molecular contacts appear to be normal; the shortest (between hydrogen atoms) is 2·68 Å.

Computer programs used in this work are those of Ahmed *et al.* (1966), Gantzel & Trueblood (*MGTLS*, thermal motion analysis) and C. K. Johnson (*ORTEP*, thermal ellipsoid plot). The problem was suggested, and specimen material supplied by Professor V. Boekelheide.

References

AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). *N.R.C. Crystallographic Programs for the IBM/360 System. IUCr World List of Crystallographic Computer Programs.* 2nd ed. Appendix, p. 52.

BERNSTEIN, J. & TRUEBLOOD, K. N. (1971). *Acta Cryst.* B27, 2078.

COULTER, C. L. & TRUEBLOOD, K. N. (1963). *Acta Cryst.* 16, 667.

GANTZEL, P. K. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* 18, 958.

HANSON, A. W. (1962). *Acta Cryst.* 15, 956.

HANSON, A. W. (1971). *Acta Cryst.* B27, 197.

HANSON, A. W. & HUML, K. (1969). *Acta Cryst.* B25, 2310.

HANSON, A. W. & HUML, K. (1971). *Acta Cryst.* B27, 459.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* 17, 1040.

HOPE, H., BERNSTEIN, J. & TRUEBLOOD, K. N. (1972). *Acta Cryst.* B28, 1733.

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

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

MATHEW, M. (1968). *Acta Cryst.* B24, 530.

MATHEW, M. & HANSON, A. W. (1968). *Acta Cryst.* B24, 1680.

MITCHELL, R. H. & BOEKELHEIDE, V. (1970). *J. Amer. Chem. Soc.* 92, 3510.

PINNOCK, P. R., TAYLOR, C. A. & LIPSON, H. (1956). *Acta Cryst.* 9, 173.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B24, 63.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175.

SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Supplement 1956–1959, M112S. London: The Chemical Society.

Hydrogen Bond Studies. LXI.* An X-ray Diffraction Study of the Isotope Effect in Lithium Hydrogen Oxalate Monohydrate, $LiHC_2O_4.H_2O$

BY J. O. THOMAS†

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala 1, Sweden

The crystal structures of the normal and deuterated forms of $LiHC_2O_4.H_2O$ have been determined from three-dimensional single-crystal X-ray diffraction data collected at room temperature using an automatic Stoe–Philips four-circle diffractometer. The unit cells in both structures are triclinic with the space group $P1$ and containing one formula unit. The cell dimensions are, for $LiHC_2O_4.H_2O$ $a = 5·056$ (1), $b = 6·140$ (1), $c = 3·411$ (1) Å, $\alpha = 95·06$ (1), $\beta = 98·93$ (1), $\gamma = 78·57$ (1)°, $V = 102·36$ Å^3 and for $LiDC_2O_4.D_2O$ $a = 5·055$ (1), $b = 6·138$ (1), $c = 3·410$ (1) Å, $\alpha = 95·05$ (1), $\beta = 98·62$ (1), $\gamma = 78·57$ (1)°, $V = 102·34$ Å^3. The undeuterated structure consists of infinite parallel chains of hydrogen oxalate ions joined by 2·490 (1) Å asymmetric hydrogen bonds. These chains are linked transversely in the plane of the hydrogen oxalate ions by weaker hydrogen bonds, 2·702 (1) and 2·777 (1) Å, *via* the water molecules and by $Li^+\cdots O$ electrostatic forces. The infinite planes so formed are in turn held together by further $Li^+\cdots O$ electrostatic forces. The structure is generally unchanged in the deuterated form except for an increase of 0·016 (1) Å in the shortest $O\cdots O$ hydrogen bond length. The conventional R values obtained from the refinement of the normal and deuterated compound are 0·024 and 0·026 respectively.

Introduction

Deuteration has long been recognized as a most useful device in hydrogen-bond studies, *e.g.* Robertson &

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† Visiting NATO/SRC (Great Britain) Research Fellow.

Ubbelohde (1939). The majority of observations of the resulting 'isotope effect' have been based, however, on cell parameter measurements combined with the assumption that any isotope effect present would appear only as changes in the hydrogen-bond lengths. More recently a number of complete structural studies of normal and deuterated compounds have been made:

α-oxalic acid dihydrate (Delaplane & Ibers, 1969), $NaHC_2O_4.H_2O$ (Tellgren & Olovsson, 1971), and $H_2SO_4.4H_2O$ (Kjällman & Olovsson, 1972). From these it is possible to obtain explicitly the effect of deuteration on the structure concerned. The present study is intended to provide further data of this type. The room temperature structures of normal and deuterated $LiHC_2O_4.H_2O$ (*LIHOX* and *LIDOX*, respectively) have been determined and refined independently from single-crystal X-ray diffractometer data.

The atomic positional parameters obtained here for *LIHOX* agree reasonably well with the less accurate results published by Follner (1970), although the structural description he has provided is slightly misleading. Significantly different bond lengths and angles are also reported in this paper.

