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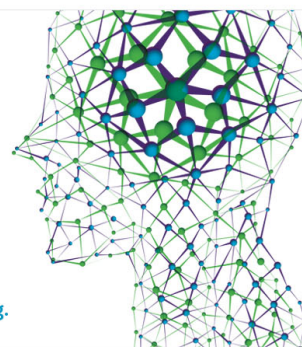
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Neutron diffraction study of lithium hydrogen phthalate monohydrate: A material with two very short intramolecular O...H...O hydrogen bonds^{a)}

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The structure of lithium hydrogen phthalate monohydrate has been refined based upon neutron diffraction data obtained at three temperatures: 15, 100, and 298 K. All bond distances have been determined with precision better than 0.002 Å. The two crystallographically independent hydrogen phthalate anions in the unit cell both possess very short intramolecular O...H...O hydrogen bonds with $O\cdots O \approx 2.4$ Å and $\angle O\cdots H\cdots O \approx 170^\circ$. One of these linkages is very decidedly asymmetric, with $O\cdots H = 1.122(1)$ Å and $H\cdots O = 1.294(1)$ Å at 15 K, reflecting the fact that the two O atoms have quite different environments in the crystal. The second O...H...O bond is more nearly symmetric, with $O\cdots H = 1.195(1)$ Å and $H\cdots O = 1.205(1)$ Å at 15 K, but the difference between the two distances is still significant. The asymmetry of the short hydrogen bonds appears somewhat more pronounced at 298 K than at the lower temperatures. A corresponding shift with temperature of the H atom in the short intramolecular hydrogen bond was found previously in 2,3-pyridinedicarboxylic acid, which has a molecular geometry similar to that found here.

INTRODUCTION

Lithium hydrogen phthalate monohydrate (LHPM) is one of a series of acid lithium phthalates possessing intramolecular hydrogen bonds with extremely short O...O distances (~ 2.4 Å). The occurrence of intramolecular hydrogen bonds in systems such as the *o*-phthalates, with carboxyl groups attached to adjacent C atoms on an aromatic ring, has been known for quite some time. The first x-ray diffraction study of a compound of this type, by Williams and Rundle on 3,4-furandicarboxylic acid,¹ indicated an intramolecular O...O separation of 2.544(4) Å. More recent investigations of the acid lithium phthalates have included x-ray and neutron diffraction studies of lithium hydrogen phthalate dihydrate^{2,3} and of a methanol adduct,^{4,5} in addition to an x-ray study of LHPM.⁶

A central consideration in systems with "short" hydrogen bonds concerns the disposition of the H atom: Is it located at the center of the bond, or is the linkage asymmetric? A thorough discussion of this question is given by Speakman⁷ in his review of structures of acid salts, while a review covering the subject of very strong hydrogen bonding in general has been published by Emsley.⁸ Generally, it is now recognized that small asymmetries in the crystalline environments of the acceptor or donor atoms may be sufficient to produce an asymmetric linkage, even in the shortest hydrogen bonds. Such has been found to be the case, for example, in the *p*-

toluidinium salt of the bifluoride ion, based on a neutron diffraction study.⁹ Similarly, several of the O...H...O bonds in the acid lithium phthalates are found to be significantly asymmetric,²⁻⁶ as is that in copper dihydrogen diphthalate dihydrate.¹⁰ In the compound 2,3-pyridinedicarboxylic acid (quinolinic acid), the short intramolecular hydrogen bond also has been found to be asymmetric, and this asymmetry has been ascribed to intramolecular effects.^{11,12} We have studied the effects of temperature and deuterium substitution on the crystal structure of quinolinic acid^{13,14} and have observed an unusual shift of the H(D) atom toward the midpoint of the O...H...O bond upon cooling the crystal to 100 K or below. In the present paper, we report results of a neutron diffraction study of LHPM, allowing precise characterization of the hydrogen bonding in this system. LHPM contains two crystallographically independent hydrogen phthalate anions. Neutron diffraction measurements have been made at three temperatures: 15, 100, and 298 K, in order to allow a comparison of the temperature effects with those observed in quinolinic acid.

TABLE I. Crystal data for lithium hydrogen phthalate monohydrate.

	15 K	100 K	298 K	298 K ^a
Empirical formula	LiC ₈ H ₅ O ₄ · H ₂ O			
Formula weight	190.08			
Space group	<i>P</i> $\bar{1}$ (<i>Z</i> = 4)			
Cell constants				
<i>a</i>	11.601(2) Å	11.667(2) Å	11.937(5) Å	11.932(2) Å
<i>b</i>	8.971(2)	8.942(2)	8.881(3)	8.874(2)
<i>c</i>	7.886(2)	7.895(1)	7.945(3)	7.943(2)
α	96.83(2) ^o	96.81(2) ^o	97.20(4) ^o	97.13(5) ^o
β	96.01(2)	95.91(3)	95.94(6)	95.88(5)
γ	94.94(2)	94.53(2)	93.08(4)	93.12(5)
<i>V</i>	806.3(2) Å ³	810.0(3) Å ³	829.3(5) Å ³	828.2(3) Å ³

^a By x rays (MoK α_1 , $\lambda = 0.70926$ Å) (Ref. 6).

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^{b)} Research Collaborator at Brookhaven National Laboratory. Recipient of travel support from the Deutsche Forschungsgemeinschaft.

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TABLE II. Experimental and refinement parameters.

	15 K	100 K	298 K
Crystal weight	31.13 mg		
Calculated crystal volume ^a	20.45 mm ³		
Measured crystal volume ^b	19.73 mm ³		
Crystal faces	{110}, {110}, (001) (117)(763)		
Number of reflections measured	4451	4544	4667
Agreement factor on averaging (R_c) ^c	0.011	0.012	0.025
Number of independent reflections	4123	4171	4297
Number of reflections with $F_0^2 > \sigma_{\text{count}}, m$	4114	4128	4083
$R(F^2) = \Sigma F_0^2 - k^2 F_c^2 / \Sigma F_0^2$	0.0440 (0.0437) ^d	0.0358 (0.0340) ^d	0.0451 (0.0427) ^d
$wR(F^2) = (\Sigma w F_0^2 - k^2 F_c^2 ^2 / \Sigma w F_0^4)^{1/2}$	0.0484 (0.0488)	0.0412 (0.0395)	0.0609 (0.0558)
$S = [\Sigma w F_0^2 - k^2 F_c^2 ^2 / (m - n)]^{1/2}$	1.1648 (1.1549)	1.0001 (0.9632)	1.1294 (0.8594)
Number of variable parameters, n	348 (448)	348 (598)	348 (598)
Scale factor, k	23.16(4) (23.19(4))	22.66(3) (22.61(3))	22.01(3) (21.94(3))
Extinction parameter, $g \times 10^{-4}$	0.52(1) (0.52(1))	0.40(1) (0.39(1))	0.23(1) (0.23(1))

^aTaken from the observed crystal weight and calculated density based on the neutron cell at 298 K (1.522 g cm⁻³).

^bBased on examination of the sample in a microscope.

^c $R_c = \sum_{i=1}^n (| \langle F_0^2 \rangle - F_{0i}^2 | / \sum n' \langle F_0^2 \rangle)$, where n' is the number of equivalent observations for a given reflection.

^dNumbers in parentheses are from the refinements including higher-order thermal parameters.

^e $w = 1/\sigma^2(F_0^2)$; $\sigma^2(F_0^2) = \sigma_{\text{count}}^2 + A \cdot F_0^8 + B \cdot F_0^4 + C$, where σ_{count}^2 is the variance based on counting statistics, $A = 1.462 \times 10^{-12}$, $B = 3.552 \times 10^{-4}$, and $C = 2.110 \times 10^4$ on the experimental scale, as defined by the factor k listed above.

EXPERIMENTAL SECTION AND DATA REDUCTION

Samples of LHPM were recrystallized from a mixture of methanol and water by means of slow evaporation at room temperature. A crystal weighing 31.13 mg was chosen for the neutron diffraction measurements. This crystal was mounted on an aluminum pin, the end of which was hollow in order to reduce the amount of metal in the neutron beam, and was oriented with the crystallographic c axis approximately parallel to the pin. The sample was sealed into an aluminum can under a helium atmosphere and placed in a closed-cycle helium refrigerator³⁵ mounted on a four-circle diffractometer^{15,16} at the Brookhaven High Flux Beam Reactor. A germanium (220) crystal monochromator was employed to obtain a neutron beam of wavelength 1.1621(2) Å (based upon KBr, $a_0 = 6.6000$ Å at 298 K). The temperatures measured during data collection were 15 ± 0.5 , 110 ± 0.5 , and 298 ± 2 K, respectively.³⁶

Unit-cell dimensions at each temperature, refined by a least-squares procedure based on $\sin \theta$ values of 32 reflections ($55^\circ < 2\theta < 72^\circ$) are listed in Table I. Reflection intensities were measured in one hemisphere of reciprocal space with $2\theta < 109^\circ$, employing a $\theta/2\theta$ step-scan technique. The scan range was varied according to $\Delta 2\theta = 1.0^\circ + 4.5^\circ \tan \theta$

for the high-angle data ($60^\circ < 2\theta < 109^\circ$) and $\Delta 2\theta = 3.2^\circ$ for the low-angle data. The step size was adjusted to give between 60 and 90 steps in each scan. At each point, counts were accumulated for approximately 0.75 s, with the exact time interval being determined by monitoring the incident beam intensity. As a general check on experimental stability, the intensities of two reflections were monitored every 150 measurements. These did not vary to any significant degree during the entire period of data collection at any given temperature. Experimental details are presented in Table II, together with information on the subsequent refinements.

Integrated intensities of reflections were obtained by a modification of the Lehmann and Larsen procedure¹⁸ with a

TABLE III. Lithium scattering lengths ($\times 10^{-12}$ cm).

		15 K	100 K	298 K
Li(1)	Real part	-0.209(2)	-0.209(2)	-0.205(2)
	Imaginary part	0.006(2)	0.001(2)	0.003(2)
Li(2)	Real part	-0.203(2)	-0.206(2)	-0.207(2)
	Imaginary part	0.006(2)	0.013(2)	0.016(2)
Mean	Real part	-0.207(1)		
	Imaginary part	0.008(2)		

program¹⁹ that employs an interactive CRT display. Observed intensities were corrected for absorption by means of numerical integration over a Gaussian grid of points²⁰ and converted to values of $F_0^2 = I \sin 2\theta$. A linear absorption coefficient of $\mu = 1.60(1) \text{ cm}^{-1}$ at the experimental wavelength was determined by measuring the attenuation through a LHPM crystal of known thickness. Values of F_0^2

were averaged for Friedel-related observations; at all three temperatures the agreement factor is less than 0.03.

