

## Refinement of Pyroelectric Lithium Perchlorate Trihydrate

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**Abstract.**  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ , hexagonal,  $P6_3mc$ ,  $a = 7.7192(4)$ ,  $c = 5.4531(5)$  Å,  $V = 281.40$  Å<sup>3</sup>,  $Z = 2$ ,  $d_m = 1.89$ ,  $d_x = 1.89$  g cm<sup>-3</sup>,  $\mu(\text{Cu } K\alpha) = 60.2$  cm<sup>-1</sup>. The absolute configuration of a crystal has been determined by means of anomalous scattering using a full three-dimensional set of diffractometer data collected with Cu  $K\alpha$  radiation. The  $R$  value for the correct configuration is 0.0170. The pyroelectric coefficient at room temperature is  $3.9 \times 10^{-6}$  Cm<sup>-2</sup> deg<sup>-1</sup>. The piezoelectric  $d_{33}$  coefficient was also detected.

**Introduction.** The determination of the absolute signs of tensor-property coefficients of noncentrosymmetric crystals provides an insight into the relation between the structure and macroscopic properties of a material (Abrahams, 1975). A prerequisite for such a study is an accurate structure determination. Further, if the anomalous scattering of the radiation used is not negligible, the absolute configuration of the crystal should be determined in the course of the least-squares refinement.

$\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  has been the subject of several X-ray and neutron diffraction studies (Sequeira, Bernal, Brown & Faggiani, 1975, and references therein). The most accurate of these studies is that of Sequeira *et al.* However, it is not stated in that paper whether the absolute configuration in the X-ray case was determined. Such neglect in polar space groups may introduce parameter errors (Cruickshank & McDonald, 1967). Of particular interest in the present case are the possible errors in the polar direction ['polar dispersion errors' (Zalkin, Hopkins & Templeton, 1966)]. As a first step in the study of some physical properties of this material, it was decided to refine the structure based on a full three-dimensional set of Cu  $K\alpha$  X-ray data.

The unit-cell dimensions were determined from a powder photograph recorded with a Guinier–Hägg XDC-700 focusing camera with Cu  $K\alpha_1$  radiation ( $\lambda = 1.54059$  Å) and using Si ( $a = 5.431065$  Å at 25°C) as an internal standard. A least-squares refinement of the observed  $\theta$  values from 28 reflexions provided the parameters given above. These values are in good

agreement with those reported by Swanson, Gilfrich, Cook, Stinchfield & Parks (1959).

The crystal used for the data collection was ground to a sphere of radius 0.121(5) mm ( $\mu R = 0.728$ ). The intensity data were collected at room temperature on a Stoe–Philips computer-controlled four-circle diffractometer with a graphite monochromator using Cu  $K\alpha$  radiation and an  $\omega$ – $2\theta$  step-scan technique. Variable scan time and filter selection were used with the intention of measuring all reflexions with approximately the same precision. Three standard reflexions were measured at regular intervals to provide a check on the stability of the experiment. These indicated a few per cent decrease in intensity and a larger spread (about  $\pm 5\sigma_{\text{count}}$ ) than is usually observed. All accessible reflexions with  $\sin \theta/\lambda$  less than 0.56 Å<sup>-1</sup> were measured, many of them twice owing to the observed variation in the standards. A total of 1517 reflexions were measured. After correction for the observed decrease in the standards, the intensities of equivalent reflexions within the two subsets  $\{hkl\}$  and  $\{\bar{h}\bar{k}\bar{l}\}$  were averaged, which resulted in 175 independent observations. The intensities were corrected for Lorentz, polarization and absorption effects. The transmission factors varied between 0.35 and 0.40. The variances of the intensities (before averaging) were estimated using the procedure of McCandlish, Stout & Andrews (1975), including contributions from counting statistics, fluctuations observed in the standards and uncertainty of the scaling parameter. The variance estimated directly from deviations among equivalent intensities within a form was used if it was larger than the variance derived for the averaged intensity. In connexion with

Table 1. Atomic coordinates ( $\times 10^4$ ) in  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$

	x	y	z
Li	0*	0	2218 (14)
Cl	$\frac{1}{3}$	$\frac{2}{3}$	0†
O(1)	$\frac{1}{3}$	$\frac{1}{3}$	2617 (6)
O(2)	4346 (1)	–4346	–894 (4)
O(3)	1218 (1)	–1218	4726 (2)
H	2290 (22)	3106 (32)	4774 (48)

\* Parameters given without an e.s.d. were not refined owing to symmetry restrictions.

† Fixed to define the origin.

