variation was noticed in their intensities. 1890 independent reflexions corresponding to $\sin \theta/\lambda < 0·81$ Å^{-1} were measured and 132 of those, for which $|F_o| \le \sigma(|F_o|)$, were assigned zero intensity, where $\sigma(|F_o|)$ is the standard deviation estimated from counting statistics. Since the linear absorption coefficient is small (μ = 1·76 cm^{-1} for Mo $K\alpha$ radiation), no absorption correction was made.

Structure determination and refinement

The structure was solved independently of the previous works by the symbolic addition method (Karle & Karle, 1966). The specification of the origin and the assignment of the unknown symbols were as follows:

h	*k*	*l*	$\lvert E_o\rvert$	φ	
2	12	0	3·38	0	Origin assignment
9	0	4	3·12	$-\pi/2$	
0	11	2	2·49	$\pi/2$	
1	6	5	2·74	*a*	
1	17	2	2·48	*b*	
4	11	7	2·40	*c*	
6	6	3	2·38	*d*	

With these assignments, 77 phase angles of the reflexions for which $|E_o| \ge 1·8$ were determined by using the relationship $\varphi_{\mathbf{H}} \sim \langle \varphi_{\mathbf{K}} + \varphi_{\mathbf{H-K}} \rangle_{\mathbf{K}}$. The tangent formula was used to refine these phase angles, and phases for additional reflexions for which $|E_o| \ge 1·5$ were obtained.

The *E* map based on the phases obtained from the tangent formula revealed an approximate structure which showed that the structures reported by Vernon & Pepinsky (1953) and by Sprenkels (1956) were essentially correct. The *R* value was 0·25 at this stage. The structure refinement was then carried out by a series of least-squares calculations, first with individual isotropic temperature factors and then with anisotropic temperature factors, by using the blockdiagonal least-squares method, which reduced the *R* value to 0·068. A three-dimensional difference Fourier synthesis was calculated, which clearly showed the positions of all the hydrogen atoms. Least-squares calculations were carried out with these hydrogen atoms included with isotropic temperature factors, and the *R* value was reduced to 0·049.

Comparison between the observed and the calculated structure factors suggested that ten reflexions, indicated by a dagger in Table 5, were affected by extinction. The final refinement was made omitting them. It was terminated when the maximum shift of the parameters became less than one third of the estimated standard deviations (e.s.d.'s) for the non-hydrogen atoms, and less than the e.s.d.'s for the hydrogen atoms. Background fluctuation in the final difference map was less than 0·4 e.Å^{-3}. The final *R* value is 0·042 (or 0·049 if reflexions of zero intensity are included). In these calculations the following weighting scheme was adopted:

$$w = \begin{cases} 0·25 & \text{when } |F_o| < 2·0 \\ 1·0 & \text{when } |F_o| \le 20·0 \\ 20·0/|F_o| & \text{when } |F_o| > 20·0 . \end{cases}$$

Atomic scattering factors used for the oxygen, nitrogen, carbon, and lithium atoms were those listed in *International Tables for X-ray Crystallography* (1962); for the hydrogen atoms the values given by Stewart, Davidson & Simpson (1965) were used. All calculations were performed on a HITAC 5020E and a FACOM 230–60 computer using the *Universal Crystallographic Computing System* (1967).

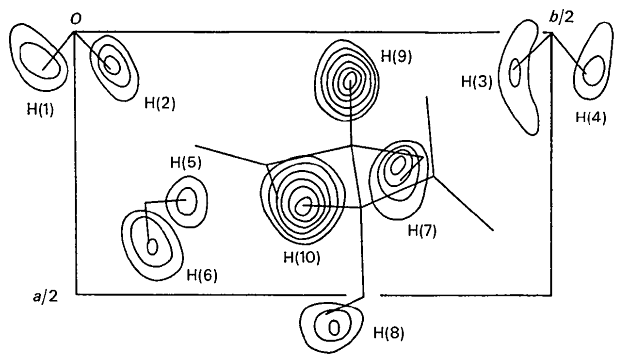

Fig. 1. Composite drawing of the final difference Fourier map viewed along the c axis. Contours are at intervals of 0·1 e.Å^{-3}, beginning at 0·2 e.Å^{-3}.