Crystal data

Lithium hydrogen oxalate monohydrate, $LiHC_2O_4.H_2O$. F.W. 114·0. Triclinic, $a=5·056$ (1),* $b=6·140$ (1), $c=3·411$ (1) Å, $\alpha=95·06$ (1), $\beta=98·93$ (1), $\gamma=78·57$ (1)°, $V=102·36$ Å^3 at 25°C. $Z=1$, $D_x=1·849$ g.cm^{-3}. Space group $P1$.
Deuterated lithium hydrogen oxalate monohydrate, $LiDC_2O_4.D_2O$. F.W. 117·0. Triclinic, $a=5·055$ (1), $b=6·138$ (1), $c=3·410$ (1) Å, $\alpha=95·05$ (1), $\beta=98·62$ (1), $\gamma=78·57$ (1)°, $V=102·34$ Å^3 at 25°C. $Z=1$, $D_x=1·898$ g.cm^{-3}. Space group $P1$.

Experimental

Crystals of *LIHOX* were prepared by dissolving oxalic acid (*pro analysi*) in hot water and adding an equivalent amount of lithium carbonate (*pro analysi*). Flat elongated crystals were formed on cooling.

Similarly shaped *LIDOX* crystals were then obtained from repeated recrystallizations from heavy water (>99·9%). The degree of deuteration in the crystals was estimated from an infrared spectrum. Comparison of the peak heights for the O–H and O–D stretching modes in the water molecule indicated a 2·5–5·0% H occupation of D atom sites. This assumes a random distribution of H atoms over all D atom sites throughout the crystal.

X-ray examination of the crystals revealed a triclinic symmetry with an extremely high incidence of twinning across the (010) plane in both *LIHOX* and *LIDOX* crystals. Initially only a very small lath-like single crystal of *LIHOX* could be found and this was used for the original structure determination. This crystal measured 0·35×0·06×0·02 mm. It was later found, however, that the final standard deviations after refinement of the data set (~0·004 Å on the bond lengths) were too large for a determinative isotope effect study. This was almost certainly due to the un-

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* Numbers in parentheses here and throughout this paper represent standard deviations in the least significant digits.

favourable counting statistics which applied as a result of using such a small crystal. Therefore, it was decided once a suitably large single crystal of *LIHOX* had been ultimately obtained by cracking a piece from a larger twinned crystal, to re-collect the data. The second *LIHOX* crystal measured 0·24×0·20×0·10 mm; a volume roughly 16 times that of the first. Henceforth only this latter data set will be considered unless otherwise stated.

A *LIDOX* single crystal (measuring 0·35 × 0·20 × 0·15 mm) could also be obtained only by cracking a piece from a larger twinned crystal. For data collection this was sealed inside a thin-walled silica glass capillary of approximate diameter 0·2 mm.

The triclinic cell parameters were measured using a Guinier–Hägg powder camera calibrated with silicon ($a=5·43054$ Å, λ for the monochromated Cu $K\alpha_1$ radiation = 1·54051 Å). These were refined in a least-squares program using 34 and 48 observed θ values for *LIHOX* and *LIDOX*, respectively. Chemical considerations suggested that, with one formula unit per cell, $P1$ was the only realistic space group.

Both data sets were collected at approximately 25°C using an automatic Stoe–Philips four-circle diffractometer controlled by a PDP8/I computer and operating in a $\omega/2\theta$ scan mode. A graphite single crystal was used to produce a monochromated Mo $K\alpha$ X-ray beam ($\lambda=0·71069$ Å) which then passed through a bank of three filters, each having a potential 2:1 cutdown effect on the incident beam intensity. Automatic filter selection thus made it possible to reduce the count rate in the detector by a ratio of up 8:1. This, in combination with automatic scan-speed selection ($\times 1$, $\times 2$ or $\times 4$), resulted in a maximum absolute internal scale factor of 32. Both intensity data sets were collected over a complete hemisphere in reciprocal space up to sin $\theta/\lambda=0·8569$. Three standard reflexions were monitored every 40 reflexions to provide a check both on the mechanical and chemical stability of the crystal and on the stability of the diffractometer system itself. A very slight tendency for the intensities of two of the test reflexions used in the *LIHOX* data collection to fall slowly was noted. This effect could be satisfactorily counteracted by a systematic redetermination of the crystal orientation matrix for every 200–300 reflexions measured. No systematic changes were observed in the test reflexions monitored during the *LIDOX* data collection.

The measured integrated peak intensities so obtained were then corrected for background and assigned standard deviations $\sigma_c(I)$ based solely on Poisson counting statistics. 1076 independent reflexions were measured for *LIHOX* of which 1023 had intensities in excess of $3\sigma_c(I)$. These were retained in the final refinements. The *LIDOX* data collection provided 1083 independent reflexions of which 1057 were in excess of $3\sigma_c(I)$.

The data sets were corrected for Lorentz, polarization and absorption effects to give the quantities F_o^2 and $\sigma_c(F_o^2)$. In both cases the crystal shape could be des-

cribed explicitly in terms of their six rational boundary planes. The transmission factors for *LIHOX* ($\mu = 1\cdot98$ cm^{-1} for Mo $K\alpha$ radiation) fell in the range 0·961–0·979 and for *LIDOX* ($\mu = 2\cdot00$ cm^{-1}) in the range 0·954–0·974. Isotropic extinction corrections were also applied to the data sets (see below).