STRUCTURE REFINEMENT

The atomic coordinates from the x-ray analysis⁶ were used as initial values for full-matrix least-squares refinements minimizing $\sum w|F_0^2 - k^2 F_c^2|^2$ and using LINEX79, a

TABLE IV. Fractional atomic coordinates and thermal parameters.^a

a. 15K										
ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23	
C(1)	0.36767(3)	0.38913(3)	0.51069(4)	0.0049(1)	0.0053(1)	0.0042(1)	0.0016(1)	0.0005(1)	0.0006(1)	
C(2)	0.34621(3)	0.45533(4)	0.67320(4)	0.0066(1)	0.0062(1)	0.0050(1)	0.0022(1)	0.0008(1)	-0.0001(1)	
C(3)	0.49029(3)	0.41324(4)	0.82361(4)	0.0074(1)	0.0083(1)	0.0044(1)	0.0024(1)	0.0011(1)	0.0001(1)	
C(4)	0.47044(3)	0.38733(4)	0.71446(4)	0.0075(1)	0.0089(1)	0.0045(1)	0.0024(1)	0.0007(1)	0.0013(1)	
C(5)	0.50324(3)	0.23975(4)	0.65429(4)	0.0066(1)	0.0079(1)	0.0046(1)	0.0025(1)	0.0005(1)	0.0008(1)	
C(6)	0.44940(3)	0.28046(4)	0.50115(4)	0.0050(1)	0.0058(1)	0.0044(1)	0.0018(1)	0.0005(1)	0.0005(1)	
C(7)	0.29855(3)	0.44376(4)	0.36153(4)	0.0055(1)	0.0058(1)	0.0044(1)	0.0028(1)	0.0005(1)	0.0006(1)	
C(8)	0.48974(3)	0.20340(4)	0.33885(4)	0.0045(1)	0.0058(1)	0.0049(1)	0.0018(1)	0.0012(1)	-0.0003(1)	
O(1)	0.25717(3)	0.56635(4)	0.38179(5)	0.0090(2)	0.0058(2)	0.0067(1)	0.0032(1)	0.0007(1)	0.0002(1)	
O(2)	0.27934(3)	0.36059(4)	0.21378(5)	0.0094(2)	0.0083(2)	0.0049(1)	0.0042(1)	-0.0013(1)	-0.0011(1)	
O(3)	0.41637(3)	0.17504(4)	0.20236(5)	0.0071(2)	0.0086(2)	0.0059(1)	0.0029(1)	-0.0003(1)	-0.0022(1)	
O(4)	0.59005(3)	0.16653(4)	0.34534(5)	0.0055(2)	0.0088(2)	0.0063(1)	0.0027(1)	0.0012(1)	-0.0010(1)	
H(1)	0.33564(7)	0.26494(9)	0.20791(9)	0.0204(3)	0.0188(3)	0.0159(3)	0.0023(3)	-0.0003(2)	-0.0001(3)	
H(2)	0.28321(7)	0.53827(9)	0.6803(1)	0.0232(3)	0.0197(3)	0.0187(3)	0.0130(3)	0.0039(3)	0.0026(3)	
H(3)	0.38024(7)	0.4638(1)	0.9477(1)	0.0200(4)	0.0266(4)	0.0114(3)	0.0101(3)	0.0051(3)	-0.0011(3)	
H(4)	0.52030(7)	0.2674(1)	0.9304(1)	0.0262(4)	0.0282(4)	0.0136(3)	0.0102(3)	-0.0015(3)	0.0066(3)	
H(5)	0.56597(7)	0.15693(9)	0.6473(1)	0.0210(4)	0.0220(3)	0.0202(3)	0.0133(3)	0.0031(3)	0.0033(3)	
OW(1)	0.32755(3)	0.92366(5)	0.96520(5)	0.0087(2)	0.0112(2)	0.0084(2)	0.0008(1)	0.0021(1)	0.0018(1)	
HU(11)	0.37220(7)	1.0069(1)	1.0386(1)	0.0234(3)	0.0232(4)	0.0233(4)	-0.0036(3)	0.0007(3)	-0.0065(3)	
HU(12)	0.36668(7)	0.9002(1)	0.8643(1)	0.0234(3)	0.0276(4)	0.0173(3)	0.0034(3)	0.0058(3)	-0.0016(3)	
LI(1)	0.26233(9)	0.7538(1)	0.5189(2)	0.0083(6)	0.0195(6)	0.0098(6)	0.0013(4)	0.0005(3)	0.0016(4)	
C(11)	-0.03577(3)	0.79525(4)	0.53743(4)	0.0049(1)	0.0059(1)	0.0045(1)	0.0019(1)	0.0004(1)	0.0000(1)	
C(12)	-0.01252(3)	0.78745(4)	0.38771(4)	0.0050(1)	0.0076(1)	0.0052(1)	0.0024(1)	0.0003(1)	-0.0010(1)	
C(13)	-0.07327(3)	0.71632(4)	0.22732(4)	0.0070(1)	0.0085(1)	0.0050(1)	0.0013(1)	0.0006(1)	-0.0011(1)	
C(14)	-0.16135(3)	0.81199(4)	0.21580(4)	0.0071(1)	0.0082(1)	0.0048(1)	0.0015(1)	-0.0002(1)	0.0003(1)	
C(15)	-0.18852(3)	0.89544(4)	0.36318(4)	0.0056(1)	0.0068(1)	0.0051(1)	0.0017(1)	-0.0004(1)	0.0004(1)	
C(16)	-0.12730(3)	0.89066(4)	0.52528(4)	0.0051(1)	0.0054(1)	0.0041(1)	0.0016(1)	0.0006(1)	0.0006(1)	
C(17)	0.04989(3)	0.78503(4)	0.69331(4)	0.0050(1)	0.0061(1)	0.0044(1)	0.0016(1)	0.0004(1)	0.0005(1)	
C(18)	-0.16596(3)	0.99655(4)	0.66813(4)	0.0056(1)	0.0053(1)	0.0046(1)	0.0015(1)	0.0008(1)	0.0001(1)	
O(11)	0.14406(3)	0.73432(4)	0.67340(5)	0.0056(1)	0.0094(2)	0.0067(1)	0.0026(1)	0.0008(1)	0.0008(1)	
O(12)	0.02519(3)	0.82965(4)	0.84557(5)	0.0071(1)	0.0096(2)	0.0045(2)	0.0037(1)	0.0008(1)	0.0002(1)	
O(13)	-0.13351(3)	0.98295(4)	0.82716(5)	0.0075(1)	0.0085(2)	0.0045(1)	0.0039(1)	0.0011(1)	0.0002(1)	
O(14)	-0.22938(3)	1.09450(4)	0.63245(5)	0.0082(2)	0.0077(2)	0.0067(1)	0.0039(1)	0.0010(1)	0.0014(1)	
H(11)	-0.05829(7)	0.90083(9)	0.8420(1)	0.0196(3)	0.0227(4)	0.0158(3)	0.0033(3)	0.0025(2)	0.0019(3)	
H(12)	-0.05656(7)	0.63410(9)	0.3972(1)	0.0194(3)	0.0234(3)	0.0197(3)	0.0116(3)	0.0014(3)	-0.0004(3)	
H(13)	-0.04829(7)	0.6526(1)	0.1131(1)	0.0244(3)	0.0278(4)	0.0137(3)	0.0081(3)	0.0039(3)	-0.0051(3)	
H(14)	-0.20397(7)	0.8221(1)	0.8912(1)	0.0248(3)	0.0288(4)	0.0120(3)	0.0077(3)	-0.0032(3)	-0.0018(3)	
H(15)	-0.25915(7)	0.96694(9)	0.3541(1)	0.0199(3)	0.0224(3)	0.0195(3)	0.0118(3)	-0.0002(3)	0.0019(3)	
OW(2)	0.17269(4)	0.63535(5)	0.95690(5)	0.0132(2)	0.0082(2)	0.0083(2)	0.0026(1)	0.0001(1)	0.0016(1)	
HU(21)	0.20343(9)	0.6059(1)	0.1658(1)	0.0306(4)	0.0297(4)	0.0199(4)	0.0024(3)	-0.0011(3)	0.0097(3)	
HU(22)	0.1745(1)	0.5536(1)	-0.0273(1)	0.0523(7)	0.0272(5)	0.0289(5)	0.0098(4)	0.0039(4)	-0.0105(4)	
LI(2)	-0.1769(1)	0.1576(1)	0.9910(3)	0.0090(6)	0.0095(6)	0.0116(6)	0.0022(4)	0.0018(4)	0.0020(4)	