The final atomic parameters, together with their e.s.d.'s, are listed in Tables 2 and 3 for the non-hydrogen atoms and in Table 4 for the hydrogen atoms. The observed and calculated structure factors are given in Table 5. Fig. 1 shows the composite drawing of the hydrogen atoms as obtained from the difference map calculated by using the final atomic parameters of the non-hydrogen atoms.

Table 2. *Final atomic coordinates and their e.s.d.'s*

	x	y	z
O(1)	0·2176 (2)	0·1260 (1)	0·1878 (2)
O(2)	0·3134 (2)	0·2113 (1)	−0·0762 (2)
O(3)	0·3736 (2)	0·4384 (1)	0·6018 (3)
O(4)	0·1218 (2)	0·3692 (1)	0·6210 (3)
O(5)	0·2355 (2)	0·3662 (1)	0·0947 (2)
O(6)	0·5046 (2)	0·3163 (1)	0·3564 (2)
O(W)	0·3265 (2)	0·0731 (1)	0·6483 (3)
N(1)	0·0000	0·0000	−0·0534 (5)
N(2)	0·0000	0·5000	−0·0842 (5)
C(1)	0·2527 (2)	0·2011 (1)	0·1027 (3)
C(2)	0·2127 (2)	0·2885 (1)	0·2255 (2)
C(3)	0·3342 (2)	0·2984 (1)	0·4147 (2)
C(4)	0·2717 (2)	0·3756 (1)	0·5560 (3)
Li	0·1266 (5)	0·0780 (2)	0·4501 (6)

Results and discussion

Fig. 2 shows the stereoscopic view of the tartrate molecule obtained by the present analysis. The atomic numbering system adopted for the carbon and oxygen atoms is the same as that used for Rochelle salt (Beevers & Hughes, 1941). The bond lengths and angles in the tartrate molecule are given in Fig. 3, while those involving the hydrogen atoms are given in Table 6. The e.s.d.'s of the bond lengths and angles involving the carbon and oxygen atoms are about 0·002 Å and 0·14° respectively.

Table 3. *Thermal parameters and their e.s.d.'s* (× 10^4)

The thermal parameters are of the form:

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

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	89 (2)	14 (1)	105 (3)	−6 (1)	13 (2)	−2 (1)
O(2)	129 (3)	23 (1)	86 (3)	−9 (1)	40 (2)	−9 (1)
O(3)	61 (2)	14 (1)	182 (4)	−3 (1)	−12 (2)	−19 (1)
O(4)	67 (2)	29 (1)	147 (3)	−8 (1)	45 (2)	−27 (1)
O(5)	116 (2)	14 (1)	93 (3)	3 (1)	−28 (2)	6 (1)
O(6)	36 (1)	28 (1)	135 (3)	3 (1)	5 (2)	−11 (1)
O(W)	93 (2)	24 (1)	148 (4)	2 (1)	−13 (3)	−15 (1)
N(1)	93 (4)	26 (1)	132 (6)	6 (2)	0	0
N(2)	82 (3)	21 (1)	162 (6)	7 (2)	0	0
C(1)	49 (2)	14 (1)	72 (3)	−3 (1)	0 (2)	−6 (1)
C(2)	46 (2)	12 (1)	72 (3)	2 (1)	−5 (2)	−3 (1)
C(3)	43 (2)	11 (1)	69 (3)	1 (1)	1 (2)	−1 (1)
C(4)	54 (2)	12 (1)	78 (3)	0 (1)	−1 (2)	−6 (1)
Li	68 (5)	19 (1)	112 (7)	−5 (2)	6 (5)	6 (3)

