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Lithium Hydrogen Phthalate–Methanol

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Abstract. $LiHC_8O_4H_4.CH_3OH$, triclinic, $P\bar{1}$, a = 13·692 (3), b = 8·023 (2), c = 8·467 (2) Å, α = 95·29 (3), β = 96·31 (3), γ = 86·72 (3)°, Z = 4, D_x = 1·474 g cm^{-3}. The structure was solved by direct methods and was refined to R = 0·038 from 2824 independent observed X-ray reflexions. Each of the two Li atoms is coordinated to four O atoms in a tetrahedral configuration. The Li—O distances range from 1·918 to 2·059 Å. Each of the two symmetrically independent hydrogen phthalate molecules exhibits a very short intramolecular hydrogen bond. The bond lengths are 2·386 (3) and 2·382 (3) Å respectively.

Introduction. The structures of about ten acid salts of phthalic acid have so far been determined. Only two of them, $Cu(HC_8O_4H_4)_2.2H_2O$ (Biagini Cingi, Guastini, Musatti & Nardelli, 1969) and $LiHC_8O_4H_4.2H_2O$ (Gonschorek & Küppers, 1975), form very short intramolecular hydrogen bonds with distances of about 2·40 Å between the O atoms of the two carboxylic groups of a particular molecule. Consequently, the hydrogen phthalate molecule attains a nearly planar configuration. In order to detect further examples of such very short hydrogen bonds, the structure of the present crystal species was investigated.

Single crystals were grown by evaporation of the solvent from a methanolic solution where phthalic acid and Li_2CO_3 were dissolved in stoichiometric proportions. The crystals are obtained as $\{10\bar{1}\}$ plates which are predominantly bounded by the faces {100} and {010}. Sometimes small faces {101}, $\{1\bar{1}\bar{1}\}$ and $\{11\bar{1}\}$ are observed. Frequently twinning occurs where $(10\bar{1})$ is the twinning plane. The crystals decompose in air; they are stable, however, if kept under a contaminating oil film.

Lattice parameters were determined by least-squares refinement from Bragg angles of several selected reflexions which were measured by an automatic diffractometer at 20°C. Intensities of 6127 X-ray reflexions (with $\theta < 27°$) from a specimen with a mean diameter of 0·4 mm were collected by an automatic Hilger & Watts Y290 four-circle diffractometer using Mo $K\alpha$ radiation. No absorption correction was applied.

The structure was solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). Refinement and further calculations were performed by *SHELX* 76 (Sheldrick, 1976). The atomic parameters were refined from 2824 independent reflexions with $I > 3\sigma$ by full-matrix least-squares procedures (anisotropic temperature parameters for the non-hydrogen atoms being assumed) to a weighted R value of 0·038 (unweighted 0·043). Reciprocal standard deviations were used as weights. Atomic scattering factors were taken from *International Tables for X-ray Crystallog-*

Table 1. *Fractional atomic coordinates* ($\times 10^4$)

Standard deviations given in parentheses refer to the last significant digits in the parameter values.

	x	y	z
C(1)	−1013 (2)	5963 (3)	6154 (3)
C(2)	−1644 (2)	4672 (3)	6247 (3)
C(3)	−1376 (2)	3370 (3)	7174 (3)
C(4)	−462 (2)	3317 (3)	8044 (4)
C(5)	174 (2)	4579 (3)	7987 (3)
C(6)	−81 (2)	5916 (3)	7060 (2)
C(7)	−1414 (2)	7228 (3)	5016 (3)
C(8)	716 (2)	7162 (3)	7129 (3)
C(11)	6034 (2)	4394 (3)	8762 (3)
C(12)	6407 (2)	2932 (3)	9421 (3)
C(13)	5908 (2)	1454 (3)	9150 (3)
C(14)	5013 (2)	1433 (3)	8212 (3)
C(15)	4627 (2)	2874 (3)	7565 (3)
C(16)	5118 (2)	4374 (3)	7814 (3)
C(17)	6667 (2)	5898 (3)	9183 (3)
C(18)	4584 (2)	5833 (3)	7036 (3)
O(1)	−2081 (1)	6880 (2)	3967 (2)
O(2)	−1064 (1)	8708 (2)	5153 (2)
O(3)	487 (1)	8660 (2)	6738 (2)
O(4)	1566 (1)	6759 (2)	7607 (2)
O(11)	7253 (1)	5927 (2)	10413 (2)
O(12)	6612 (1)	7069 (2)	8260 (2)
O(13)	5073 (1)	7016 (2)	6645 (2)
O(14)	3676 (1)	5848 (2)	6755 (2)