Structure determination and refinements

The positions of the heavy atoms of the hydrogen oxalate ion in *LIHOX* were obtained directly from a three-dimensional Patterson synthesis. All remaining atoms were then located unambiguously from a series of difference Fourier syntheses.

Full-matrix least-squares refinements were performed on both data sets using the program *LINUS* in which the function minimized was $\sum w(|F_o^2| - |F_c^2|)^2$, where the weighting factor $w = 1/\sigma_c^2(F^2)$. In the latter stages cf refinement this quantity was modified so that $\sigma^2(F^2) = \sigma_c^2(F^2) + (kF^2)^2$, where k is an empirical constant given the value 0·05. This is intended to take account of other random errors in the data. Subsequent analysis of the resulting weighting indicated that this modification had been effective. The starting values for both refinements were the final refined parameters which had been obtained for *LIHOX* using data collected from the very small crystal (conventional R index 0·046). The progress of the refinements is summarized in Table 1. The agreement factors given are calculated from the expressions:

$$R(F^2) = \sum||F_o^2| - |F_c^2||/\sum|F_o^2|$$
and
$$R_w(F^2) = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^4|]^{1/2}.$$

The final conventional R values based on F were 0·024 for *LIHOX* and 0·026 for *LIDOX*. The data recol-

lection for *LIHOX* therefore had the desired effect of improving the precision of the refined parameters.

In the final refinement of *LIHOX* the value obtained for the isotropic extinction parameter g (Coppens & Hamilton, 1970) was 2570(440). The corresponding value for *LIDOX* was 3210(440). For both refinements the final shifts were all less than $0\cdot1\sigma$ for the non-hydrogen atoms and of the order of $0\cdot3\sigma$ for the hydrogen atoms. The resulting positional and thermal parameters are given in Tables 2 and 3 together with the lengths of the principal axes of the thermal motion ellipsoids. The final observed and calculated structure factors are presented in Table 4.

Table 2. *Atomic coordinates* ($\times 10^5$)

For hydrogen and deuterium atoms the coordinates are ($\times 10^3$)

LIHOX

	x	y	z
Li	86692 (40)	69920 (33)	91086 (59)
O(1)	0	0	0
O(2)	-18998 (19)	34025 (15)	-21069 (32)
O(3)	21309 (18)	51117 (14)	16583 (29)
O(4)	41837 (19)	18547 (15)	41536 (32)
C(1)	-104 (22)	19629 (16)	-1473 (33)
C(2)	23126 (21)	30990 (17)	20697 (34)
O(W)	63552 (21)	74659 (16)	36361 (33)
H(1)	688 (6)	275 (5)	658 (11)
H(2)	530 (5)	659 (4)	340 (8)
H(3)	534 (5)	875 (4)	364 (7)

LIDOX

	x	y	z
Li	86672 (39)	69927 (32)	91167 (56)
O(1)	0	0	0
O(2)	-18893 (18)	34112 (14)	-20873 (31)
O(3)	21258 (18)	51142 (13)	16615 (28)
O(4)	41818 (18)	18557 (15)	41431 (31)
C(1)	-14 (21)	19617 (15)	-1382 (31)
C(2)	23151 (20)	31001 (15)	20678 (31)
O(W)	63473 (20)	74671 (15)	36650 (31)
D(1)	690 (5)	278 (5)	662 (10)
D(2)	527 (5)	661 (4)	347 (8)
D(3)	545 (5)	875 (4)	360 (8)

Table 1. *Agreement factors at successive stages of the refinements*

The expressions for $R(F^2)$ and $R_w(F^2)$ are given in the text. The position of atom O(1) is fixed at the origin in all refinements.

Parameters refined	LIHOX		LIDOX	
	$R(F^2)$	$R_w(F^2)$	$R(F^2)$	$R_w(F^2)$
(a) One scale factor, 21 non-H atom coordinates, 48 non-H anisotropic B factors. Hydrogen atoms omitted. (3 cycles)	0·076	0·092	–	–
(b) One scale factor, all 30 atom coordinates, 3 isotropic B factors for H atoms, 48 non-H anisotropic B factors. (3 cycles).	0·068	0·071	0·088	0·079
(c) As (b) but including an isotropic extinction correction parameter (3 cycles).	0·044	0·069	0·052	0·073

The atomic scattering factor values used for Li$^+$ were those given in *International Tables for X-ray Crystallography* (1962); for C and O those suggested by Hanson, Herman, Lea & Skillman (1964). For H (and D) the spherical scattering factors proposed by Stewart, Davidson & Simpson (1965) were used.

Computer programs

All large calculations were performed using the CDC 3600 computer in Uppsala. The programs used are given below.

DATAPH: corrections for Lorentz, polarization and absorption effects. Isotropic and anisotropic extinction components are also calculated for subsequent use in *LINUS*. Written by Coppens, Leiserowitz & Rabinovich (1965) and adapted by P.-G. Jönsson.