Table 4. *Final parameters of the hydrogen atoms*

The e.s.d.'s for the positional parameters are in parentheses. The thermal parameters, B, are of the form: $\exp[-B(\sin\theta/\lambda)^2]$.

	x	y	z	B	$\sigma(B)$	Bonded to
H(1)	0·059 (4)	−0·034 (2)	−0·139 (5)	2·5	0·7	N(1)
H(2)	0·075 (4)	0·037 (2)	0·027 (6)	3·2	0·9	N(1)
H(3)	0·066 (6)	0·462 (3)	−0·032 (7)	6·6	1·6	N(2)
H(4)	0·078 (7)	0·530 (4)	−0·190 (8)	9·9	1·8	N(2)
H(5)	0·320 (5)	0·112 (3)	0·746 (6)	6·2	1·0	O(W)
H(6)	0·409 (5)	0·074 (2)	0·581 (6)	6·2	0·7	O(W)
H(7)	0·284 (4)	0·342 (2)	−0·013 (6)	4·3	0·9	O(5)
H(8)	0·552 (4)	0·259 (2)	0·346 (4)	2·4	0·6	O(6)
H(9)	0·095 (3)	0·288 (2)	0·262 (4)	1·2	0·4	C(2)
H(10)	0·327 (3)	0·238 (2)	0·488 (4)	1·2	0·5	C(3)

Table 5. *Final observed and calculated structure factors* (×10)

Reflexions indicated by a dagger (†) seemed to be affected by extinction and were omitted in the final stage of refinement, and those indicated by an asterisk (*) were given the weight 0·25.

Table 5 (*cont.*)

Tartrate molecule

The bond lengths and angles in the tartrate molecule obtained in this work are on the whole the same as those given by Sprenkels (1956) and are close to those found in Rochelle salt (Beevers & Hughes, 1941; Krstanovič, Okaya & Pepinsky, 1960). The average values of the four C–O bonds of the two carboxylate groups, of the two C–O bonds of the carbinol groups,

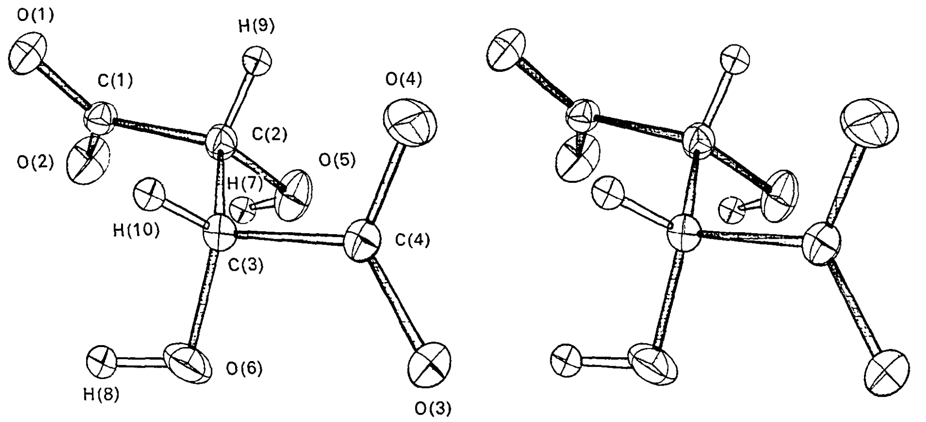

Fig. 2. Stereoscopic view of the tartrate molecule. The non-hydrogen atoms are shown as 50% probability ellipsoids. This figure was drawn by using the program *ORTEP* (Johnson, 1965).