b. 100K										
ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23	
C(1)	0.36904(3)	0.38877(4)	0.51131(4)	0.0099(1)	0.0094(1)	0.0074(1)	0.0023(1)	0.0016(1)	0.0006(1)	
C(2)	0.34757(3)	0.45488(4)	0.67371(4)	0.0129(1)	0.0117(1)	0.0092(1)	0.0034(1)	0.0028(1)	0.0002(1)	
C(3)	0.49133(3)	0.41214(4)	0.82357(4)	0.0149(1)	0.0167(2)	0.0079(1)	0.0031(1)	0.0023(1)	0.0003(1)	
C(4)	0.47895(3)	0.38188(4)	0.71375(4)	0.0150(1)	0.0188(2)	0.0085(1)	0.0042(1)	0.0011(1)	0.0027(1)	
C(5)	0.50382(3)	0.23810(4)	0.65372(4)	0.0128(1)	0.0152(2)	0.0096(1)	0.0050(1)	0.0012(1)	0.0025(1)	
C(6)	0.45042(3)	0.27944(4)	0.50134(4)	0.0094(1)	0.0118(1)	0.0082(1)	0.0018(1)	0.0013(1)	0.0006(1)	
C(7)	0.30045(3)	0.44416(4)	0.36291(4)	0.0110(1)	0.0102(1)	0.0092(1)	0.0045(1)	0.0015(1)	0.0008(1)	
C(8)	0.48975(3)	0.20265(4)	0.33905(4)	0.0101(1)	0.0113(1)	0.0093(1)	0.0031(1)	0.0014(1)	-0.0008(1)	
O(1)	0.25897(4)	0.56704(5)	0.38353(5)	0.0166(2)	0.0122(2)	0.0128(2)	0.0067(1)	0.0009(1)	0.0012(1)	
O(2)	0.28171(4)	0.36141(5)	0.21546(5)	0.0194(2)	0.0164(2)	0.0103(2)	0.0077(1)	-0.0030(1)	-0.0022(1)	
O(3)	0.41850(4)	0.17467(5)	0.20310(5)	0.0148(2)	0.0177(2)	0.0115(2)	0.0062(1)	-0.0017(1)	-0.0050(1)	
O(4)	0.59061(3)	0.16557(5)	0.34483(5)	0.0111(2)	0.0175(2)	0.0118(2)	0.0053(1)	0.0019(1)	-0.0019(1)	
H(1)	0.33771(7)	0.2653(1)	0.2089(1)	0.0294(4)	0.0255(4)	0.0209(3)	0.0053(3)	-0.0010(3)	-0.0016(3)	
H(2)	0.28492(8)	0.5385(1)	0.6811(1)	0.0318(4)	0.0270(4)	0.0249(4)	0.0161(3)	0.0064(3)	0.0029(3)	
H(3)	0.38115(8)	0.4628(1)	0.9476(1)	0.0390(4)	0.0401(5)	0.0155(3)	0.0123(4)	0.0075(3)	-0.0017(3)	
H(4)	0.52866(8)	0.2655(1)	0.9295(1)	0.0376(4)	0.0429(5)	0.0184(3)	0.0132(4)	0.0013(3)	0.0091(3)	
H(5)	0.56619(8)	0.1540(1)	0.6464(1)	0.0300(4)	0.0320(4)	0.0266(4)	0.0177(3)	0.0038(3)	0.0060(3)	
OW(1)	0.32612(4)	0.92718(6)	0.96379(6)	0.0163(2)	0.0237(2)	0.0151(2)	-0.0009(2)	0.0043(2)	-0.0064(2)	
HU(11)	0.37127(8)	1.0080(1)	1.0385(1)	0.0299(4)	0.0323(4)	0.0267(4)	-0.0005(3)	0.0001(3)	-0.0081(3)	
HU(12)	0.36525(8)	0.9021(1)	0.8640(1)	0.0293(4)	0.0349(4)	0.0220(4)	0.0059(3)	0.0007(3)	-0.0032(3)	
LI(1)	0.2630(1)	0.7615(1)	0.5206(3)	0.0151(6)	0.0164(6)	0.0150(6)	0.0042(4)	0.0013(4)	0.0007(4)	
C(11)	-0.03386(3)	0.79358(4)	0.53759(4)	0.0090(1)	0.0114(2)	0.0094(1)	0.0021(1)	0.0010(1)	-0.0001(1)	
C(12)	-0.01197(3)	0.78441(4)	0.38813(4)	0.0120(1)	0.0139(1)	0.0092(1)	0.0023(1)	0.0012(1)	-0.0002(1)	
C(13)	-0.07089(3)	0.71122(4)	0.23017(5)	0.0141(1)	0.0199(2)	0.0108(1)	-0.0001(1)	0.0010(1)	-0.0033(1)	
C(14)	-0.15886(3)	0.81767(4)	0.21650(4)	0.0150(1)	0.0176(2)	0.0090(1)	-0.0008(1)	-0.0008(1)	0.0003(1)	
C(15)	-0.18635(3)	0.89173(4)	0.36369(4)	0.0124(1)	0.0135(1)	0.0104(1)	0.0013(1)	-0.0009(1)	0.0019(1)	
C(16)	-0.12553(3)	0.88872(4)	0.52547(4)	0.0095(1)	0.0103(1)	0.0085(1)	0.0013(1)	0.0006(1)	0.0013(1)	
C(17)	0.05126(3)	0.78541(4)	0.69471(4)	0.0102(1)	0.0119(1)	0.0101(1)	0.0029(1)	0.0006(1)	0.0011(1)	
C(18)	-0.16483(3)	0.99561(4)	0.66707(4)	0.0109(1)	0.0111(1)	0.0104(1)	0.0030(1)	0.0014(1)	0.0010(1)	
O(11)	0.14561(4)	0.73578(5)	0.67562(5)	0.0113(2)	0.0193(2)	0.0140(2)	0.0060(1)	0.0013(1)	0.0021(1)	
O(12)	0.02599(4)	0.83044(5)	0.84635(5)	0.0146(2)	0.0196(2)	0.0096(2)	0.0075(1)	0.0007(1)	0.0017(1)	
O(13)	-0.13278(4)	0.98317(5)	0.82600(5)	0.0153(2)	0.0178(2)	0.0098(2)	0.0070(1)	0.0018(1)	0.0005(1)	
O(14)	-0.22866(4)	1.09299(5)	0.63021(5)	0.0158(2)	0.0157(2)	0.0153(2)	0.0078(1)	0.0024(1)	0.0033(1)	
H(11)	-0.05760(7)	0.9016(1)	0.8418(1)	0.0284(3)	0.0302(4)	0.0185(3)	0.0056(3)	0.0030(3)	0.0023(3)	
H(12)	0.05898(8)	0.6312(1)	0.4013(1)	0.0268(3)	0.0338(4)	0.0297(4)	0.0141(3)	0.0016(3)	-0.0045(3)	
H(13)	-0.04599(8)	0.6459(1)	0.1171(1)	0.0341(4)	0.0446(5)	0.0213(4)	0.0074(4)	0.0046(3)	-0.0100(3)	
H(14)	-0.20625(8)	0.8154(1)	0.8932(1)	0.0358(4)	0.0420(5)	0.0175(3)	0.0053(4)	-0.0049(3)	0.0040(3)	
H(15)	-0.25708(7)	0.9638(1)	0.3535(1)	0.0278(4)	0.0296(4)	0.0267(4)	0.0119(3)	-0.0034(3)	0.0025(3)	
OW(2)	0.17626(4)	0.63688(5)	0.95813(6)	0.0300(4)	0.0309(4)	0.0165(3)	0.0059(2)	0.0007(2)	0.0027(2)	
HU(21)	0.20620(9)	0.6004(1)	0.1667(1)	0.0331(5)	0.0403(5)	0.0287(4)	0.0096(4)	-0.0011(4)	0.0139(4)	
HU(22)	0.1730(1)	0.5532(1)	-0.0249(2)	0.0746(8)	0.0371(6)	0.0405(6)	0.0117(5)	0.0061(5)	-0.0124(5)	
LI(2)	-0.1770(1)	0.1567(1)	0.9912(3)	0.0165(6)	0.0187(7)	0.0169(6)	0.0060(4)	0.0014(4)	0.0027(4)	

TABLE IV (continued).

