

**Hydrogen Bond Studies.**  
**CXLII.\* Neutron Diffraction Study of the Two Very Short Hydrogen Bonds in  
 Lithium Hydrogen Phthalate–Methanol**

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### Abstract

The structure of  $\text{LiHC}_8\text{H}_4\text{O}_4 \cdot \text{CH}_3\text{OH}$  has been determined by single-crystal neutron diffraction techniques at 298 K. The crystals are triclinic, space group  $P\bar{1}$ , with  $Z = 4$ ,  $a = 13.692$  (3),  $b = 8.023$  (2),  $c = 8.467$  (2) Å,  $\alpha = 95.29$  (3),  $\beta = 96.31$  (3),  $\gamma = 86.72$  (3)°. The final unweighted  $R(F^2)$  is 0.065 for the 2551 reflections with  $I > 3\sigma(I)$ . There are two formula units in the asymmetric unit. The two non-equivalent hydrogen phthalate ions have very short intramolecular hydrogen bonds; one of these is virtually centred [ $\text{O}\cdots\text{O}$  2.393 (4) Å;  $\text{O}-\text{H}$  1.195 (5) and 1.205 (5) Å;  $\angle\text{O}-\text{H}-\text{O}$  171.3 (5)°] whereas the second is significantly asymmetric [ $\text{O}\cdots\text{O}$  2.388 (4) Å;  $\text{O}-\text{H}$  1.172 (5) and 1.226 (5) Å;  $\angle\text{O}-\text{H}-\text{O}$  169.3 (6)°]. This asymmetry results from minor differences in the coordination geometries around the two carboxyl groups. It is evident that the potential governing the position of the H atom in these short hydrogen bonds is very sensitive to asymmetries in the molecular environment.

### Introduction

The X-ray structure analysis of lithium hydrogen phthalate–methanol (Adiwidjaja & Küppers, 1978) revealed that, in each of the two independent hydrogen phthalate ions, the carboxyl groups are interconnected by very short intramolecular hydrogen bonds ( $\text{O}\cdots\text{O}$  2.386 and 2.382 Å). The present neutron diffraction work was undertaken to study these short hydrogen bonds in greater detail.

### Experimental

Single crystals of suitable size were grown from a solution of a stoichiometric mixture of  $\text{Li}_2\text{CO}_3$  and phthalic acid in methanol by slow evaporation of the solvent. A prismatic crystal slightly elongated along the  $b$  direction and with a total volume of 20.8 mm<sup>3</sup> was used for the data collection. The crystal was bounded by six natural faces,  $\{010\}$ ,  $\{10\bar{1}\}$ , and  $\{100\}$ .

Cell dimensions as given in the *Abstract* were determined from X-ray diffraction data (Adiwidjaja & Küppers, 1978). The linear absorption coefficient,  $\mu = 0.191$  mm<sup>-1</sup>, was determined experimentally by measuring the attenuation of a narrow beam of neutrons passing through the crystal. Assuming absorption cross sections for Li, O and C as tabulated in *International Tables for X-ray Crystallography* (1962), the mean incoherent scattering cross section for H in lithium hydrogen phthalate–methanol was found to be  $4.08 \times 10^{-27}$  m<sup>2</sup> at a neutron wavelength of 1.210 Å.

Intensity data were collected using a  $\theta$ - $2\theta$  scan technique on an automated four-circle diffractometer at the Studsvik R2 reactor. Two copper crystals with their (220) planes in reflecting positions were used to obtain a monochromatized beam of wavelength  $\lambda = 1.210$  Å.

The total scan interval ( $\Delta 2\theta$ ) was 4.0° for  $2\theta < 80^\circ$ , and 5.0° for  $2\theta > 80^\circ$ . The step size was chosen to give 40 and 50 steps in the two regions respectively. Data were collected over a complete hemisphere of reciprocal space up to  $\sin \theta/\lambda = 0.692$  Å<sup>-1</sup>. Three standard reflections were measured at regular intervals to provide a check on crystal and electronic stability. Only variations expected from counting statistics could be observed.