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Table 2. Thermal parameters ( $\times 10^4$ ) in  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ 

The form of the temperature factor is  $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$ . The r.m.s. components  $R_i$  ( $\times 10^3$ ) of thermal displacement along the ellipsoid axes are also listed. The hydrogen isotropic temperature factor  $B$  is  $1.37$  (48)  $\text{\AA}^2$ .

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$R_1$ ( $\text{\AA}$ )	$R_2$ ( $\text{\AA}$ )	$R_3$ ( $\text{\AA}$ )
Li	130 (6)	130*	235 (15)	65	0	0	172 (4)	172 (4)	188 (6)
Cl	90 (2)	90	237 (4)	45	0	0	143 (2)	143 (2)	189 (2)
O(1)	217 (5)	217	211 (15)	109	0	0	178 (6)	222 (3)	222 (3)
O(2)	154 (3)	154	402 (7)	97 (3)	24 (2)	-24	154 (3)	194 (2)	250 (2)
O(3)	124 (3)	124	254 (5)	72 (3)	-1 (2)	1	153 (3)	172 (3)	196 (2)

\* Parameters given without an e.s.d. were not refined owing to symmetry restrictions.

Table 3. Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ 

Li—O(3) ( $\times 3$ )	2.127 (5)*	O(3)—Li—O(3)	83.1 (2)
Li—O(3)' ( $\times 3$ )	2.121 (5)	O(3)—Li—O(3)'	96.8 (2)
		O(3)—Li—O(3)''	179.8 (3)
		O(3)'—Li—O(3)''	83.4 (2)
Cl—O(1)	1.427 (3)	O(1)—Cl—O(2)	109.8 (1)
Cl—O(2) ( $\times 3$ )	1.439 (2)	O(2)—Cl—O(2)	109.1 (1)
O(3)—H ( $\times 2$ )	0.725 (15)	H—O(3)—H	103 (4)
O(3)···O(2) ( $\times 2$ )	2.994 (1)	O(3)—H···O(2)	160 (3)
O(3)···O(1)	3.053 (2)	O(3)—H···O(1)	111 (2)
O(2)···H	2.303 (16)		
O(1)···H	2.715 (24)		

\* The e.s.d.'s are based on the variance-covariance matrix from the last least-squares refinement. The uncertainties in the unit-cell dimensions are also included.

the absorption correction, a contribution to the total variance was added. This estimation is associated with errors in measurement of the crystal dimensions and uncertainty in the linear absorption coefficient.

The structure was refined, starting with the parameters reported by Sequeira *et al.*, by minimizing  $\sum w(|F_o| - |F_c|)^2$  using the full-matrix least-squares program *UPALS* (Lundgren, 1976). Each reflexion was assigned a weight  $w = 1/\sigma^2(F)$ , where  $\sigma(F) = \sigma(F^2)/2F$ . Refinement of the structure using the coordinates listed in Table 1 together with the Miller indices of the 175 independent structure factors resulted in  $R(F) = 0.0170$ ,  $R_w(F) = 0.0233$  and the standard deviation of an observation of unit weight  $S = 0.376$ .\* Refinement with the opposite polarity resulted in  $R(F) = 0.0465$ ,  $R_w(F) = 0.1027$  and  $S = 1.654$ . The correct absolute configuration thus corresponds unambiguously to the first choice of coordinates and Miller indices. The total number of parameters varied was 26, including an isotropic extinction correction with a final coefficient of 0.275 (27) (Coppens & Hamilton, 1970). The atomic scattering factors for  $\text{Li}^+$ ,

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32926 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

$\text{Cl}^0$ ,  $\text{O}^{-0.25}$  (by interpolation) and  $\text{H}^0$  together with corrections for anomalous scattering were taken from *International Tables for X-ray Crystallography* (1974). The final fit between  $F_o$  and  $F_c$  was examined by means of the  $\delta R = (F_o - F_c)/\sigma(F_o)$  normal probability plot (Abrahams & Keve, 1971). In the absence of systematic error in the data or model and for correctly estimated variances this plot should be linear with a zero intercept and unit slope. In the present case the plot is linear, except for a few points at the extremes, with a zero intercept but with a slope of 0.34 indicating an overestimation of  $\sigma(F)$  as is also indicated by the value of  $S$ . The final positional parameters are given in Table 1, thermal parameters in Table 2, and the bond distances and angles in Table 3.