DRF: performs Fourier calculations. Written by A. Zalkin, Berkeley, Calif. and modified for local use by J.-O. Lundgren and R. Liminga.

LINUS: full-matrix least-squares refinement with options for isotropic and anisotropic extinction refinement. Originally written by Busing, Martin & Levy (1962) and extended by Coppens & Hamilton (1970).

ORFFE: crystallographic function and error program written by Busing, Martin & Levy (1964).

ORTEP: a thermal ellipsoid plot program for stereoscopic illustration of crystal structures written by C. K. Johnson (1965).

WAL: A weighting scheme analysis program written locally by P.-G. Jönsson.

Smaller calculations (*e.g.* cell parameter refinements) were performed using the departmental IBM 1800 computer.

Discussion of the structure

General

The structures are closely isomorphous; their essential features are depicted in Figs. 1 and 2. The important interatomic distances and angles are provided for both structures in Table 5. The standard deviations have been calculated directly from the variance-covariance matrix obtained at the end of the least-squares refinements; errors in the cell parameters are also taken into account in this calculation.

Table 3. *Anisotropic thermal parameters* ($\times 10^4$)

The form of the temperature factor is $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$. The r.m.s. components ($R_i \times 10^3$ Å) of thermal displacement along the principal axes of the thermal vibration ellipsoids are also given along with the isotropic thermal parameters (B Å^2) for the hydrogen and deuterium atoms.

LIHOX

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B	R_1	R_2	R_3
Li	165 (6)	111 (4)	401 (13)	−13 (4)	−45 (7)	45 (6)		119 (3)	148 (2)	172 (2)
O(1)	200 (2)	71 (1)	511 (6)	−53 (1)	−67 (3)	42 (2)		102 (1)	137 (1)	197 (1)
O(2)	120 (2)	86 (1)	447 (5)	−27 (1)	−108 (2)	44 (2)		92 (1)	122 (1)	188 (1)
O(3)	135 (2)	66 (1)	546 (6)	−37 (1)	−73 (3)	41 (2)		100 (1)	117 (1)	194 (1)
O(4)	129 (2)	78 (1)	471 (5)	−13 (1)	−122 (2)	28 (2)		92 (1)	121 (1)	195 (1)
C(1)	97 (2)	68 (1)	250 (5)	−25 (1)	−30 (2)	19 (2)		94 (1)	109 (1)	136 (1)
C(2)	85 (2)	61 (1)	281 (5)	−18 (1)	−25 (2)	9 (2)		92 (1)	106 (1)	137 (1)
O(*W*)	151 (2)	70 (1)	444 (5)	−25 (1)	−21 (2)	17 (2)		112 (1)	129 (1)	170 (1)
H(1)							4·4 (6)			
H(2)							2·8 (4)			
H(3)							2·8 (4)			

LIDOX

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B	R_1	R_2	R_3
Li	164 (5)	112 (4)	418 (12)	−15 (4)	−43 (6)	46 (5)		122 (2)	148 (2)	173 (2)
O(1)	202 (2)	77 (1)	523 (5)	−58 (1)	−65 (3)	39 (2)		104 (1)	140 (1)	196 (1)
O(2)	123 (2)	87 (1)	456 (5)	−28 (1)	−110 (2)	42 (2)		94 (1)	123 (1)	189 (1)
O(3)	137 (2)	69 (1)	547 (5)	−39 (1)	−74 (2)	37 (2)		101 (1)	120 (1)	194 (1)
O(4)	129 (2)	84 (1)	465 (5)	−14 (1)	−123 (2)	26 (2)		92 (1)	125 (1)	195 (1)
C(1)	98 (2)	74 (1)	253 (4)	−28 (1)	−28 (2)	16 (2)		95 (1)	114 (1)	136 (1)
C(2)	84 (2)	66 (1)	283 (4)	−19 (1)	−28 (2)	8 (2)		91 (1)	110 (1)	138 (1)
O(*W*)	146 (2)	71 (1)	440 (4)	−24 (1)	−23 (2)	16 (2)		113 (1)	127 (1)	169 (1)
D(1)							3·8 (5)			
D(2)							2·5 (4)			
D(3)							2·3 (3)			

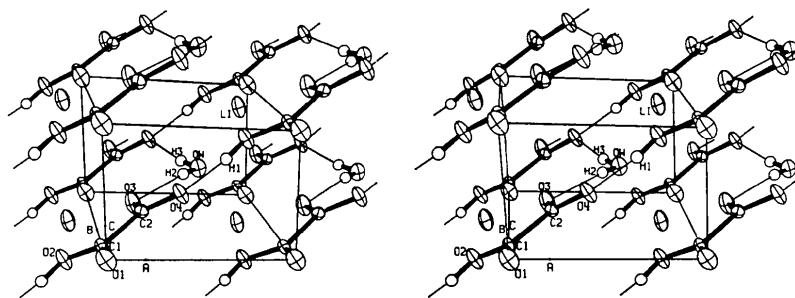LIHC2O4.H2O   LIHC2O4.H2O

Fig. 1. A stereoscopic illustration showing the distinct layered nature of the structure. The labelled atoms correspond to the chosen asymmetric unit with origin at O(1). Covalent bonds: thick solid lines; hydrogen bonds: thin unbroken lines. Thermal ellipsoids for the non-hydrogen atoms are scaled to include 50% probability.