Background corrections were made using a method (Lehmann & Larsen, 1974) which separates the peak and the background in such a way that  $\sigma_c(I)/I$  is

\* Part CXXI: Selenius & Lundgren (1980).

minimized, where  $I$  is the integrated intensity and  $\sigma_c(I)$  its e.s.d. based on counting statistics.

Squared structure amplitudes were obtained as  $F_o^2 = I \sin 2\theta$  and were corrected for absorption by the Gaussian integration method using a grid of 216 points. The transmission factors fell in the range 0.612 to 0.692 for the 4830 collected data. Averaging yielded 4265 independent reflections.

### Refinement and description of the structure

The structure was refined by minimizing  $\sum w(F_o^2 - |F_c|^2)^2$  with the program *UPALS* (Lundgren, 1976). The agreement factors of the full-matrix least-squares refinement are given in Table 1. Only reflections with  $I > 3\sigma(I)$  were used in the refinements. In the last cycles of refinement an isotropic extinction correction (type I, Lorentzian distribution) was introduced according to Becker & Coppens (1974, 1975). The neutron scattering lengths used were  $b_c = 6.648$ ,  $b_o = 5.803$ ,  $b_H = -3.740$ ,  $b_{Li} = 1.940$  fm. Final fractional coordinates are listed in Table 2. An equivalent isotropic temperature factor ( $U_{eq}$ ) was computed from the anisotropic temperature parameters.\* Bond lengths and angles of the two independent phthalate ions (I and II) and atoms adjacent to the carboxyl groups are presented in Fig. 1(a) and (b).

The coordination of the Li ions is characterized by the lengths and angles listed in Table 3. Li(2) has four neighbours with comparable distances and exhibits a fairly regular coordination tetrahedron. As well as four nearest neighbours, Li(1) has two more-distant neighbours. At the same time the tetrahedron created by the four nearest neighbours is extremely distorted.

The two Li ions contribute in different ways to the packing within the structure, as may be seen in the

\* Lists of intensities and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35962 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Refinement data*

Number of independent reflections: $N' = 4265$
Number of independent reflections with $I > 3\sigma(I)$ : $N = 2551$
Number of variables: $V = 434$
$R_1 = \sum (F_o^2 - F_c^2) / \sum F_o^2 = 0.065$
$R_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2]^{1/2} = 0.105$
$R_3 = \sum (F_o - F_c) / \sum F_o = 0.048$
$S = [\sum w(F_o^2 - F_c^2)^2 / (N - V)]^{1/2} = 1.343$
$w^{-1} = \sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (0.055F_o^2)^2$ ; $\sigma_c(F_o^2)$ is based on counting statistics
Isotropic extinction coefficient: $g = 876$ (111)
R.m.s. mosaic spread (Lorentzian) = $66''$

stereofigure of Adiwidjaja & Küppers (1978). Two cations, Li(1), link two molecules of type I and, together with four methanol molecules, form a quasi-dimer. The cations Li(2), on the other hand, provide the linkage perpendicular to the layers formed by these dimers and the molecules of type II. The average plane for molecule (II) is approximately parallel to that for molecule (I). The angle between their average planes is  $16.5^\circ$ .

Table 2. *Fractional atomic coordinates and equivalent isotropic temperature parameters  $U_{eq}$  ( $\text{\AA}^2$ ) calculated from the refined anisotropic thermal parameters*