Table 1 (*cont.*)

	x	y	z
O*M*(1)	7097 (1)	933 (2)	3994 (3)
C*M*(1)	6601 (2)	520 (4)	5271 (4)
O*M*(2)	8142 (2)	8974 (3)	11073 (2)
C*M*(2)	8486 (2)	9449 (4)	9678 (4)
Li(1)	8296 (3)	−37 (5)	3258 (5)
Li(2)	7444 (3)	5050 (5)	2479 (5)
H(1)	−316 (28)	8781 (47)	6094 (46)
H(2)	7711 (20)	4716 (33)	5595 (32)
H(3)	8184 (23)	2493 (41)	7220 (38)
H(4)	9752 (21)	2443 (37)	8690 (35)
H(5)	845 (19)	4462 (32)	8589 (32)
H(11)	5905 (28)	7043 (46)	7398 (45)
H(12)	7059 (19)	2907 (31)	104 (30)
H(13)	6231 (18)	485 (32)	9575 (30)
H(14)	4701 (21)	357 (37)	8001 (35)
H(15)	3963 (19)	2848 (32)	6874 (31)
HO*M*(1)	6869 (23)	1823 (41)	3654 (38)
HO*M*(2)	7908 (24)	8231 (42)	961 (40)
H*M*(11)	2948 (33)	10354 (58)	4202 (54)
H*M*(12)	6005 (39)	10214 (67)	4878 (64)
H*M*(13)	6511 (34)	1572 (64)	6057 (60)
H*M*(21)	8619 (37)	647 (69)	−87 (61)
H*M*(22)	8954 (34)	8535 (60)	−761 (55)
H*M*(23)	7967 (30)	9567 (50)	−1119 (50)

raphy (1962). The final positional parameters are listed in Table 1.*

Discussion. Fig. 1 shows a stereoscopic view of the unit cell drawn by *ORTEP* (Johnson, 1965). Some atoms of neighbouring cells are included in order to characterize the complete environment of the Li ions. All of the H atoms were drawn with a uniform radius of 0·1 Å.

The two hydrogen phthalate molecules of the asymmetric unit are packed approximately parallel to each other. The equations of the least-squares planes through the C atoms are, respectively, $-0{\cdot}3876x_1 + 0{\cdot}4985x_2 + 0{\cdot}7754x_3 = -2{\cdot}8231$ and $-0{\cdot}4715x_1 + 0{\cdot}2362x_2 + 0{\cdot}8496x_3 = -6{\cdot}1386$, if referred to a Cartesian coordinate system with $\mathbf{e}_1 \parallel \mathbf{a}^*$, $\mathbf{e}_3 \parallel \mathbf{c}$, $\mathbf{e}_2 \parallel \mathbf{e}_3 \times \mathbf{e}_1$. The angle between the normals is 16·4°.

Table 2. *Bond lengths* (Å) *and angles* (°) *involving the* Li *ions*

Li(1)–O(2)	2·059 (4)	Li(2)–O(1)	1·936 (4)
Li(1)–O(3)	2·050 (4)	Li(2)–O(4)	1·929 (5)
Li(1)–O*M*(1)	1·918 (5)	Li(2)–O(11)	1·931 (4)
Li(1)–O*M*(2)	1·939 (5)	Li(2)–O(14)	1·931 (4)
O(2)–Li(1)–O(3)	92·0 (2)	O(1)–Li(2)–O(4)	110·2 (2)
O(2)–Li(1)–O*M*(1)	103·4 (2)	O(1)–Li(2)–O(11)	105·8 (2)
O(2)–Li(1)–O*M*(2)	123·8 (2)	O(1)–Li(2)–O(14)	109·3 (2)
O(3)–Li(1)–O*M*(1)	121·9 (2)	O(4)–Li(2)–O(11)	107·8 (2)
O(3)–Li(1)–O*M*(2)	101·5 (2)	O(4)–Li(2)–O(14)	106·1 (2)
O*M*(1)–Li(1)–O*M*(2)	113·8 (2)	O(11)–Li(2)–O(14)	117·6 (2)

The Li ions are in tetrahedral coordination which is characterized by the distances and angles given in Table 2.

Apparently, the coordination polyhedron of Li(2) more nearly resembles a regular tetrahedron than does that of Li(1). This fact might be explained as follows. Li(2) is surrounded by comparable O atoms, *i.e.* by the four outer O atoms O(1), O(4), O(11), and O(14) of the different carboxylic groups. Li(1), however, is surrounded by the two O atoms of the methanol molecules and the two inner O atoms O(2) and O(3) which are also involved in the intramolecular hydrogen bond.