Table 4. *Observed and calculated structure factors for* LiHC$_2$O$_4$.H$_2$O *and* LiDC$_2$O$_4$.D$_2$O

The four columns are in the order: the indices k and l, $100|F_o|$ and $100|F_c|$. Reflexions with $F^2 < 3\sigma_c(F^2)$ are marked with an asterisk and were not included in the least-squares refinement. Reflexions whose intensities were found to be subject to a 5% or greater extinction effect are marked with an E.

LiHC$_2$O$_4$.H$_2$O

LiDC$_2$O$_4$.D$_2$O

It will be noticed that the O–H (and O–D) distances after refinement are all ~0·2 Å shorter than expected. This is a familiar result in X-ray diffraction studies and is symptomatic of the oversimplified scattering model used. An attempt was made partially to compensate for this deficiency by allowing the site occupation parameters for all oxygen and hydrogen atoms participating in hydrogen bonding to vary in the least-squares refinement. Small increases in the O–H distances (~0·05 Å) were obtained but these were not sufficiently significant to merit publication in detail.

The distinct layer-like nature of the structure arises as a result of the near planar hydrogen oxalate ions linking together *via* short asymmetric O–H···O bonds to form infinite chains running in the [101] direction. These chains are linked transversely by means of O–H···O hydrogen bonds *via* the water molecules and Li⁺···O electrostatic forces. The infinite planes so formed are held together chiefly by the zigzag ···Li⁺ ···O(W)···Li⁺··· chains running in the [001] direction, the interaction again being electrostatic. It is thus interesting to note that the entire formula unit is roughly coplanar. In *LIHOX* the oxygen of the water molecule lies 0·62 Å out of the least-squares plane through the non-hydrogen atoms of the hydrogen oxalate ion and the Li⁺ ion lies only 0·30 Å out of this plane in the opposite direction.

Table 5. *Interatomic distances and angles*

A prime indicates that the atom lies in an adjacent hydrogen oxalate chain within the same atom plane; a double prime indicates that the atom lies in an adjacent atom plane

(a) Distances

	LIHOX	*LIDOX*
Li···O(W)	2·055 (2) Å	2·055 (2) Å
Li···O(W″)	2·046 (2)	2·048 (2)
Li···O(1)	2·070 (2)	2·070 (2)
Li···O(2′)	2·273 (2)	2·265 (2)
Li···O(3′)	2·014 (2)	2·015 (2)
C(1)–O(1)	1·210 (1)	1·209 (1)
C(1)–O(2)	1·309 (1)	1·312 (1)
C(1)–C(2)	1·547 (1)	1·547 (1)
C(2)–O(3)	1·240 (1)	1·239 (1)
C(2)–O(4)	1·259 (1)	1·259 (1)

(b) Angles

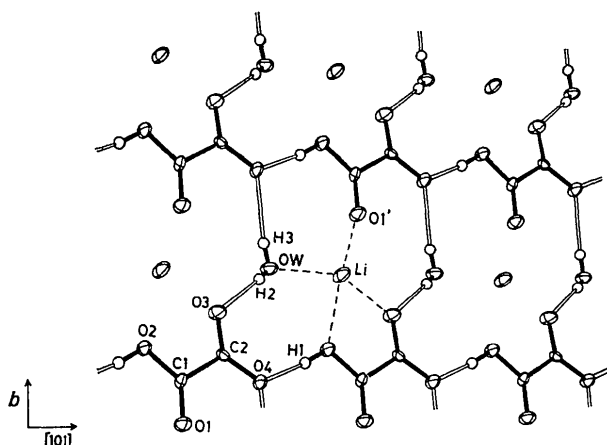|	*LIHOX*	*LIDOX*
O(W) ···Li···O(W″)	112·58 (9)°	112·41 (9)°
O(W) ···Li···O(1)	98·93 (8)	99·03 (8)
O(W) ···Li···O(2′)	84·44 (7)	84·48 (7)
O(W) ···Li···O(3′)	140·35 (10)	140·64 (10)
O(W″)···Li···O(1)	97·26 (8)	97·30 (8)
O(W″)···Li···O(2′)	91·80 (8)	91·83 (8)
O(W″)···Li···O(3′)	101·18 (8)	101·03 (8)
O(1) ···Li···O(2′)	168·20 (10)	168·05 (10)
O(1) ···Li···O(3′)	96·71 (8)	96·61 (8)
O(2′) ···Li···O(3′)	74·03 (7)	73·99 (6)
O(1)——C(1)–O(2)	126·52 (8)	126·46 (7)
O(1)——C(1)–C(2)	122·61 (6)	122·90 (6)
O(2)——C(1)–C(2)	110·87 (6)	110·64 (6)
O(3)——C(2)–O(4)	127·10 (7)	127·22 (7)
O(3)——C(2)–C(1)	117·49 (6)	117·42 (6)
O(4)——C(2)–C(1)	115·40 (6)	115·35 (6)
Li ···O(W)···Li″	112·58 (9)	112·41 (9)
Li ···O(W)···O(3)	116·97 (6)	117·45 (6)
Li ···O(W)···O(4′)	102·53 (6)	102·87 (6)
Li″ ···O(W)···O(3)	109·03 (6)	108·71 (6)
Li″ ···O(W)···O(4′)	106·57 (6)	106·20 (6)
O(3)···O(W)···O(4′)	108·40 (3)	108·41 (3)