	$U_{eq} = 1/6\pi^2 \sum_i \sum_j \beta_{ij} a_i \cdot a_j$			
	$x$	$y$	$z$	$U_{eq}$
C(1)	-0.1012 (1)	0.5963 (3)	0.6152 (2)	0.0248
C(2)	-0.1647 (2)	0.4681 (3)	0.6241 (3)	0.0342
C(3)	-0.1381 (2)	0.3360 (4)	0.7180 (3)	0.0462
C(4)	-0.0462 (2)	0.3313 (3)	0.8053 (3)	0.0469
C(5)	0.0177 (2)	0.4586 (3)	0.7990 (3)	0.0353
C(6)	-0.0079 (1)	0.5921 (3)	0.7055 (2)	0.0245
C(7)	-0.1413 (1)	0.7232 (3)	0.5015 (2)	0.0286
C(8)	0.0712 (1)	0.7161 (3)	0.7129 (2)	0.0265
C(11)	0.6032 (1)	0.4402 (3)	0.8766 (2)	0.0240
C(12)	0.6409 (2)	0.2931 (3)	0.9428 (3)	0.0319
C(13)	0.5912 (2)	0.1460 (3)	0.9156 (3)	0.0352
C(14)	0.5012 (2)	0.1436 (3)	0.8219 (3)	0.0371
C(15)	0.4627 (1)	0.2875 (3)	0.7567 (3)	0.0321
C(16)	0.5119 (1)	0.4377 (3)	0.7813 (2)	0.0241
C(17)	0.6666 (1)	0.5896 (3)	0.9179 (2)	0.0284
C(18)	0.4584 (2)	0.5835 (3)	0.7038 (2)	0.0298
O(1)	-0.2076 (2)	0.6877 (4)	0.3963 (3)	0.0387
O(2)	-0.1067 (2)	0.8698 (3)	0.5149 (3)	0.0400
O(3)	0.0490 (2)	0.8660 (3)	0.6739 (3)	0.0383
O(4)	0.1567 (2)	0.6760 (4)	0.7608 (3)	0.0374
O(11)	0.7253 (2)	0.5921 (3)	1.0408 (3)	0.0367
O(12)	0.6615 (2)	0.7065 (4)	0.8256 (3)	0.0421
O(13)	0.5069 (2)	0.7015 (4)	0.6647 (4)	0.0468
O(14)	0.3679 (2)	0.5852 (4)	0.6764 (3)	0.0369
OM(1)	0.7095 (2)	0.0934 (5)	0.3996 (4)	0.0470
CM(1)	0.6601 (2)	0.0521 (4)	0.5271 (4)	0.0438
OM(2)	0.8146 (2)	0.8972 (4)	1.1065 (3)	0.0440
CM(2)	0.8490 (2)	0.9459 (5)	0.9689 (4)	0.0463
Li(1)	0.8296 (5)	-0.0045 (11)	0.3259 (9)	0.0334
Li(2)	0.7440 (5)	0.5055 (10)	0.2466 (9)	0.0319
H(1)	-0.0305 (4)	0.8773 (6)	0.6006 (6)	0.0468
H(2)	0.7638 (4)	0.4727 (8)	0.5565 (7)	0.0581
H(3)	0.8123 (5)	0.2389 (9)	0.7213 (9)	0.0791
H(4)	0.9764 (5)	0.2298 (9)	0.8785 (9)	0.0817
H(5)	0.0885 (4)	0.4569 (8)	0.8679 (7)	0.0598
H(11)	0.5864 (3)	0.7013 (7)	0.7324 (6)	0.0519
H(12)	0.7112 (4)	0.2963 (7)	0.0147 (6)	0.0518
H(13)	0.6225 (5)	0.0335 (7)	0.9666 (7)	0.0621
H(14)	0.4617 (4)	0.0287 (7)	0.7979 (8)	0.0648
H(15)	0.3930 (4)	0.2852 (7)	0.6830 (7)	0.0548
HOM(1)	0.6834 (4)	0.2000 (8)	0.3671 (7)	0.0557
HOM(2)	0.7797 (4)	0.7944 (7)	0.0813 (6)	0.0532
HM(11)	0.3042 (10)	1.0390 (19)	0.4195 (18)	0.1813
HM(12)	0.5898 (7)	1.0263 (19)	0.4959 (11)	0.1333
HM(13)	0.6543 (11)	0.1476 (19)	0.6106 (13)	0.1533
HM(21)	0.8772 (14)	0.0538 (19)	-0.0072 (13)	0.1830
HM(22)	0.9004 (11)	0.8736 (25)	-0.0706 (16)	0.1808
HM(23)	0.7967 (7)	0.9487 (22)	-0.1250 (10)	0.1492

Distances and angles involving the methanol groups and their intermolecular hydrogen bonds are listed in Table 4.