c. 298K

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
C(1)	0.37425(4)	0.38711(6)	0.51285(6)	0.0268(3)	0.0262(2)	0.0238(2)	0.0043(2)	0.0046(2)	0.0022(2)
C(2)	0.35246(5)	0.45196(7)	0.67437(7)	0.0363(3)	0.0376(3)	0.0253(2)	0.0083(2)	0.0085(2)	0.0016(2)
C(3)	0.40490(6)	0.40680(8)	0.82193(7)	0.0438(3)	0.0536(4)	0.0238(2)	0.0080(3)	0.0069(2)	0.0027(2)
C(4)	0.48135(6)	0.29479(8)	0.81041(7)	0.0428(3)	0.0591(4)	0.0247(3)	0.0105(3)	0.0029(2)	0.0114(2)
C(5)	0.50661(5)	0.23223(7)	0.65074(7)	0.0346(2)	0.0440(3)	0.0289(3)	0.0120(2)	0.0029(2)	0.0101(2)
C(6)	0.45454(4)	0.27629(6)	0.50055(6)	0.0264(2)	0.0279(2)	0.0232(2)	0.0057(2)	0.0028(2)	0.0028(2)
C(7)	0.30681(5)	0.44573(6)	0.36709(7)	0.0313(2)	0.0305(3)	0.0266(2)	0.0085(2)	0.0024(2)	0.0038(2)
C(8)	0.49421(5)	0.20070(6)	0.33841(7)	0.0306(2)	0.0301(3)	0.0265(2)	0.0079(2)	0.0029(2)	-0.0029(2)
O(1)	0.26439(6)	0.56872(8)	0.38916(9)	0.0468(4)	0.0370(4)	0.0394(3)	0.0190(3)	0.0024(3)	0.0050(3)
O(2)	0.28980(7)	0.36456(9)	0.21946(9)	0.0553(4)	0.0502(4)	0.0294(3)	0.0228(3)	-0.0026(3)	-0.0026(3)
O(3)	0.42528(7)	0.1746(1)	0.20381(9)	0.0445(4)	0.0533(4)	0.0329(3)	0.0177(3)	-0.0059(3)	-0.0150(3)
O(4)	0.59280(6)	0.16329(9)	0.34269(9)	0.0335(3)	0.0475(4)	0.0349(3)	0.0144(3)	-0.0053(2)	-0.0057(3)
H(1)	0.3452(1)	0.2674(2)	0.2112(2)	0.0639(8)	0.0503(7)	0.0386(6)	0.0130(6)	-0.0059(5)	-0.0054(5)
H(2)	0.2906(1)	0.5374(2)	0.6839(2)	0.0637(8)	0.0613(8)	0.0458(7)	0.0262(7)	0.0178(6)	0.0033(6)
H(3)	0.3849(2)	0.4574(2)	0.9463(2)	0.081(1)	0.095(1)	0.0347(6)	0.0251(9)	0.0158(6)	-0.0028(7)
H(4)	0.5221(2)	0.2563(2)	0.9240(2)	0.080(1)	0.103(1)	0.0383(6)	0.028(1)	0.001(7)	0.0247(7)
H(5)	0.5685(1)	0.1467(2)	0.6411(2)	0.0594(9)	0.0697(9)	0.0549(7)	0.0327(7)	0.0055(6)	0.0179(6)
HU(1)	0.32181(7)	0.9365(1)	0.9624(1)	0.0429(6)	0.0672(6)	0.0410(4)	-0.0023(4)	0.0106(3)	-0.0176(4)
HU(11)	0.3275(1)	1.0119(2)	1.0383(2)	0.0537(7)	0.0647(9)	0.0524(7)	0.0041(7)	-0.0008(6)	-0.0123(7)
HU(12)	0.3609(1)	0.9081(2)	0.8657(2)	0.0549(7)	0.0672(9)	0.0428(7)	0.0117(6)	0.0100(6)	0.0066(6)
LI(1)	0.2641(2)	0.7649(2)	0.5249(4)	0.043(1)	0.043(1)	0.035(1)	0.0153(8)	0.0018(7)	0.0051(7)
C(11)	-0.02757(4)	0.78960(6)	0.54253(7)	0.0256(2)	0.0323(3)	0.0276(2)	0.0031(2)	0.0019(2)	0.0017(2)
C(12)	-0.00308(5)	0.69613(8)	0.39840(8)	0.0334(3)	0.0483(4)	0.0362(3)	0.0056(2)	-0.0023(2)	-0.0094(2)
C(13)	-0.06374(6)	0.69542(9)	0.23948(8)	0.0404(3)	0.0626(4)	0.0333(3)	-0.0015(3)	0.0027(2)	-0.0112(3)
C(14)	-0.15281(6)	0.78914(9)	0.22249(8)	0.0419(3)	0.0580(4)	0.0282(3)	-0.0052(3)	-0.0041(2)	0.0008(2)
C(15)	-0.18026(5)	0.87929(7)	0.36525(7)	0.0343(3)	0.0420(3)	0.0305(3)	0.0007(2)	-0.0060(2)	0.0070(2)
C(16)	-0.12007(4)	0.88261(6)	0.52639(7)	0.0257(2)	0.0308(3)	0.0266(2)	0.0021(2)	0.0009(2)	0.0046(2)
C(17)	-0.05593(5)	0.78781(7)	0.69849(7)	0.0287(2)	0.0350(3)	0.0306(3)	0.0076(2)	0.0007(2)	0.0043(2)
C(18)	-0.16142(5)	0.99239(7)	0.66366(7)	0.0294(2)	0.0339(3)	0.0314(3)	0.0000(2)	0.0041(2)	0.0058(2)
O(11)	0.15015(6)	0.7419(1)	0.6818(1)	0.0306(3)	0.0584(5)	0.0413(4)	0.0157(3)	0.0016(3)	0.0074(3)
O(12)	0.02941(7)	0.8340(1)	0.84721(9)	0.0432(4)	0.0629(5)	0.0280(3)	0.0233(4)	-0.0007(3)	0.0059(3)
O(13)	-0.13076(7)	0.98322(9)	0.82155(9)	0.0438(4)	0.0548(4)	0.0276(3)	0.0206(3)	0.0049(3)	0.0022(3)
O(14)	-0.22574(7)	1.08831(1)	0.6250(1)	0.0457(4)	0.0476(4)	0.0477(4)	0.0226(3)	0.0055(3)	0.0111(3)
H(11)	-0.0555(1)	0.9037(2)	0.8402(2)	0.0566(7)	0.0655(9)	0.0362(6)	0.0143(6)	0.0051(5)	0.0077(5)
H(12)	-0.0675(1)	0.6241(2)	0.4122(2)	0.0523(7)	0.077(1)	0.0655(9)	0.0266(7)	0.0014(6)	0.0159(7)
H(13)	-0.0395(2)	0.6248(2)	0.1309(2)	0.071(1)	0.114(2)	0.0512(9)	0.009(1)	0.0054(9)	-0.0308(9)
H(14)	-0.1997(2)	0.7927(2)	0.0983(2)	0.075(1)	0.102(1)	0.0393(7)	0.0008(9)	-0.0145(7)	0.0037(7)
H(15)	-0.2513(1)	0.9493(2)	0.3528(2)	0.0556(8)	0.0692(9)	0.0540(8)	0.0167(7)	-0.0139(6)	0.0079(7)
HU(2)	0.18745(9)	0.6409(1)	0.0585(1)	0.0797(6)	0.0520(5)	0.0447(5)	0.0211(5)	-0.0035(4)	0.0115(4)
HU(21)	0.2137(2)	0.6133(3)	0.1650(3)	0.083(1)	0.096(1)	0.071(1)	0.021(1)	-0.0050(9)	0.038(1)
HU(22)	0.1903(3)	0.5612(3)	-0.0189(4)	0.145(2)	0.089(2)	0.122(2)	0.025(2)	0.023(2)	-0.026(2)
LI(2)	-0.1793(2)	0.1525(3)	0.9924(5)	0.040(1)	0.048(1)	0.049(1)	0.0126(9)	0.0033(8)	0.0101(9)

* Thermal parameters are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$.

modified version of ORFLS.²¹ Weights were taken as $w = 1/\sigma^2(F_0^2)$. At each temperature, a scale factor (k), real and imaginary parts of the coherent neutron scattering lengths of Li atoms and a type I isotropic extinction parameter²² were varied together with positional and anisotropic thermal parameters for all atoms. The refinements were pursued to convergence; final difference-Fourier syntheses were essentially featureless. Neutron scattering lengths²³ used are $b_C = 0.665$, $b_H = -0.374$, and $b_O = 0.580$ ($\text{all} \times 10^{-12}$ cm). For Li atoms, refined values are listed in Table III. The real part of the scattering length with a mean value of $-0.207(1) \times 10^{-12}$ cm agrees well with the value of $-0.203(5) \times 10^{-12}$ cm given by Koester,²⁴ while the imaginary part is very nearly zero, as expected.

Third- and fourth-order thermal tensors were introduced for the O atoms of the carboxyl groups and H atoms in the intramolecular hydrogen bonds using an expansion developed by Johnson,^{25,26} and these higher-order terms were refined with the other parameters for the O and H atoms, in order to assess the importance of curvilinear or anharmonic thermal motion. The weighted R values after these refinements are included in Table II. Hamilton's R value test²⁷ indicates that, for the data obtained at 298 K, the model including higher-order terms gives significantly better fit than does the conventional model at the 99.5% confidence level. However, there appears to be no significant improvement for the data obtained at lower temperatures. Positional and anisotropic thermal parameters for all atoms from the conventional refinements are given in Table IV. A listing of observed and calculated squared structure factors is available.²⁸

RESULTS AND DISCUSSION

The main features of the structure have been described by Küppers in his paper⁶ reporting the x-ray diffraction study. The present discussion will be particularly concerned with the geometry of the hydrogen bonds and in general with those aspects of the structure that are observed to change with temperature.

The molecular structure of the hydrogen phthalate anions in the crystalline state at 15, 100, and 298 K is illustrated in Fig. 1,²⁹ and the approximately tetrahedral environment of the lithium cations is shown stereoscopically in Fig. 2. The reduction of thermal motion upon cooling the crystal is quite evident. Bond distances and angles in the anions calculated from the coordinates of Table IV are shown in Figs. 3 and 4, respectively, while the dimensions of the Li^+ coordination spheres and of the water molecules are given in Table V. The carboxyl groups are rotated so that the hydrogen phthalate anions are distinctly nonplanar; displacements of individual atoms from the least-squares planes through the C atoms of the six-membered rings are indicated in Fig. 5.

There is no major change in covalent bond distances or angles observed upon cooling the crystal, although a degree of foreshortening due to the effects of thermal motion is detectable at 298 K (*vide infra*), most notably in the water molecules. Generally good agreement is found between 298 K x-ray⁶ and neutron values of bonding parameters involving nonhydrogen atoms, with the differences $|\Delta P|/\sigma = |P_X - P_N|/[\sigma^2(X) + \sigma^2(N)]^{1/2} < 3$ for all distances and angles. There is a very slight systematic tendency for the x-ray⁶ values of C-C distances in the six-membered ring to be shorter

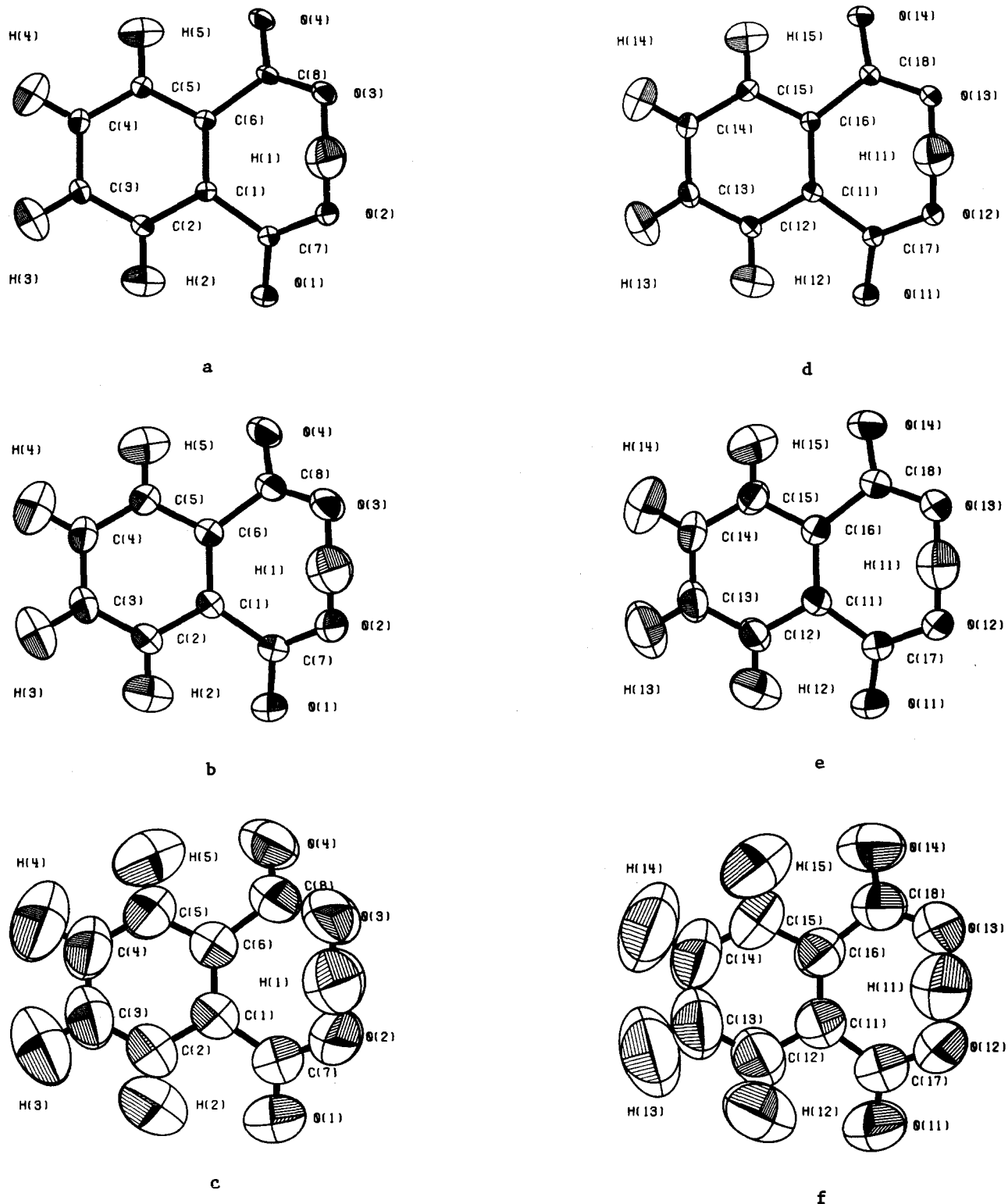


FIG. 1. Views of the hydrogen phthalate anions: (a) anion (I) at 15 K; (b) anion (I) at 100 K; (c) anion (I) at 298 K; (d) anion (II) at 15 K; (e) anion (II) at 100 K; (f) anion (II) at 298 K. Thermal ellipsoids are drawn to the 97% probability level.

than the corresponding neutron values, possibly reflecting the influence of the aspherical valence charge density on the x-ray refinement.