Table 6. *Bond lengths and angles involving the hydrogen atoms*

N(1)-H(1)	0·90 Å	C(2)-O(5)-H(7)	102°
N(1)-H(2)	0·91	C(3)-O(6)-H(8)	105
N(2)-H(3)	0·83		
N(2)-H(4)	1·01	C(1)-C(2)-H(9)	107
		C(3)-C(2)-H(9)	113
O(*W*)-H(5)	0·87	O(5)-C(2)-H(9)	104
O(*W*)-H(6)	0·87	C(2)-C(3)-H(10)	105
O(5)—H(7)	0·88	C(4)-C(3)-H(10)	110
O(6)—H(8)	0·89	O(6)-C(3)-H(10)	111
		⟨e.s.d.⟩ =	1·6
C(2)-H(9)	0·99		
C(3)-H(10)	0·99		
⟨e.s.d.⟩ =	0·04		

and of the three C–C bonds are 1·254 ± 0·003, 1·417 ± 0·002, and 1·526 ± 0·004 Å respectively. There are three planar groups in the tartrate molecule, that is two carboxylate groups and the C–C chain. The equations of the least-squares planes and the deviations of the atoms from the planes are given in Table 7.

Ammonium ion

There are four ammonium ions in the unit cell. These ions occupy two sets of different equivalent positions on the twofold symmetry axes, and the distribution of the hydrogen atoms around the central nitrogen atoms is different in the two sets. As seen in Table 3, the temperature factors of the two types of nitrogen atoms, N(1) and N(2), do not differ much, while those of the hydrogen atoms bonded to these nitrogen atoms show a pronounced difference as seen in Table 4 and Fig. 1. This suggests the possibility that there is a certain disorder in the orientation of the ammonium ion, $NH_4^+(2)$.

Hydrogen bonds and packing

Figs. 4 and 5 illustrate the crystal structure projected onto (001) and (100) respectively. They show the packing of the molecules and the hydrogen bonds (broken lines). As can be seen in these figures, there is a three-dimensional network of hydrogen bonds in the crystal. The dimensions of the hydrogen bonds

Table 7. *Least-squares planes in the tartrate molecule*

The equations of the planes are of the form: $lX+mY+nZ=D$, where direction cosines, l, m and n, are referred to the axes a, b and c, and X, Y and Z are expressed in Å, D being the origin-to-plane distance.

Carboxylate group I

$$0{\cdot}9225X-0{\cdot}0376Y+0{\cdot}3840Z=1{\cdot}9776$$

Deviations of the atoms from the plane

O(1) −0·001, O(2) −0·001, C(1) 0·003, C(2) −0·001 Å

Carboxylate group II

$$0{\cdot}3115X-0{\cdot}5164Y+0{\cdot}7977Z=0{\cdot}6942$$

Deviations of the atoms from the plane

O(3) 0·003, O(4) 0·003, C(3) 0·002, C(4) −0·008 Å

C–C chain

$$0{\cdot}6100X+0{\cdot}5809Y-0{\cdot}5390Z=2{\cdot}6332$$

Deviations of the atoms from the plane

C(1) 0·071, C(2) −0·074, C(3) −0·066, C(4) 0·069 Å

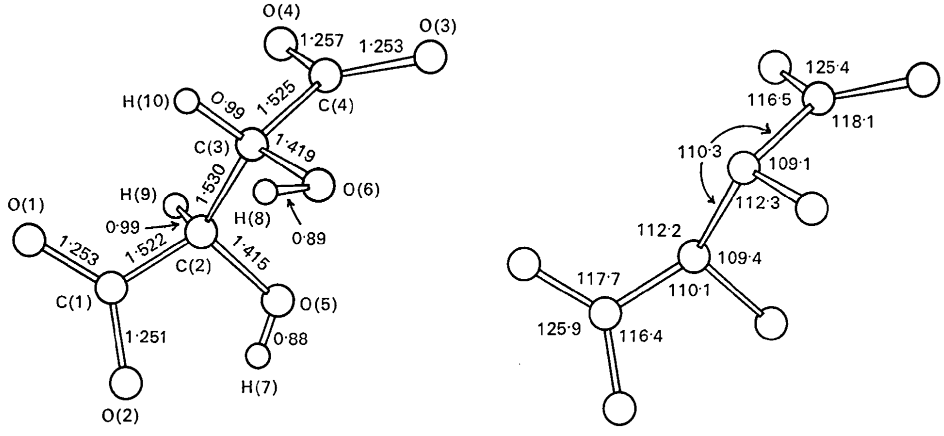

Fig. 3. Bond lengths (left) and angles (right) in the tartrate molecule.