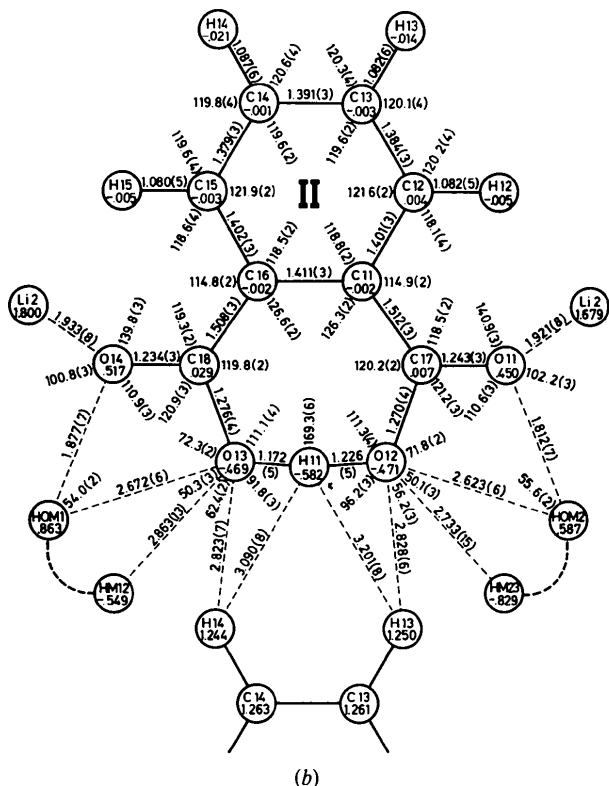
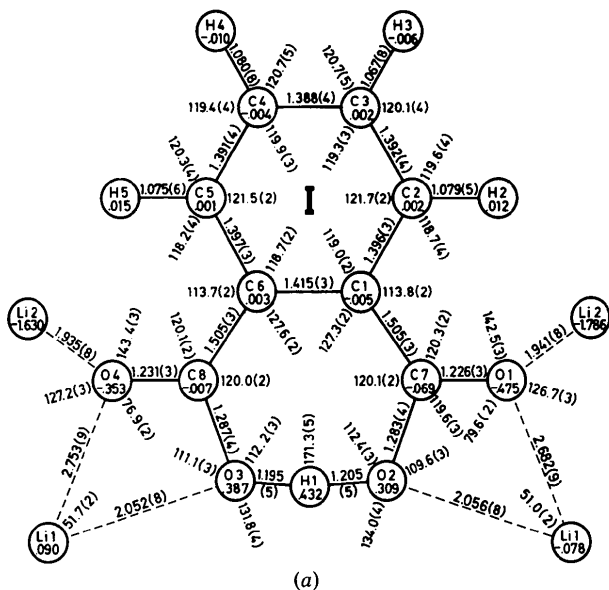


Fig. 1. Bond lengths (Å) and angles ( $^{\circ}$ ) within and around the hydrogen phthalate ions. Numbers within the circles indicate the height (in Å) of the particular atom above or below the least-squares plane through the C atoms of the benzene ring. (a) Molecule (I), (b) molecule (II).

Table 3. Bond lengths (Å) and angles ( $^{\circ}$ ) around the Li ions

Li(1)—O(2)	2.056 (8)	Li(2)—O(1)	1.941 (8)
Li(1)—O(3)	2.052 (8)	Li(2)—O(4)	1.935 (8)
Li(1)—OM(1)	1.922 (8)	Li(2)—O(11)	1.921 (9)
Li(1)—OM(2)	1.944 (8)	Li(2)—O(14)	1.933 (8)
Li(1)—O(1)	2.682 (9)		
Li(1)—O(4)	2.823 (9)		
O(2)—Li(1)—O(3)	92.2 (3)	O(1)—Li(2)—O(4)	109.5 (4)
O(2)—Li(1)—OM(1)	103.5 (4)	O(1)—Li(2)—O(11)	106.2 (4)
O(2)—Li(1)—OM(2)	123.9 (4)	O(1)—Li(2)—O(14)	109.4 (4)
O(3)—Li(1)—OM(1)	121.6 (5)	O(4)—Li(2)—O(11)	108.0 (4)
O(3)—Li(1)—OM(2)	101.3 (4)	O(4)—Li(2)—O(14)	105.8 (4)
OM(1)—Li(1)—OM(2)	114.0 (4)	O(11)—Li(2)—O(14)	117.8 (4)