Fig. 2. A view perpendicular to the (10T) plane showing the chains of hydrogen oxalate ions running in the [101] direction. Covalent bonds: thick solid lines; hydrogen bonds: thick unfilled lines; ionic bonds: thin broken lines.

Table 5 (*cont.*)

(c) Hydrogen bond distances and angles

LIHOX			*LIDOX*	
O(2)...O(4)	2·490 (1)		O(2)...O(4)	2·506 (1)
O(2)——H(1)	0·85 (3)		O(2)——D(1)	0·84 (3)
H(1)...O(4)	1·65 (3)		D(1)...O(4)	1·67 (3)
O(2)——H(1)...O(4)	171·3 (3·0)		O(2)——D(1)...O(4)	172·0 (3·0)
O(W)...O(3)	2·777 (1)		O(W)...O(3)	2·778 (1)
O(W)——H(2)	0·82 (3)		O(W)——D(2)	0·82 (3)
H(2) ...O(3)	1·98 (3)		D(2) ...O(3)	1·99 (3)
O(W)——H(2)···O(3)	162·7 (2·6)		O(W)——D(2)···O(3)	162·6 (2·7)
O(W)···O(4′)	2·702 (1)		O(W)···O(4′)	2·700 (1)
O(W)——H(3)	0·85 (2)		O(W)——D(3)	0·83 (3)
H(3) ···O(4′)	1·88 (2)		D(3) ···O(4′)	1·89 (3)
O(W)——H(3)···O(4′)	161·6 (2·2)		O(W)——D(3)···O(4′)	166·0 (2·4)

A fascinating comparison can be made here with the related structure of $NaHC_2O_4.H_2O$ (Tellgren & Olovsson, 1971). This structure (referred to henceforth as *NAHOX*) has the space group $P\bar{1}$, the symmetry centre occurring midway between planes of hydrogen oxalate chains. Thus, in *NAHOX*, the hydrogen bond linkage runs in opposite directions in adjacent planes; whereas on *LIHOX* (having no symmetry centre) the hydrogen bonding is in the same direction in adjacent planes.
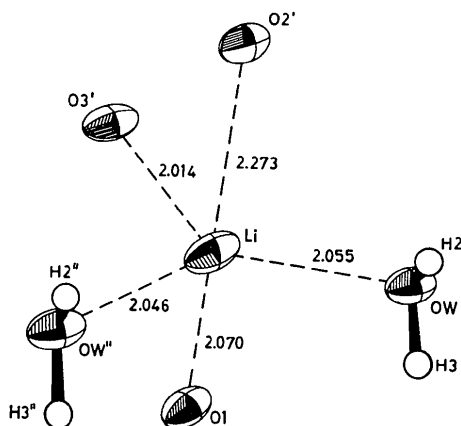

Fig. 3. Distances around the lithium ion (for atom labelling notation see Table 5).
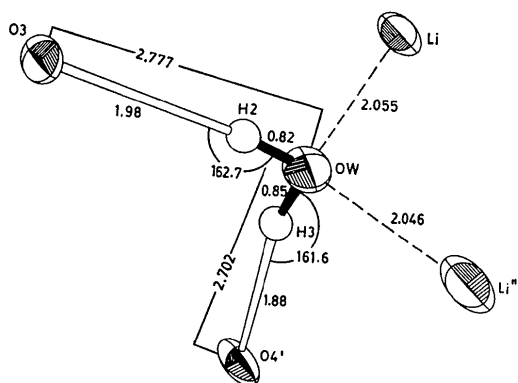
Fig. 4. The bonding situation around the water molecule.

The lithium ion

The immediate environment of the Li^+ ion is shown in Fig. 3. Of the five near contacts four lie within the same plane containing the atoms O(1), O(2'), O(3'), and O(W'); the fifth contact $Li^+\cdots O(W'')$ provides the electrostatic interaction between the layers of atoms. It is clear that the *LIHOX* and *NAHOX* structures differ as a direct result of the different effective radii of the Li^+ and Na^+ ions (~ 0.60 and ~ 0.95 Å, respectively). The Na^+ ion in *NAHOX* is surrounded by six oxygen atoms in distorted octahedral coordination, of which two lie in different adjacent planes. The mean $Na^+\cdots O$ distance is 0.30 Å greater than the mean $Li^+\cdots O$ distance, the difference corresponding approximately to the difference in ionic radii.