The crystal structure of LHPM is characterized by layers of hydrogen phthalate anions, lying roughly in the (110) plane, interconnected by coordination to the Li^+ ions and hydrogen bonding through the water molecules. Figure 6

presents a stereoscopic view of the structure, while intermolecular hydrogen bonding parameters are given in Table VI. Four short $\text{H}\cdots\text{O}$ contacts falling between 2.46 and 2.56 Å, somewhat beyond the normal range for hydrogen bonds, are also tabulated. Three of the H atoms of the two crystallographically independent water molecules are donated to carboxylic O atoms on hydrogen phthalate anion (I), but the

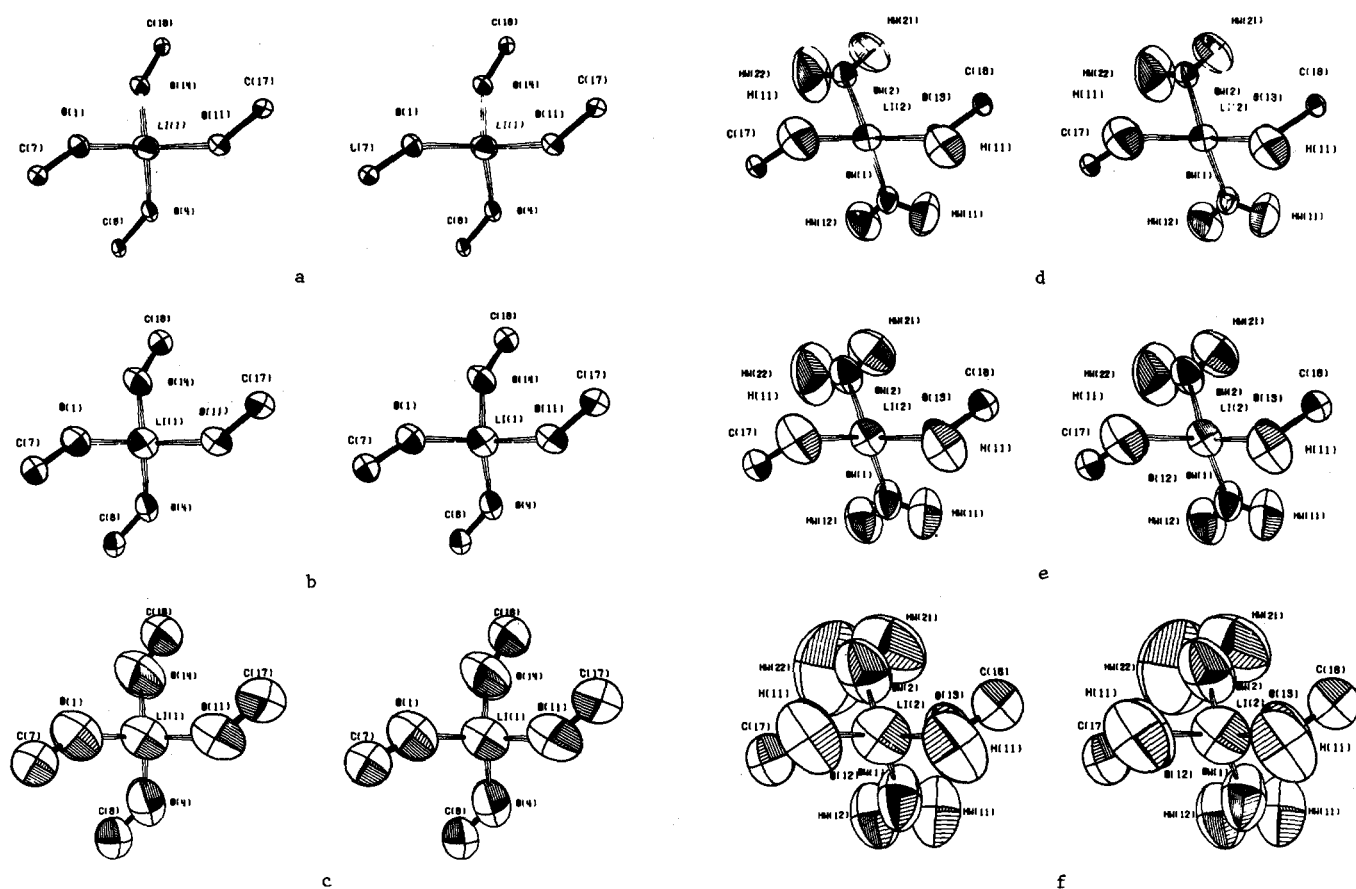


FIG. 2. Stereoscopic views of the environment surrounding the Li^+ ions, with ellipsoids drawn as in Fig. 1: (a) around Li(1) at 15 K; (b) around Li(1) at 100 K; (c) around Li(1) at 298 K; (d) around Li(2) at 15 K; (e) around Li(2) at 100 K; (f) around Li(2) at 298 K.

fourth [HW(22)] is not involved in any hydrogen bond and accordingly shows the largest thermal motion, as can be seen in Fig. 2.

The coordination around Li(2) is considerably more distorted from tetrahedral geometry than is that around Li(1). Two additional oxygens, namely O(11) and O(14), are locat-

ed within 2.9 Å of Li(2) and cause this distortion (see Table V).

The two independent hydrogen phthalate anions both possess very short intramolecular hydrogen bonds with $\text{O}\cdots\text{O}$ separations of approximately 2.4 Å and $\text{O}\cdots\text{H}\cdots\text{O}$ an-

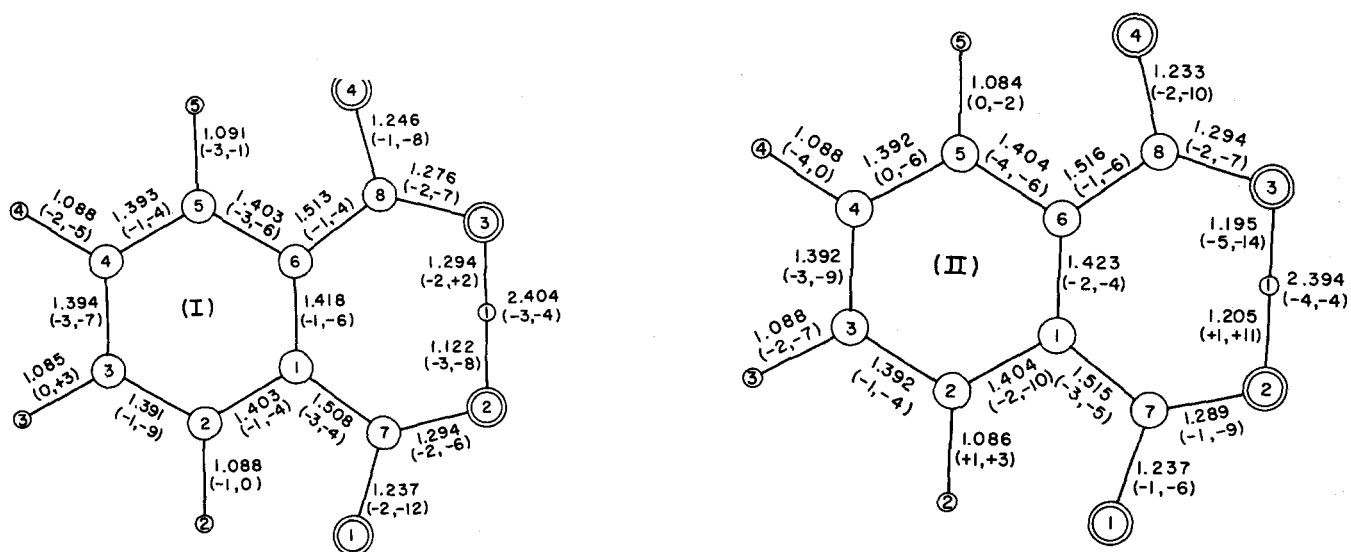


FIG. 3. Bond distances in hydrogen phthalate anions at 15 K. The differences $\Delta D(T) = D(T) - D(15)$ in units of 0.001 Å for $T = 100$ and 298 K, respectively, are given in parentheses below the values at 15 K (298 K values calculated employing the neutron cell parameters). Estimated standard deviations are 0.001–0.002 Å: (a) anion (I); (b) anion (II). [Add 10 to atom numbers in the circles for anion (II).]