Table 4. Bond lengths (Å) and angles ( $^{\circ}$ ) of the methanol molecules and intermolecular hydrogen bonds

CM(1)—HM(11)	0.975 (15)	CM(2)—HM(21)	0.964 (17)
CM(1)—HM(12)	0.997 (10)	CM(2)—HM(22)	0.956 (17)
CM(1)—HM(13)	0.999 (13)	CM(2)—HM(23)	1.010 (9)
CM(1)—OM(1)	1.409 (5)	CM(2)—OM(1)	1.399 (5)
OM(1)—HOM(1)	0.960 (7)	OM(2)—HOM(2)	0.972 (7)
OM(1)···O(14)	2.834 (5)	OM(2)···O(11)	2.781 (5)
HOM(1)···O(14)	1.877 (7)	HOM(2)···O(11)	1.812 (7)
OM(1)—HOM(1)···O(14)	174.7 (6)	OM(2)—HOM(2)···O(11)	174.6 (5)

## Discussion

As the O···O distance of a hydrogen bond decreases, the H atom moves away from the donor towards the acceptor atom. In very short hydrogen bonds the question arises as to whether or not the H atom forms a centred bond. (The term 'centred' is used here to indicate effectively equal O—H distances rather than a situation in which the H atom lies exactly at the centre of the bond, on the line connecting the O atoms.)

Table 5 provides geometrical data (obtained by neutron diffraction) for different crystal structures which contain comparable intramolecular hydrogen bonds. The quantity  $\Delta = (H \cdots O) - (O-H)$  gives a measure of the asymmetry of the bond.  $\phi_{sh}$  and  $\phi_{lo}$  are the angles between the average planes through the molecular rings (or maleate group) with the planes of the carboxyl groups which form the short (O—H) or long (H···O) part of the hydrogen bond, respectively.

The position of the H atom within an intramolecular hydrogen bond is influenced by both internal and external forces. Quinolinic acid (Kvick, Koetzle, Thomas & Takusagawa, 1974) exemplifies an internal influence, where the asymmetry of the molecule (due to the asymmetric position of the N within the ring) may cause the observed non-centred position for the H atom in the intramolecular hydrogen bond. On the other hand, an isolated phthalate ion is symmetric. A non-centred intramolecular hydrogen bond in acid phthalates must therefore result from the influence of neighbouring molecules or ions. Copper di(hydrogen phthalate) dihydrate (CuHP) (Bartl & Küppers, 1980)

provides a perfect example of such an influence since both O atoms of one carboxyl group are coordinated to the Cu ion, whereas the O atoms of the second carboxyl groups do not form bonds to the cation. The H atoms are accordingly somewhat closer to the O atoms of the less-ionized carboxyl group.

In contrast to CuHP, the present structure exhibits only minor differences in the crystalline environments of the two carboxyl groups of each of the two molecules. This can be seen in Fig. 1(a) and (b), where all adjacent atoms which can conceivably influence the atoms of the carboxyl groups are included. A stereoscopic illustration of the packing is given in Fig. 2.

In molecule (I), the outer oxygen atoms O(1) and O(4) are primarily coordinated to the Li(2) cation at identical distances. The inner oxygen atoms O(2) and O(3) are coordinated to the Li(1) cation, again at

distances equal to within one standard deviation. It is therefore no surprise that the intramolecular hydrogen bond in this molecule is effectively centred.