The water molecule

As in the case of *NAHOX*, the water molecules provide the hydrogen bond bridging between adjacent chains of hydrogen oxalate ions. Their tetrahedral environment (Fig. 4) comprises two Li^+ ions and two oxygen atoms. O(3) and O(4'). The O(W)–H(2)$\cdots$O(3) and O(W)–H(3)$\cdots$O(4') hydrogen bond distances are 2.777(1) and 2.702(1) Å respectively.

The hydrogen oxalate ion

Evidence from the C–O distances within the hydrogen oxalate ion (Fig. 5) and from the position of the well resolved H(1) atom peak in the difference Fourier synthesis confirms that the hydrogen bond linking the hydrogen oxalate ions is asymmetric and of the form O(2)–H(1)$\cdots$O(4). The O(2)$\cdots$O(4) distance of 2.490(1) Å indicates furthermore that the bonding is strong. The C(1)–O(1) distance, 1.210(1) Å, and the

Table 6. *Changes observed in hydrogen bond lengths (l) in complete structural studies of the normal and deuterated compounds*

Also provided, in the extreme right-hand column, is the quantity $(l_D'-l_H)$ Å, where l_D' is the calculated bond length using the atomic fractional coordinates of the undeuterated structure together with the dimensions of the deuterated cell.

Compound	Reference	$l_H=(O\cdots O)_H$	$l_D=(O\cdots O)_D$	(l_D-l_H)	$(l_D'-l_H)$
α–Oxalic acid. $2H_2O$	Delaplane & Ibers (1969)	2.512 (1) Å	2.531 (1) Å	+0.019 (2) Å	+0.013 (Å)
		2.864 (2)	2.880 (2)	+0.016 (3)	+0.002
		2.883 (1)	2.907 (1)	+0.024 (2)	+0.015
$NaHC_2O_4.H_2O$	Tellgren & Olovsson (1971)	2.571 (2)	2.593 (2)	+0.022 (3)	+0.009
		2.808 (2)	2.809 (2)	+0.001 (3)	−0.002
		2.826 (2)	2.826 (2)	0.000 (3)	+0.002
$H_2SO_4.4H_2O$	Kjällman & Olovsson (1972)	2.431 (3)	2.426 (3)	−0.005 (5)	−0.001
		2.655 (2)	2.655 (2)	0.000 (3)	−0.001
		2.664 (2)	2.666 (2)	+0.002 (3)	0.000
$LiHC_2O_4.H_2O$	This work	2.490 (1)	2.506 (1)	+0.016 (1)	+0.005
		2.702 (1)	2.700 (1)	−0.002 (2)	−0.001
		2.777 (1)	2.778 (1)	+0.001 (2)	+0.002

C(1)–O(2) distance, 1·309(1) Å, typify a double and a single bond respectively, whereas the C(2)–O(3) and C(2)–O(4) distances (1·240(1) Å and 1·259(1) Å, respectively) resemble bond lengths found in hydrogen bond accepting carboxylate and oxalate ions [cf. $CH_3COON_2H_5$ (Abdel Hady, Nahringbauer & Olovsson, 1969) and $K_2C_2O_4.H_2O$ (Sequeira, Srikanta & Chidambaram, 1970)]. The precise values of these bond lengths will clearly depend on the detailed character of the hydrogen bonding present.

The hydrogen oxalate ion in *LIHOX* is considerably more planar than in *NAHOX*. The angle between the O(1)–C(1)–O(2) plane and the O(3)–C(2)–O(4) plane is only 2·1° compared with 12·9° in *NAHOX*. Such a difference is in no way alarming, however: it is known from other investigations that the $HC_2O_4^-$ ion can be easily distorted. A dihedral twist of 12·6° has been reported in KHC_2O_4 (Pedersen, 1968) and of 6·1° in $KHC_2O_4.H_2C_2O_4.2H_2O$ (Haas, 1964).

Discussion of the isotope effect

As seen from Table 5, the short asymmetric hydrogen bond O(2)–H(1)···O(4) between the hydrogen oxalate ions undergoes an elongation of 0·016(1) Å on deuteration, whereas the longer hydrogen bonds from the water molecules, O(W)–H(2)···O(3) and O(W)–H(3)···O(4′), show insignificant changes of +0·001(2) and −0·002(2) Å respectively. Small, although possibly significant, changes of +0·29(8) and −0·23(8)° are observed in the O(1)–C(1)–C(2) and O(2)–C(1)–C(2) angles of the hydrogen oxalate ion. These would suggest that the isotope effect in the O(2)–H(1)···O(4) bonds linking the $HC_2O_4^-$ ions is capable of bringing about a small distortion in the internal geometry of the ions themselves. Minor changes are also observed in the angles centred on the oxygen atom of the water molecule.

It is of interest to compare these results with those from other systematic structural studies of the isotope effect. These are summarized in Fig. 6 and Table 6. It would clearly be unrealistic on the basis of so few results to attempt to derive some functional correlation between hydrogen bond length and change in length on deuteration. A number of suggestive points do emerge, however.