and other close contacts are listed in Table 8. The lithium ion is surrounded by five oxygen atoms, and the shortest Li···O distance is 1·957 Å. The hydroxyl group, O(5)–H(7), which was considered to play an important role in the ferroelectric effect of Rochelle salt (Shirane, Jona & Pepinsky, 1955), forms an intramolecular hydrogen bond with O(2) as can be seen in Figs. 4 and 5. The atom O(5) is also linked to N(1) and N(2) by hydrogen bonds as can be seen in Table 8 and Figs.4 and 5.

On the ferroelectric effect

In the ferroelectric phase of LAT spontaneous polarization takes place along the *b* axis. According to

Table 8. *Dimensions of the hydrogen bonds and other close contacts*

X	*Y*	at*	*X*–*Y*	H–*Y*	∠*X*–H···*Y*
N(1)—H(1)···	O(5)	IV (0$\bar{1}\bar{1}$)	2·867 Å	2·23 Å	125°
N(1)—H(2)···	O(1)	I (000)	2·950	2·04	174
N(2)—H(3)···	O(5)	I (000)	2·925	2·10	149
N(2)—H(4)···	O(1)	IV (00$\bar{1}$)	2·961	2·13	137
O(*W*)–H(5)···	O(2)	I (001)	2·680	1·82	171
O(*W*)–H(6)···	O(4)	III (000)	3·018	2·29	142
O(5)—H(7)···	O(2)	I (000)	2·583	1·96	127
O(6)—H(8)···	O(4)	III (000)	2·859	1·99	164
N(2)·········	O(4)	I (00$\bar{1}$)	2·850		
O(*W*)········	O(3)	IV (0$\bar{1}$0)	2·984		
O(3)·········	O(3)	II (000)	2·682		
O(6)·········	O(2)	III (00$\bar{1}$)	3·051		
Li···········	O(1)	I (000)	1·957		
Li···········	O(*W*)	I (000)	2·026		
Li···········	O(3)	III ($\bar{1}$00)	2·036		
Li···········	O(6)	III ($\bar{1}$00)	2·199		
Li···········	O(3)	IV (0$\bar{1}$0)	2·060		

* The Roman numerals indicate the symmetry operations:

I	x	y	z
II	$1-x$	$1-y$	z
III	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$
IV	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$1-z$.

The figures in parentheses denote the translation along the *a*, *b* and *c* axes respectively.