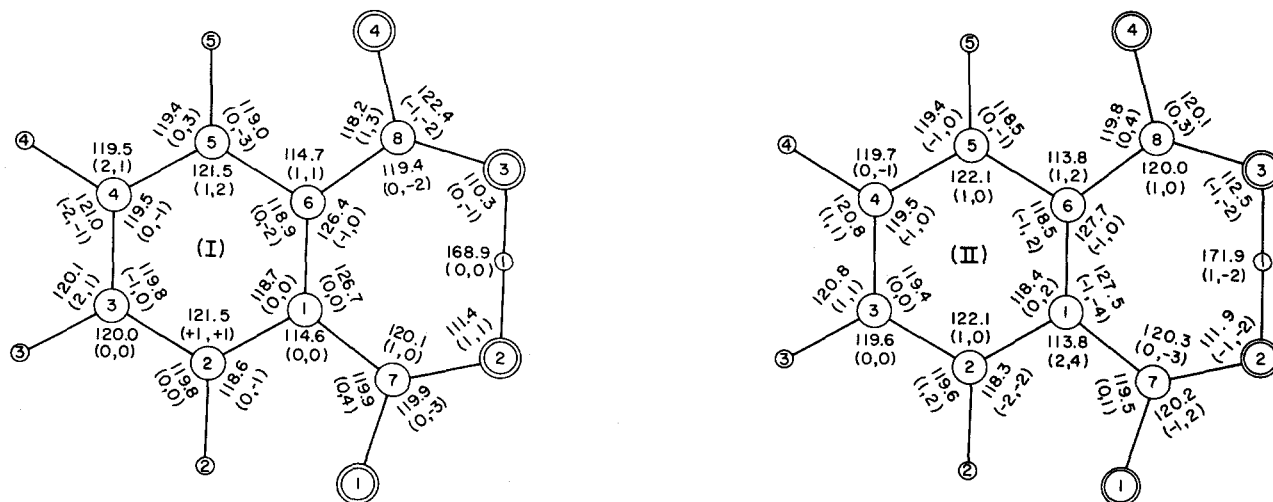


FIG. 4. Bond angles in hydrogen phthalate anions at 15 K. The differences $\Delta A(T) = A(T) - A(15)$ in units of 0.1° for $T = 100$ and 298 K, respectively, are given in parentheses below the values at 15 K (298 K values are calculated employing the neutron cell parameters). Estimated standard deviations are less than 0.1° : (a) anion (I); (b) anion (II). [Add 10 to atom numbers in the circles for anion (II).]

TABLE V. Geometry of the Li^+ coordination spheres and the water molecules.

Li-O distances (\AA)		15 K	100 K	298 K ^a
Symmetry				
Li(1)-O(1)	$[x, y, z]$	1.926(2)	1.931(2)	1.932(3)
Li(1)-O(4)	$[1-x, 1-y, 1-z]$	1.941(2)	1.938(2)	1.944(3)
Li(1)-O(11)	$[x, y, z]$	1.945(2)	1.946(2)	1.957(3)
Li(1)-O(14)	$[-x, 2-y, 1-z]$	1.908(2)	1.903(2)	1.915(3)
Li(2)-O(12)	$[-x, 1-y, 2-z]$	2.056(2)	2.057(2)	2.075(3)
Li(2)-O(13)	$[x, -1+y, z]$	2.042(2)	2.040(2)	2.043(3)
Li(2)-OW(1)	$[-x, 1-y, 2-z]$	1.916(2)	1.923(2)	1.924(3)
Li(2)-OW(2)	$[-x, 1-y, 1-z]$	1.937(2)	1.931(2)	1.934(3)
Li(2)-O(11)	$[-x, 1-y, 2-z]$	2.684(2)	2.669(2)	2.621(3)
Li(2)-O(14)	$[x, -1+y, z]$	2.808(2)	2.831(2)	2.893(3)
O-Li-O angles (deg)		15 K	100 K	298 K ^a
O(1)-Li(1)-O(4)		116.0(1)	115.8(1)	114.6(1)
O(1)-Li(1)-O(11)		105.0(1)	105.0(1)	106.0(1)
O(1)-Li(1)-O(14)		108.0(1)	108.0(1)	108.5(1)
O(4)-Li(1)-O(11)		108.8(1)	108.8(1)	108.7(1)
O(4)-Li(1)-O(14)		106.6(1)	106.9(1)	107.6(1)
O(11)-Li(1)-O(14)		112.6(1)	112.4(1)	111.6(1)
O(12)-Li(2)-O(13)		94.1(1)	94.2(1)	94.0(1)
O(12)-Li(2)-OW(1)		125.8(1)	125.6(1)	125.5(1)
O(12)-Li(2)-OW(2)		99.9(1)	100.7(1)	102.2(1)
O(13)-Li(2)-OW(1)		100.2(1)	100.0(1)	100.6(1)
O(13)-Li(2)-OW(2)		124.3(1)	123.8(1)	121.9(1)
OW(1)-Li(2)-OW(2)		113.3(1)	113.3(1)	113.0(1)
Water molecules		15 K	100 K	298 K ^a
OW(1)-HW(11)		0.964(1) \AA	0.961(1) \AA	0.949(2) \AA
OW(1)-HW(12)		0.968(1)	0.963(1)	0.955(2)
OW(2)-HW(21)		0.970(1)	0.962(1)	0.937(2)
OW(2)-HW(22)		0.932(1)	0.927(1)	0.882(3)
HW(11)-OW(1)-HW(12)		108.9(1) $^\circ$	109.2(1) $^\circ$	108.6(2) $^\circ$
HW(21)-OW(2)-HW(22)		107.3(1)	107.6(1)	107.7(3)

^a Calculated employing the neutron cell parameters (Table I).

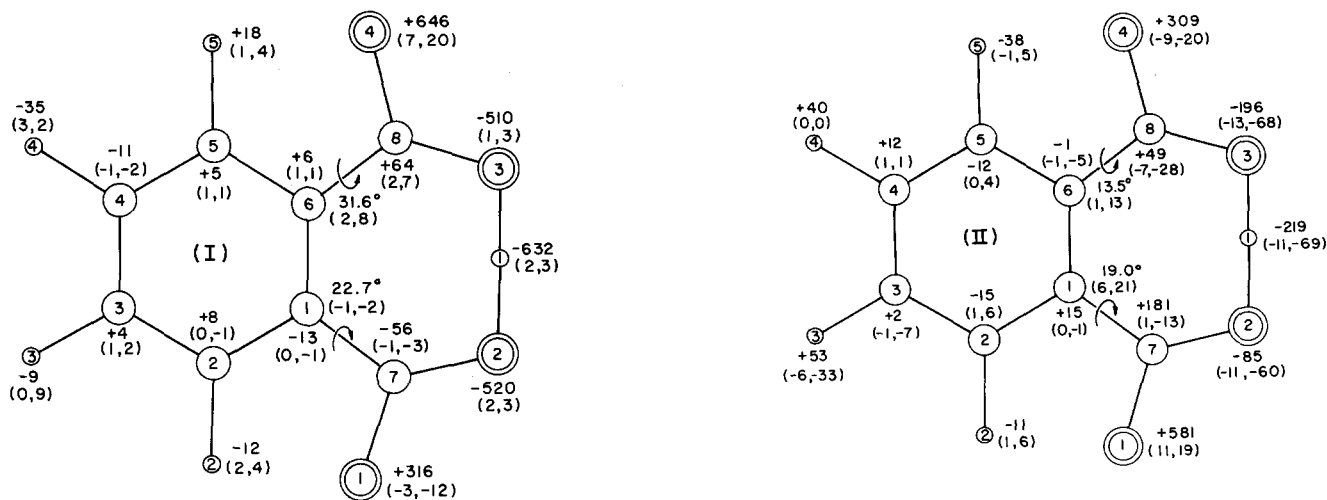


FIG. 5. Displacements of individual atoms in the anions from the least-squares planes through the C atoms of the six-membered rings at 15 K. Changes in displacements (displacement at T —displacement at 15 K) for $T = 100$ and 298 K, respectively, are given in parentheses below the values at 15 K. Units are 0.001 Å, and 298 K values are calculated employing the neutron cell parameters. Dihedral angles for out-of-plane rotations of the carboxyl groups are also shown: (a) anion (I); (b) anion (II). [Add 10 to atom numbers in the circles for anion (II).]

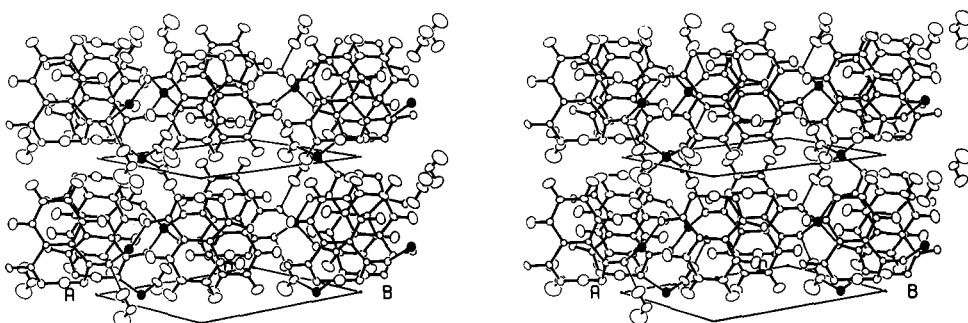


FIG. 6. Stereoscopic view of the crystal structure at 100 K. Thermal ellipsoids are drawn at the 74% probability level. Thin lines indicate Li...O bonds and intermolecular O-H...O bonds. Li⁺ ions have been filled in for clarity.

TABLE VI. Intermolecular hydrogen bonds and short H...O contacts.

(a) Intermolecular hydrogen bonds

- (I) OW(1)—HW(11) ... O(3)—C(8) [$x, 1 + y, 1 + z$]
 (II) OW(1)—HW(12) ... O(4)—C(8) [$1 - x, 1 - y, 1 - z$]
 (III) OW(2)—HW(21) ... O(1)—C(7) [x, y, z]

Hydrogen bond	Temperature	O...O	O—H	H...O	O—C	∠O—H...O	∠H...O—C
(I)	15 K	2.801(1) Å	0.964(1) Å	1.864(1) Å	1.276(1) Å	163.5(1)°	135.1(1)°
	100 K	2.800(1)	0.961(1)	1.865(1)	1.274(1)	164.0(1)	136.3(1)
	298 K ^a	2.809(2)	0.949(2)	1.877(2)	1.269(1)	166.5(1)	139.7(1)
(II)	15 K	2.778(1)	0.968(1)	1.826(1)	1.246(1)	167.5(1)	113.8(1)
	100 K	2.776(1)	0.963(1)	1.827(1)	1.245(1)	167.7(1)	114.3(1)
	298 K ^a	2.788(2)	0.955(2)	1.847(2)	1.223(1)	168.0(1)	115.6(1)
(III)	15 K	2.804(1)	0.970(1)	1.837(1)	1.237(1)	174.7(1)	106.1(1)
	100 K	2.808(1)	0.962(1)	1.848(1)	1.235(1)	175.5(1)	106.1(1)
	298 K ^a	2.855(2)	0.937(2)	1.919(2)	1.225(1)	176.5(1)	105.5(1)

(b) Short H...O contacts (Å)

	15 K	100 K	298 K ^a
C(2)—H(2) ... O(11) [x, y, z]	2.489(1)	2.492(1)	2.534(2)
C(5)—H(5) ... O(14) [$x, -1 + y, z$]	2.495(1)	2.509(1)	2.549(2)
C(12)—H(12) ... O(1) [x, y, z]	2.467(1)	2.460(1)	2.455(2)
OW(2)—HW(21) ... O(2) [x, y, z]	2.495(1)	2.499(1)	2.503(3)

^a Calculated employing the neutron cell parameters (Table I).