**Discussion.** In the X-ray and neutron study by Sequeira *et al.* (1975) a set of 'best values' were derived for the heavy-atom positional parameters by taking a weighted average of the two determinations and a set of

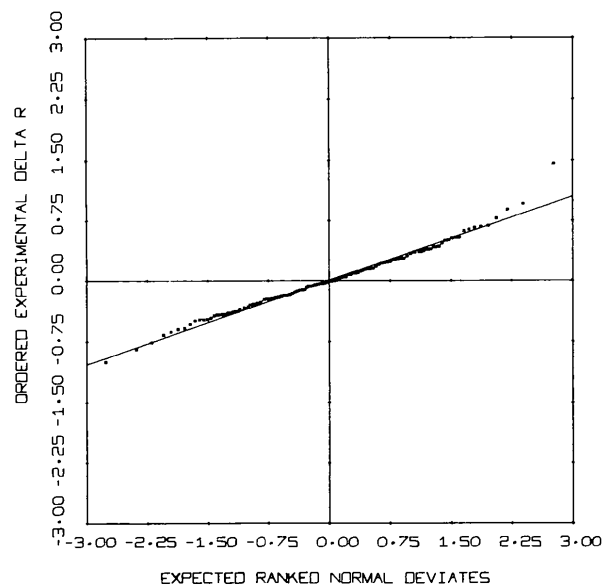


Fig. 1. Normal probability plot of the ordered residuals  $(F_o - F_c)/\sigma(F)$ .

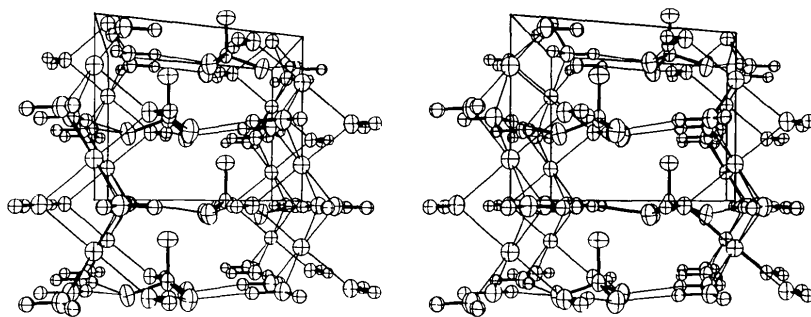


Fig. 2. Stereoscopic view of the  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  structure prepared with the program *ORTEP*. The origin is at the lower, left-hand corner with the *a* axis pointing towards the reader, the *b* axis to the right and the *c* axis up. Covalent bonds are filled, ionic and H bonds are drawn as single lines. The ellipsoids are scaled to include 50% probability.

X-ray-determined parameters by Prosen (1955). A comparison of these 'best values' with the present set of parameters using a half-normal probability plot (Abrahams & Keve, 1971) may indicate the presence of some systematic error. For this reason and because of the linear plot of Fig. 1, it is preferred not to average the present parameters with the previously reported values.

The  $\text{Li}^+$  ions are situated on sixfold screw axes, octahedrally coordinated to water O atoms. The octahedron is rather symmetrical (see Table 1 and Fig. 2). Each water O is coordinated to two  $\text{Li}^+$  ions. Chains of  $\text{Li}(\text{H}_2\text{O})_6^+$  octahedra sharing faces are thus formed along the *c* axis.

The Cl and O(1) atoms of the  $\text{ClO}_4^-$  ions are located on threefold axes, with the Cl—O(1) bonds pointing in the positive *c* direction (Fig. 2). The two crystallographically different Cl—O bonds are unequal at the limit of significance [1.427 (3), 1.439 (2) Å]. This result does not agree with that of Sequeira *et al.* (1975), who found these two bonds to be of the same length. As was already pointed out by Sequeira *et al.*, a difference in these two bond lengths would not be surprising considering the different chemical environment of the two O atoms. The water molecules (the O atoms on mirror planes) are hydrogen-bonded to O(2), with an O(3)···O(2) distance of 2.994 (1) Å. The neutron-diffraction-determined H···O(2) distance is 2.04 Å, and the O(3)—H···O(2) angle is 164° (Sequeira *et al.*, 1975). With the generally accepted criterion for hydrogen bonding, *i.e.* the H···O distance should be less than the sum of the van der Waals radii of H and O, the O(3)···O(1) contact of 3.053 (2) Å should not be considered as a hydrogen bond in contradiction to the proposal by Sequeira *et al.* The H···O(1) distance as reported in the neutron study mentioned above is 2.62 Å and the O(3)—H···O(1) angle is 106°. An H···O contact should be shorter than 2.4 Å to be taken as a possible indication of hydrogen bonding (Baur, 1972). The observed distortion of the perchlorate ion, with Cl—O(2) being 0.012 (4) Å longer than

Cl—O(1), is expected as O(2) is hydrogen-bonded to the water molecules whereas O(1) is not.