The distances and angles within the two hydrogen phthalate molecules are shown in Fig. 2. Each contains an extremely short hydrogen bond. The bond lengths are 2·386 (3) and 2·382 (3) Å respectively. The considerable strain which is produced by the intramolecular hydrogen bonds within the molecules causes displacements of the inner O atoms [O(2), O(3) and O(12), O(13)] of the carboxylic groups out of the plane of the C atoms. The deviations of O(1), O(2), O(3) and O(4) from the average benzene ring plane are −0·476, +0·305, +0·380, and −0·357 Å, and the deviations of O(11), O(12), O(13), and O(14) are +0·457, −0·464, −0·473, and 0·512 Å respectively. The angular distor-

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33444 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

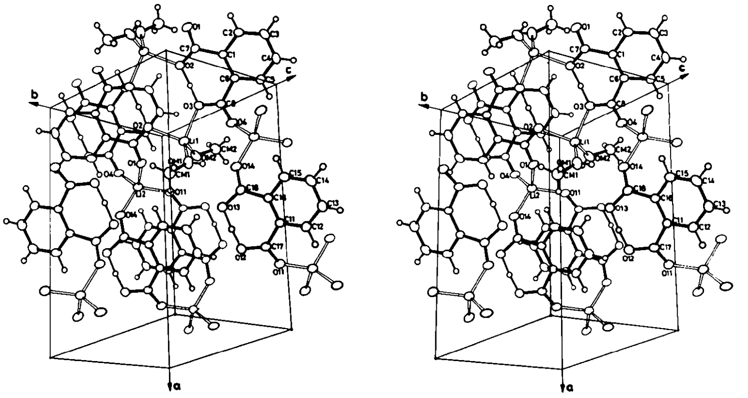

Fig. 1. Stereoscopic view of the unit cell.

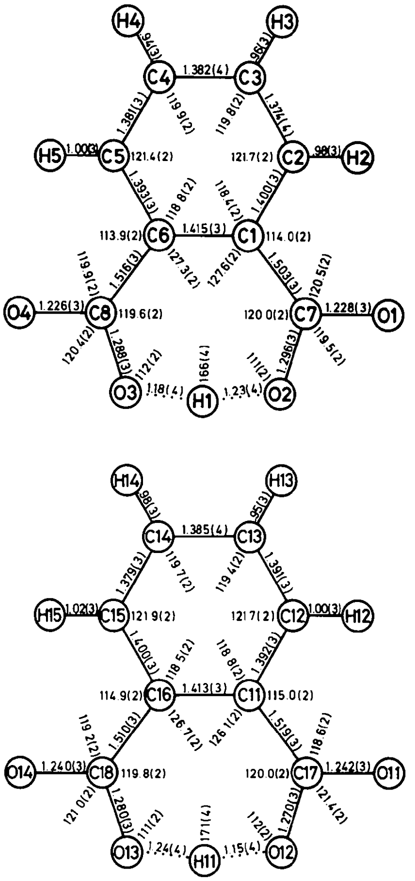

Fig. 2. Distances (Å) and angles (°) in the two hydrogen phthalate molecules.

tions of the planes of the carboxylic groups with respect to the planes of the benzene rings are 21·2 and −19·8° for the first and 24·9 and −26·7° for the second molecule. As has already been observed in $LiHC_8O_4H_4.2H_2O$ (Gonschorek & Küppers, 1975), as a consequence of the intramolecular strain, the distances C(1)–C(6) and C(11)–C(16) are increased, the C–C distances in the reverse part of the benzene ring are decreased, and the angles around C(1), C(6), C(11), and C(16) deviate considerably from 120°, if compared with the unstrained phthalate molecule as found in phthalic acid or those acid salts which do not form the intramolecular hydrogen bond.

Although the calculated distances of H(1) and H(11) to the neighbouring O atoms are shown in Fig. 2, these values are too uncertain to allow a decision as to whether the hydrogen bonds are symmetrical or not, or to which of the two O atoms the H atom lies closer. This question has to be answered by a neutron diffraction analysis which is being undertaken. In the case of $Cu(HC_8O_4H_4)_2.2H_2O$ (Bartl & Küppers, 1978), one can predict to which O atom of the intramolecular hydrogen bond the H will tend from the asymmetry of the environment in the lattice. In the present crystal (*cf.* Fig. 1) the distances of the two carboxylic groups of the hydrogen phthalate ions to the neighbouring cations or methanol molecules are extremely similar. A prediction of the probable position of the H atoms is, therefore, not possible from environmental considerations. It is to be expected that these hydrogen bonds have a high degree of symmetry.

The O atoms of the methanol molecules form weak hydrogen bonds with the following lengths: O*M*(1)–HO*M*(1)···O(14) 2·834 (3), O*M*(2)–HO*M*(2)···O(11) 2·776 (3) Å.

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References

Bartl, H. & Küppers, H. (1978). To be published.

Biagini Cingi, M., Guastini, C., Musatti, A. & Nardelli, M. (1969). *Acta Cryst.* B**25**, 1833–1840.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Gonschorek, W. & Küppers, H. (1975). *Acta Cryst.* B**31**, 1068–1072.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Sheldrick, G. M. (1976). *SHELX* 76, Univ. of Cambridge.