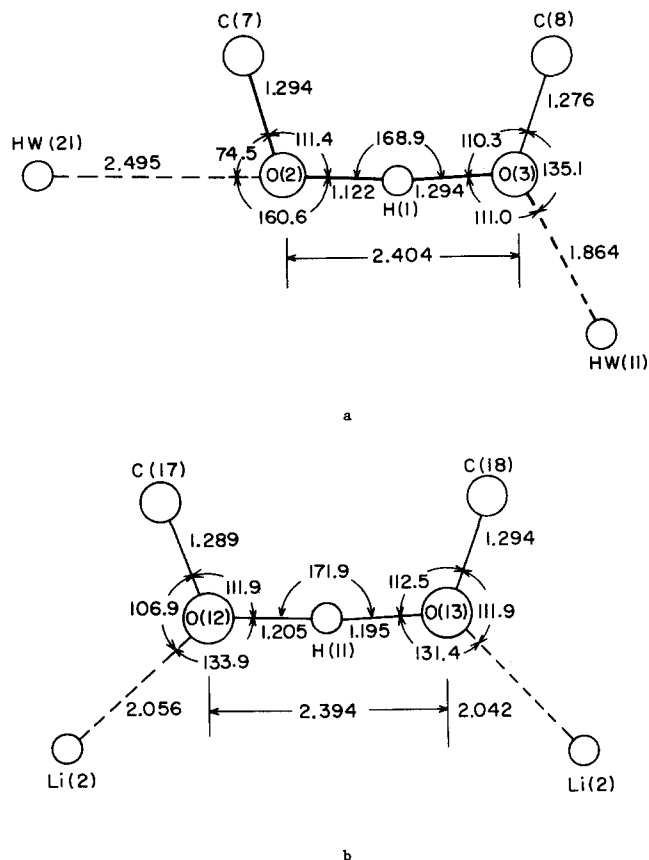


FIG. 7. Geometry of the intramolecular hydrogen bonds at 15 K. Esd's are 0.001 Å in distances and less than 0.1° in angles: (a) anion (I); (b) anion (II).

gles of about 170°. As shown in Fig. 7, the linkage in anion (I) is very decidedly asymmetric, with O(2)⋯H(1) 1.122(1) Å and H(1)⋯O(3) 1.294(1) Å at 15 K, reflecting the fact that oxygens O(2) and O(3) have quite different environments in the crystal. This asymmetry was also apparent from the x-ray determination.⁶ Oxygen O(3) accepts a normal hydrogen bond from the water molecule W1, but O(2) is involved only in a very weak interaction with W2. The “outer” oxygens O(1) and O(4) are hydrogen bonded to W2 and W1, respectively, with O(1)⋯HW(21) 1.837(1) Å and O(4)⋯HW(12) 1.826(1) Å at 15 K, and O(1) and O(4) also are both coordinated to Li(1) in a similar fashion. In anion (II), the intramolecular hydrogen bond is more nearly symmetric with O(13)⋯H(11) 1.195(1) Å and H(11)⋯O(12) 1.205(1) Å at 15 K. Oxygens O(12) and O(13) display similar contacts with Li(2), as do O(11) and O(14) with Li(1) (see Table V). However, H(11) is still not quite centered, but is displaced 0.005 Å or 5σ from the plane equidistant between O(12) and O(13) at 15 K. The displacement is 0.008 Å at 100 K and 0.018 Å at 298 K (*vide infra*). This small asymmetry is also evident in the C–O distances: C(17)–O(12) 1.289(1) Å, C(18)–O(13) 1.294(1) Å, C(17)–O(11) 1.237(1) Å, and C(18)–O(14) 1.233(1) Å at 15 K.

It is interesting to compare the situation in LHPM with that in the methanol adduct.^{4,5} This latter material also exhibits two crystallographically independent hydrogen phthalate anions with intramolecular hydrogen bonds, one of which is quite asymmetric (with O⋯H distances of 1.172(5) and 1.226(5) Å at 298 K⁵) and the other virtually

centered [O⋯H 1.195(5) and 1.205(5) Å]. The principal difference in the two structures stems from the fact that in the methanol adduct each methanol molecule possesses only one H atom to form hydrogen bonds, while the water molecules in LHPM have two such H atoms. In the methanol adduct, the “outer” oxygens of the asymmetric hydrogen phthalate anion each accept one hydrogen bond from a methanol molecule; these bonds are of different length, thereby causing the intramolecular hydrogen bond to be asymmetric. In LHPM, the considerably higher degree of asymmetry in anion (I) results from the situation where one carboxyl group [C(8), O(3), O(4)] accepts two intermolecular hydrogen bonds, while the other group [C(7), O(1), O(2)] accepts only one such bond, as indicated above.

The data presented here, together with available neutron diffraction results for comparable intramolecular O⋯H⋯O bonds unconstrained by crystallographic symmetry^{3,10,12–14,30–32} give strong evidence that the potential governing the H atom is extremely sensitive to asymmetries in the molecular environment.

For the hydrogen phthalate anions in LHPM, thermal parameters U_{ij} have been analyzed in terms of rigid-body motions by the method of Schomaker and Trueblood.³³ Results of these calculations are summarized in Table VII. As expected, all translational and librational tensor components are markedly reduced when the crystal is cooled. The fit assuming that the nonhydrogen atom framework of each anion behaves as a rigid body is quite good at both 15 and 100 K, but at 298 K it is evident that the carboxyl groups are moving somewhat independently of the six-membered rings. When the carboxyl groups were analyzed separately, the large librational motion at 298 K around the C–C bonds was seen to be greatly reduced upon cooling, just as was found to be the case in quinolinic acid.^{13,14}

The tensor components obtained from the nonhydrogen atom framework have been employed to correct the bond distances in each anion for the foreshortening effects of librational motion. The magnitude of these effects at 100 and 298 K may be estimated in terms of $R_T = \sum_{i=1}^n D_{iT} / \sum_{i=1}^n D_{i15}$, where D_{iT} is the i th bond distance found at temperature T and the summation extends over the 36 bonds in both anions. R_{100} and R_{298} are 0.9988 and 0.9961, respectively, for uncorrected distances. After correction, R_{100} (0.9994) and R_{298} (0.9990) are both closer to the ideal value of 1.0. Individual bond distances averaged over the three experimental temperatures are listed in Table VIII.

The temperature dependence of thermal motion was further investigated by fitting the atomic U_{ij} values to the expression $U_{ij}(T) = a_{ij}T^n + b_{ij}$, where the coefficients a_{ij} and b_{ij} for each individual atom and the overall exponent n were determined by least-squares methods. A value of $n = 1.46$ was obtained, close to the value of 1.5 shown to hold for Debye–Waller factors in a diverse set of inorganic crystalline solids by Bastow, Mair, and Wilkins, who interpreted this empirical relationship within the framework of the Debye theory modified to include quasi-harmonic effects.³⁴

The dimensions of the intramolecular hydrogen bonds exhibit interesting systematic changes with temperature. At

TABLE VII. Results of rigid-body analyses of thermal motion in the hydrogen phthalate anions.