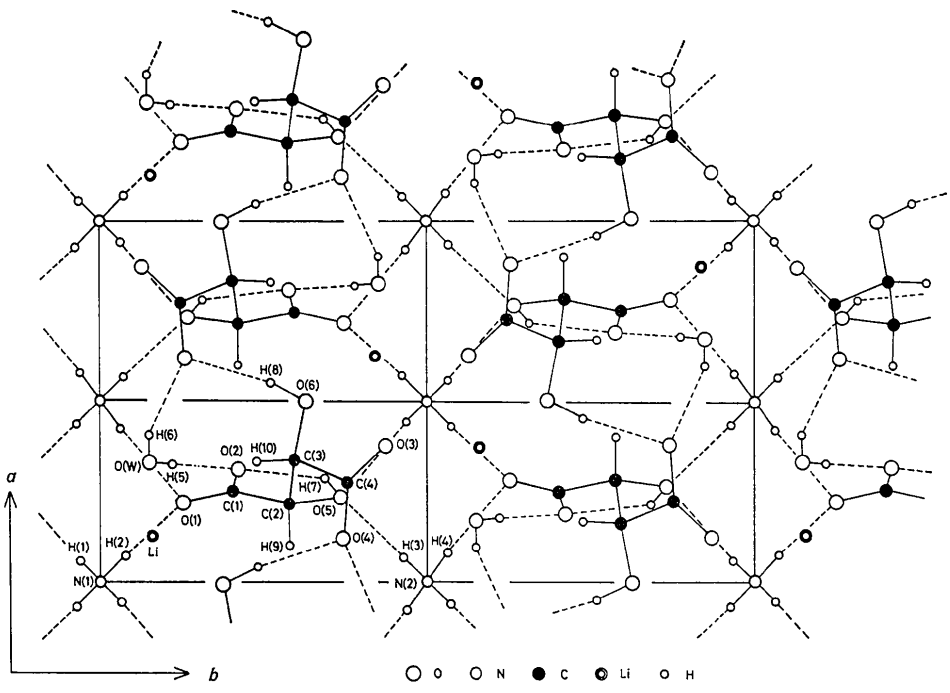

Fig. 4. Structure projected onto (001). The hydrogen bonds are shown as broken lines.

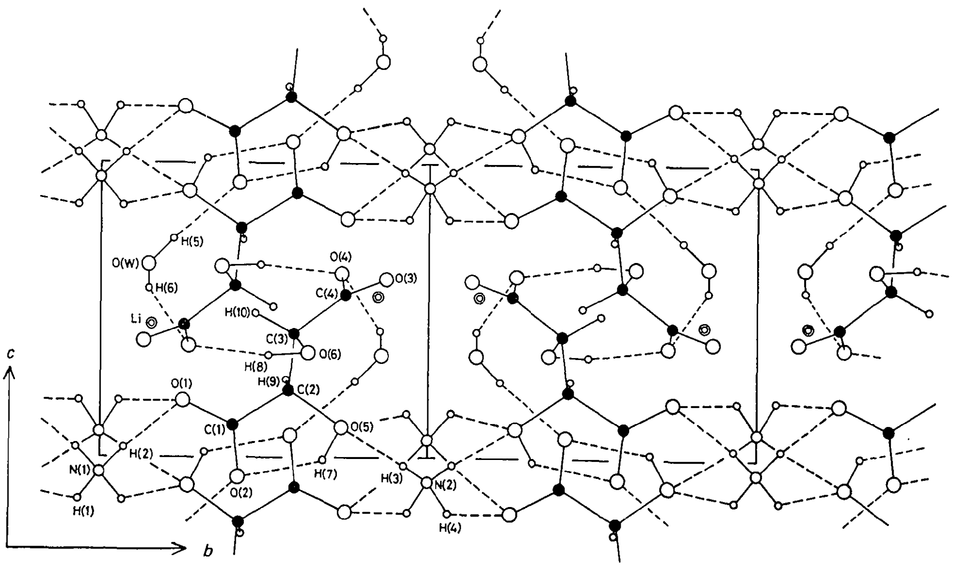

Fig. 5. Structure projected onto (100).

Shirane, Jona & Pepinsky (1955), neutron diffraction experiments at low temperature, (about 80°K) show the occurence of *h*00 reflexions with *h* odd. This means the space group is $P12_11$ in the ferroelectric phase.

Megaw (1957) pointed out the possibility that LAT is essentially antiferroelectric along the *a* axis, resulting in weak ferroelectricity along the *b* axis. It seems difficult, however, to discuss the mechanism of ferroelectricity of LAT only on the basis of the data presented in this paper. Accurate structure analysis is in progress on Rochelle salt and ammonium Rochelle salt in our laboratories to provide more information.

The authors wish to thank Professor Y. Makita of Science University of Tokyo for supplying valuable information on LAT, and Drs T. Ueki and T. Hamanaka for their helpful advice. They are indebted to the Computer Centre of the University of Tokyo and the Hokkaido University Computing Centre for making the HITAC 5020E and the FACOM 230-60 computers available.

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