The magnitude of the unique pyroelectric coefficient in  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  was determined to be  $3.9 (2) \times 10^{-6} \text{ Cm}^{-2} \text{ deg}^{-1}$  over the temperature range 265–293 K. The experimental method using an operational amplifier has been described by Abrahams (1975). The piezoelectric  $d_{33}$  coefficient was also detected. A full report of these experiments and the relation of the absolute signs of these tensor coefficients with the atomic arrangement is in progress.

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## 2,3-Dimethyl-4a,9a-diaza-1,4,4a,9,9a,10-hexahydroanthracene-9,10-dione\*

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**Abstract.** C<sub>14</sub>H<sub>14</sub>O<sub>2</sub>N<sub>2</sub>, monoclinic,  $P2_1/c$ ,  $a = 12.216$  (2),  $b = 12.627$  (2),  $c = 7.890$  (1) Å,  $\beta = 101.62$  (1)°,  $Z = 4$ ,  $D_x = 1.34$  g cm<sup>-3</sup>, Cu  $K\alpha$  radiation.  $R = 0.056$  for 1888 observed reflexions. The molecule can be described as a 'strip' twisted about 15° from end to end.

**Introduction.** The determination of the crystal structure of the title compound is a continuation of a study on tetracycline analogues mentioned in a previous work (Foces-Foces, Cano & García-Blanco, 1977).

\* Crystal and Molecular Structure of Diazapolycyclic Compounds. III.

A crystal 0.40 × 0.20 × 0.40 mm was used, and the lattice parameters and intensities were measured on a Philips PW 1100 diffractometer, with graphite-monochromated Cu  $K\alpha$  radiation ( $\omega/2\theta$  scan mode); no decomposition was observed. Of the 2036 reflexions recorded with  $\theta < 65^\circ$ , 1888 had  $I > 2\sigma(I)$  and were classified as observed. Lorentz and polarization factors were applied but no absorption correction was made ( $\mu = 7.5$  cm<sup>-1</sup>). The structure was solved with *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974) and refined by full-matrix least-squares methods. All H atoms were located in a difference Fourier map. A mixed refinement converged to  $R = 0.056$  and  $R_w = 0.068$ . The reflexions were weighted as follows:  $w = K/(f|F_o|)^2 f(S)$  where  $f(F_o) = 0.25 + 0.05|F_o|$  and

Table 1. Final positional parameters ( $\times 10^4$ , for H  $\times 10^3$ ) with their standard deviations and bond distances (Å) for the hydrogen atoms

	x	y	z		x	y	z	Bond length
C(1)	5525 (1)	5309 (1)	2526 (2)	H(1a)	555 (2)	458 (2)	273 (3)	0.94 (2)
C(2)	6618 (1)	5751 (1)	3442 (2)	H(1b)	541 (2)	543 (2)	132 (3)	0.95 (2)
C(3)	6675 (1)	6566 (1)	4513 (2)	H(4a)	571 (2)	780 (2)	456 (3)	0.93 (2)
C(4)	5659 (1)	7097 (1)	4876 (2)	H(4b)	562 (2)	699 (2)	611 (3)	1.00 (2)
C(5)	1604 (1)	7329 (2)	3486 (2)	H(5)	164 (2)	800 (2)	397 (3)	0.93 (3)
C(6)	583 (2)	6853 (2)	2886 (3)	H(6)	-8 (2)	721 (2)	293 (4)	0.93 (3)
C(7)	523 (2)	5856 (2)	2115 (3)	H(7)	-20 (2)	556 (2)	167 (3)	0.96 (2)
C(8)	1483 (1)	5326 (2)	1960 (2)	H(8)	144 (2)	464 (2)	147 (4)	0.95 (3)
C(9)	3546 (1)	5245 (1)	2374 (2)	H(15a)	754 (2)	515 (2)	186 (4)	0.87 (3)
C(10)	3671 (1)	7292 (1)	3989 (2)	H(15b)	761 (3)	450 (3)	331 (4)	0.91 (3)
C(11)	2580 (1)	6799 (1)	3319 (2)	H(15c)	832 (2)	545 (2)	352 (4)	0.95 (3)
C(12)	2521 (1)	5799 (1)	2577 (2)	H(16a)	785 (2)	777 (2)	507 (4)	0.95 (3)
N(13)	4595 (1)	6732 (1)	3831 (2)	H(16b)	842 (2)	669 (2)	544 (3)	0.98 (3)
N(14)	4539 (1)	5701 (1)	3125 (2)	H(16c)	774 (2)	706 (2)	673 (4)	0.99 (3)
C(15)	7602 (1)	5189 (2)	2983 (2)					
C(16)	7731 (1)	7079 (2)	5477 (2)					
O(17)	3528 (1)	4410 (1)	1565 (1)					
O(18)	3766 (1)	8161 (1)	4720 (2)					