The packing around molecule (II) is somewhat more complicated. The outer oxygen atoms, O(11) and O(14), are again coordinated by Li(2) at virtually identical coordination distances,  $\text{Li}(2)\text{—O}(11) = 1.921(9)$  and  $\text{Li}(2)\text{—O}(14) = 1.933(8)$  Å. However, these O atoms are also hydrogen bonded to the methanol molecules. The hydrogen bonds are slightly different in length: the  $\text{HOM}(2)\text{—O}(11)$  distance of  $1.812(7)$  Å is significantly shorter than the  $\text{HOM}(1)\text{—O}(14)$  distance of  $1.877(7)$  Å. Methanol molecule (II) is evidently slightly closer to O(11) and O(12) than methanol molecule (I) is to O(13) and O(14). This small difference in the external packing situation is apparently sufficient to displace the hydrogen atom H(11) significantly towards the oxygen atom O(13) giving rise to a non-centred bond [ $\text{O}(13)\text{—H}(11)$   $1.172(5)$  and  $\text{O}(14)\text{—H}(11)$   $1.226(5)$  Å]. The potential governing the position of the H atom in a very short bond of this type is extremely sensitive to asymmetry in the molecular environment (Kvick *et al.*, 1974). It is thus to be expected that truly centred bonds are rare in structures where centring is not a requirement of symmetry.

The C—O distances in molecule (II) are in agreement with the observation that  $\text{O}(13)\text{—H}(11)$  is the shorter part of the hydrogen bond.  $\text{C}(18)\text{—O}(13)$  is longer than  $\text{C}(17)\text{—O}(12)$  and  $\text{C}(18)\text{—O}(14)$  is shorter than  $\text{C}(17)\text{—O}(11)$ . This indicates that O(11) should be slightly more ionized than O(14). It is also worth drawing attention to the close agreement between the average values of the two C—O distances in each carboxyl group: 1.255, 1.259, 1.257 and 1.255 Å for the bonds originating from C(7), C(8), C(17) and C(18), respectively. Although this tendency is well known (Manojlović & Speakman, 1967), the close agreement in this case may be taken as an indication of the good internal consistency of the experimental results.

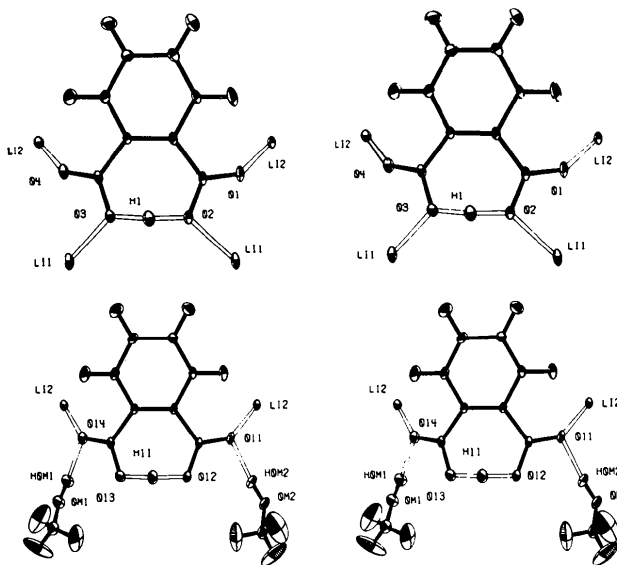


Fig. 2. Stereoscopic views of the hydrogen phthalate ions and their neighbours. The thermal ellipsoids are drawn to enclose 80% probability.

Table 5. Compilation of the geometrical features (Å and deg) of comparable intramolecular hydrogen bonds

$\varphi_{\text{sh}}$  and  $\varphi_{\text{lo}}$  are defined in the text.