	Temp. K	$\langle \Delta U^2 \rangle^{1/2}$ \AA^2	<i>L</i> principal axes				<i>T</i> principal axes ^a				$ S_{\text{max}} $ ^b \AA	$\langle \Delta U^2 \rangle^{1/2}$, \AA^2 C atoms only ^c
			$(L_i)^{1/2}$ deg	Direction cosines			$(T_i)^{1/2}$ \AA	Direction cosines				
C and O atoms (I) ^d	15	0.0005	1.7(1)	-0.23	0.97	0.05	0.077(1)	-0.14	-0.09	0.99	0.012	0.0002
			1.1(1)	0.61	0.10	0.79	0.066(1)	-0.90	-0.42	-0.16		
			0.8(1)	0.76	0.21	-0.61	0.058(1)	0.42	-0.91	-0.02		
	100	0.0008	2.5(1)	-0.18	0.98	0.09	0.102(2)	-0.12	-0.05	0.99	0.022	0.0002
			1.6(1)	0.61	0.04	0.79	0.091(2)	-0.68	-0.72	-0.12		
			1.3(1)	0.77	0.20	-0.61	0.083(2)	0.72	-0.69	0.05		
	298	0.0023	4.5(1)	-0.10	0.98	0.15	0.167(4)	0.09	0.12	-0.99	0.033	0.0005
			3.0(2)	0.62	-0.06	0.78	0.154(4)	-0.37	-0.92	-0.15		
			2.4(2)	0.78	0.17	-0.60	0.143(4)	-0.92	0.38	-0.04		
Carboxyl group C(1), C(7), O(1), O(2) ^e	15	0.0006	3.9(3)	1.00	0.00	0.00	0.081(3)	-0.12	-0.89	0.44	g	...
			f				0.070(3)	-0.93	-0.06	-0.37		
			f				0.064(3)	0.35	-0.45	-0.82		
	100	0.0013	5.8(4)	1.00	0.00	0.00	0.111(5)	-0.11	-0.88	0.45	g	...
			f				0.099(4)	-0.95	-0.04	-0.31		
			f				0.090(4)	0.29	-0.47	-0.83		
	298	0.0040	10.2(7)	1.00	0.00	0.00	0.187(9)	-0.08	-0.80	0.60	g	...
			f				0.169(7)	-0.84	-0.27	-0.47		
			f				0.154(7)	0.54	-0.54	-0.65		
Carboxyl group C(6), C(8), O(3), O(4) ^e	15	0.0005	3.5(2)	1.00	0.00	0.00	0.083(3)	-0.23	0.96	0.15	g	...
			f				0.074(2)	0.40	-0.04	0.91		
			f				0.061(2)	0.88	0.27	-0.38		
	100	0.0012	5.4(4)	1.00	0.00	0.00	0.115(4)	-0.32	0.92	0.23	g	...
			f				0.102(3)	0.32	-0.13	0.94		
			f				0.086(4)	0.89	0.37	-0.25		
	298	0.0041	9.6(7)	1.00	0.00	0.00	0.194(9)	-0.41	0.85	0.34	g	...
			f				0.171(7)	0.33	-0.20	0.92		
			f				0.145(7)	0.85	0.49	-0.20		
C and O atoms (II) ^d	15	0.0004	1.5(1)	0.29	0.95	-0.12	0.078(1)	0.05	-0.08	-1.00	0.010	0.0002
			1.1(1)	0.89	-0.21	0.41	0.065(1)	0.83	0.56	0.00		
			0.9(1)	0.36	-0.23	-0.90	0.062(1)	0.56	-0.82	0.10		
	100	0.0008	2.3(1)	0.39	0.88	-0.27	0.104(2)	0.14	-0.17	-0.97	0.030	0.0002
			1.7(1)	0.82	-0.20	0.53	0.094(2)	0.20	0.97	-0.14		
			1.6(1)	0.41	-0.43	-0.80	0.091(2)	0.97	-0.17	0.17		
	298	0.0025	4.3(1)	0.29	0.91	-0.29	0.173(4)	-0.26	0.34	0.90	0.051	0.0005
			3.1(2)	0.91	-0.17	0.37	0.162(4)	-0.58	0.69	-0.43		
			2.8(2)	0.29	-0.37	-0.88	0.153(4)	-0.77	-0.64	0.02		
Carboxyl group C(11), C(17), O(11), O(12) ^e	15	0.0005	3.3(2)	1.00	0.00	0.00	0.083(2)	-0.13	-0.98	0.17	g	...
			f				0.071(2)	-0.92	0.05	-0.39		
			f				0.066(2)	0.38	-0.20	-0.90		
	100	0.0009	5.0(3)	1.00	0.00	0.00	0.114(4)	0.20	0.96	-0.19	g	...
			f				0.104(3)	0.73	-0.02	0.68		
			f				0.094(3)	0.65	-0.27	-0.71		
	298	0.0033	9.4(6)	1.00	0.00	0.00	0.192(8)	0.27	0.94	-0.21	g	...
			f				0.182(5)	0.53	0.03	0.85		
			f				0.157(6)	0.80	-0.34	-0.49		
Carboxyl group C(16), C(18), O(13), O(14) ^e	15	0.0005	3.5(2)	1.00	0.00	0.00	0.081(2)	-0.28	0.95	0.13	g	...
			f				0.071(2)	0.43	0.00	0.90		
			f				0.065(2)	0.86	0.31	-0.41		
	100	0.0012	5.1(4)	1.00	0.00	0.00	0.111(5)	-0.48	0.87	0.12	g	...
			f				0.105(3)	0.54	0.19	0.82		
			f				0.094(3)	0.69	0.46	-0.56		
	298	0.0038	9.4(7)	1.00	0.00	0.00	0.191(9)	-0.71	0.70	-0.03	g	...
			f				0.180(6)	0.42	0.46	0.78		
			f				0.158(6)	0.56	0.55	-0.62		

^aObtained using the nonintersecting axes description of the motion, as defined in Ref. 33.^bMaximum effective screw translation along the principal axes of *L*.^cThe rms fit for a rigid body composed of the eight C atoms alone is included for purposes of comparison, to allow an assessment of the importance of independent motions of the O atoms.^dThe coordinate system is defined with the *z* axis normal to the plane of the six-membered ring, the *x* axis along [C(2)–C(5)] × *z* or [C(12)–C(15)] × *z*, and the *y* axis along *z* × *x*.^eThe coordinate system is defined with *x* along (C–C), *y* along the normal to the plane defined by the two C atoms and the "outer" oxygen and *z* along *x* × *y*. The origin lies along the *x* axis.^fOnly L_{11} was refined; all other librational components were set to zero.^gThe *S* tensor was not included.

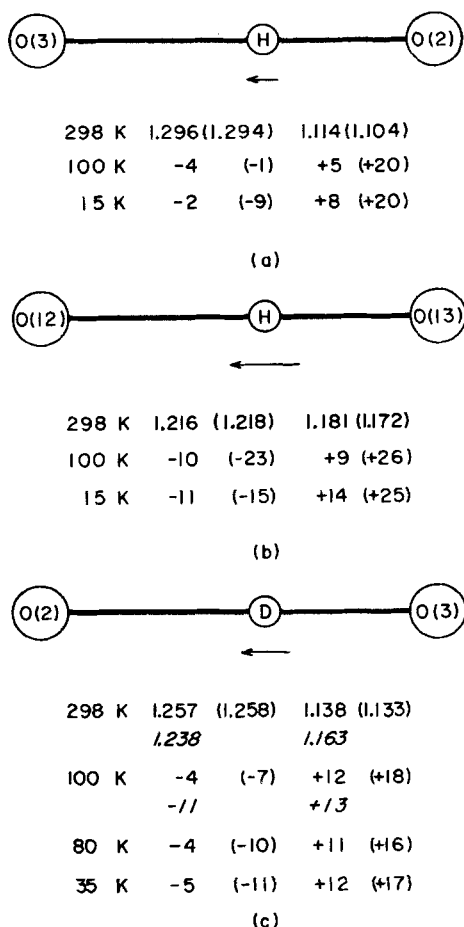


FIG. 8. Dimensions of the intramolecular hydrogen bonds with the changes in H(D)...O distances upon cooling. The changes are given in units of 0.001 Å and results of refinements incorporating higher-order thermal tensors are included in parentheses. (a) LHPM anion (I); (b) LHPM anion (II); (c) deuterated quinolinic acid (Ref. 14) with values for the H compound (Refs. 12 and 13) also included in italics. Esd's are 0.001–0.002 Å, except in the case of H-quinolinic acid where they are 0.003–0.005 Å.

TABLE VIII. Bond distances averaged over $T = 15, 100,$ and 298 K.

Bond	Mean distance, Å ^a			
	Uncorrected		Corrected for thermal motion	
	Anion (I)	Anion (II) ^b	Anion (I)	Anion (II) ^b
C(1)–C(2)	1.4015(11)	1.4000(31)	1.4038(2)	1.4026(16)
C(2)–C(3)	1.3878(29)	1.3902(11)	1.3904(14)	1.3924(2)
C(3)–C(4)	1.3906(21)	1.3883(25)	1.3921(13)	1.3902(15)
C(4)–C(5)	1.3911(11)	1.3900(18)	1.3935(3)	1.3925(4)
C(5)–C(6)	1.4001(16)	1.4005(16)	1.4028(6)	1.4027(8)
C(1)–C(6)	1.4157(20)	1.4210(11)	1.4172(11)	1.4230(1)
C(1)–C(7)	1.5059(11)	1.5122(13)	1.5086(9)	1.5145(5)
C(6)–C(8)	1.5116(12)	1.5135(18)	1.5139(3)	1.5163(2)
C(7)–O(1) ^c	1.2327(36)	1.2345(18)	1.2341(28)	1.2362(8)
			1.2398(2)	1.2404(17)
C(7)–O(2) ^c	1.2913(16)	1.2852(34)	1.2936(5)	1.2876(20)
			1.2988(24)	1.2913(4)
C(8)–O(3) ^c	1.2729(21)	1.2911(22)	1.2753(8)	1.2932(9)
			1.2795(15)	1.2973(13)
C(8)–O(4) ^c	1.2431(25)	1.2290(29)	1.2446(16)	1.2308(19)
			1.2496(12)	1.2349(14)
C(2)–H(2)	1.0876(3)	1.0874(12)	1.0888(8)	1.0889(20)
C(3)–H(3)	1.0861(9)	1.0849(18)	1.0879(20)	1.0870(7)
C(4)–H(4)	1.0858(16)	1.0869(14)	1.0879(5)	1.0885(20)
C(5)–H(5)	1.0894(9)	1.0833(7)	1.0906(11)	1.0848(2)

^a Esd's are calculated as $\sigma(\langle x \rangle) = (\sum_{i=1}^3 (x_i - \langle x \rangle)^2 / 6)^{1/2}$, where the summation runs over the values at 15, 100, 298 K.

^b Add 10 to the atom numbers in the left-hand column for anion (II).

^c The first line gives the bond distance corrected for librational motion assuming all C and O atoms make up a rigid body, and the second line gives the distance corrected for the libration of the carboxyl group alone.

15 and 100 K the O...O distances increase marginally³⁷ (0.003–0.004 Å, uncorrected values) relative to the values at 298 K, while the hydrogens H(1) and H(11) shift toward the plane equidistant between the two O atoms. The resulting changes in H...O distances, which are small but quite significant judging from their esd's, are indicated in Fig. 8 together with similar corresponding values found in quinolinic acid.^{12–14} Distances calculated from the positional parameters obtained in the refinements including third- and fourth-order thermal tensors^{25,26} are also shown and follow the same trend as the results from the conventional refinement, although the changes with temperature are larger in magnitude for the high-order refinements. It is perhaps noteworthy that while cooling causes the intramolecular hydrogen bonds to become more symmetric, deuteration appears to have the opposite effect, making the bonds more asymmetric, based on the results for quinolinic acid^{12–14} and imidazolium hydrogen maleate.³¹

Dimensions of some of the intermolecular hydrogen bonds and short O...H contacts show substantial variation with temperature (Table VI) reflecting the effects of thermal motion on the crystal packing. On the other hand, the eight nearest-neighbor Li–O distances are shortened on the average by only 0.4% in going from 298 to 15 K, as might be expected for these strong bonded interactions.³⁸ In the hydrogen phthalate anions, and especially in anion(II), there are significant changes in the out-of-plane displacements (Fig. 5) of atoms of the carboxyl groups, for which the librational motion about the C–C bonds is much reduced upon cooling. (It should be noted that perturbations of the carboxyl groups are quite strongly coupled with one another via the linkages involving the Li⁺ ions.) Finally, the distances between the planes of anions related by a center of inversion are 3.568, 3.571, and 3.592 Å at 15, 100, and 298 K, respectively, for anion (I), and 3.286, 3.306, and 3.389 Å for anion (II); appreciable contraction is evident upon cooling.

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³⁷This apparent increase probably reflects some foreshortening of the 298 K values due to thermal motion.

³⁸The weaker Li(2)–O(11) and Li(2)–O(14) interactions change much more with temperature: Li(2)–O(14) contracts approximately 3% on cooling, while Li(2)–O(11) actually increases 2%.