	O...O	O—H	H...O	O—H...O	$\Delta\left(\frac{\text{O—H}}{\text{H...O}}\right)$	$\varphi_{\text{sh}}$	$\varphi_{\text{lo}}$
KH chloromaleate <sup>(a)</sup>	2.403 (3)	1.199 (5)	1.206 (5)	175.4 (4)	0.007	9.3	7.0
H-Quinolinic acid <sup>(b)</sup>	2.398 (3)	1.163 (5)	1.238 (5)	174.4 (4)	0.075	10.7	8.0
D-Quinolinic acid <sup>(c)</sup>	2.393 (2)	1.138 (2)	1.257 (2)	175.2 (2)	0.119	10.6	8.5
$\text{Cu}(\text{HC}_8\text{H}_4\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ <sup>(d)</sup>	2.391 (2)	1.108 (4)	1.290 (4)	172.1 (4)	0.182	18.3	15.9
$\text{LiHC}_8\text{H}_4\text{O}_4 \cdot \text{H}_2\text{O}$ <sup>(e)</sup> I	2.400 (2)	1.114 (2)	1.296 (2)	168.9 (1)	0.182	22.3	32.4
$\text{LiHC}_8\text{H}_4\text{O}_4 \cdot \text{H}_2\text{O}$ <sup>(e)</sup> II	2.390 (2)	1.181 (2)	1.216 (2)	171.7 (1)	0.035	14.8	21.1
$\text{LiHC}_8\text{H}_4\text{O}_4 \cdot \text{CH}_3\text{OH}$ <sup>(f)</sup> I	2.393 (4)	1.195 (5)	1.205 (5)	171.3 (5)	0.010	19.8	21.4
$\text{LiHC}_8\text{H}_4\text{O}_4 \cdot \text{CH}_3\text{OH}$ <sup>(f)</sup> II	2.388 (4)	1.172 (5)	1.226 (5)	169.3 (6)	0.054	26.9	24.9

(a) Ellison & Levy (1965). (b) Kvick *et al.* (1974). (c) Takusagawa & Koetzle (1979) (recrystallized from  $\text{D}_2\text{O}$ ). (d) Bartl & Küppers (1980). (e) Küppers, Takusagawa & Koetzle (1981). (f) Present work.

Attention should be drawn to one remarkable difference between molecules (I) and (II). The number of intermolecular bonds is considerably larger for molecule (I) than for molecule (II). It should be noted particularly that the oxygen atoms O(12) and O(13) which form the non-centred hydrogen bond do not participate in intermolecular bonds. Distances to more remote H atoms are also included in the lower part of Fig. 1(b) in order to demonstrate that there is no significant bonding to O(12) or O(13).

Several hydrogen bonds have previously been reported as being centred. In most of these cases, however, the H atom is assumed to be in a special position (inversion centre  $\bar{1}$  or twofold axis). Doubts have been raised as to the centricity in these cases (Kroon, Kanters & Peerdeman, 1971). Potassium hydrogen chloromaleate (Ellison & Levy, 1965) was the first example to exhibit a centred hydrogen bond which was not constrained by a symmetry operation. The present crystal provides a second example. It is emphasized that, within the standard deviations, nearly all distances and angles within molecule (I) obey the symmetry of a mirror plane perpendicular to the plane of the molecule.

The relatively large tilting angles  $\varphi$  (Table 5) in the present structure can be explained by the cations Li(2) which link the hydrogen phthalate ions perpendicular to their average plane (see Fig. 2).

In hydrogen bonds with O...O distances longer than 2.5 Å, the distances O—H increase with decreasing O...O in a well correlated manner. Table 5 clearly demonstrates that, in very short hydrogen bonds, such a correlation no longer exists. All examples cited show comparable O...O distances, whereas the O—H distances scatter considerably. Furthermore, no correlation can be observed between O—H distance and

other geometric features such as the  $\varphi$  or O—H...O angles.

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## The Structures of the Mono- and Disodium Salts of Hadacidin, an Antibiotic Hydroxamic Acid

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#### Abstract

The crystal structures of the mono- and disodium salts of *N*-formyl-*N*-hydroxyglycine (hadacidin), an L-aspartate antagonist for the enzyme adenylosuccinate

synthetase, were determined at 138 (2) K. For  $C_3H_4NNaO_4 \cdot 2H_2O$ ,  $M_r = 177.12$ , monoclinic,  $P2_1/c$ ,  $Z = 4$ ,  $a = 8.915$  (9),  $b = 10.474$  (11),  $c = 8.485$  (7) Å,  $\beta = 115.29$  (7)°,  $V = 716.4$  Å<sup>3</sup>,  $D_c = 1.642$  Mg m<sup>-3</sup>; final  $R$  value was 0.055 for all 1470 data. For  $C_3H_3NNa_2O_4 \cdot 2H_2O$ ,  $M_r = 198.97$ , monoclinic,  $P2_1/c$ ,  $Z = 4$ ,  $a = 7.562$  (4),  $b = 7.574$  (3),  $c =$

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