The observation of an insignificant isotope effect in the *short symmetric* O···H···O hydrogen bond in $H_2SO_4.4H_2O$, 2·431(3) Å, is unfortunately the only reliable measurement made to date on a bond of this type. If we assume the bond to be symmetric with a single potential minimum, then the result would appear to support the suggestion made by Rundle (1964) that a negligible isotope effect is to be expected in such a bond. Further comment should, however, await the availability of additional data, especially in view of the slightly larger standard deviations in the bond lengths in this case.

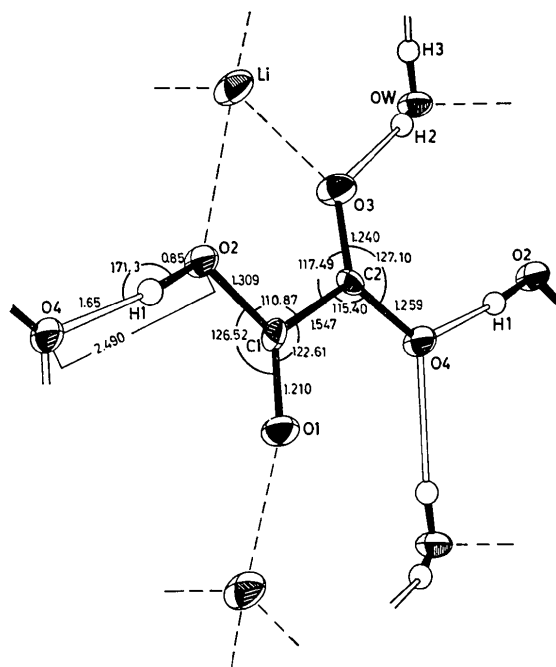For *short asymmetric* hydrogen bonds in the range

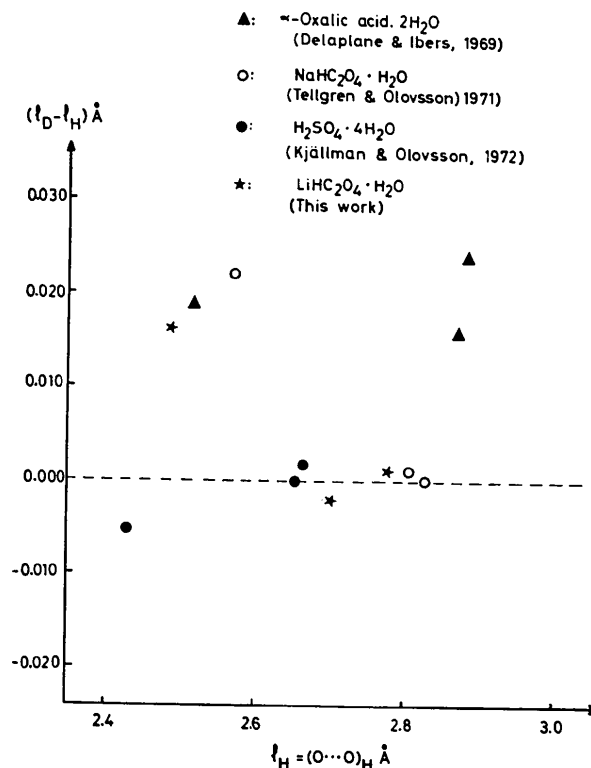Fig. 5. The bonding situation around the hydrogen oxalate ion.

Fig. 6. Changes observed in O···O hydrogen-bond lengths (l_H) in complete structural studies of the normal and deuterated compound.

2·5–2·6 Å, there appears to be a consistent lengthening on deuteration: an effect which has also been predicted theoretically (Singh & Wood, 1969).

The situation for *medium* and *long asymmetric* hydrogen bond is clearly in dispute. It would have been tempting, in the light of the results for *LIHOX, NA-HOX* and $H_2SO_4.H_2O$, to suggest that no significant changes are to be expected in hydrogen bonds of length greater than ∼2·6 Å. The evidence from α-oxalic acid dihydrate immediately disposes of this suggestion. In this case lengthening of the order of 0·020 Å is observed in all three hydrogen bonds of lengths 2·512, 2·864 and 2·883 Å. Inspection of the structure, however, suggests that a high degree of coupling must prevail within the hydrogen-bonding scheme. Each water molecule serves both as donor to the two longer bonds and as acceptor of the shorter bond. The structure is thus far from ideal in isolating the effect of deuteration on individual hydrogen bonds. The apparent anomalous situation which thus arises for medium and long hydrogen bonds can be resolved by invoking the hypothesis that only for bonds up to ∼2·6 Å can an observed isotope effect be considered in some way characteristic of that particular bond. Secondary effects can appear in longer (weaker) bonds, but these no longer uniquely characterize the bonds themselves. Rather, they are a result of cooperative rearrangement distributed throughout the structure. Such rearrangement would be only indirectly related to the specific lengths of the longer hydrogen bonds involved; being determined rather by 'genuine' isotope-effect shifts localized within the shorter hydrogen bonds and by more general packing, symmetry and electrostatic considerations. The possibility of some degree of feedback from longer to shorter bonds in this type of situation should not be discounted completely, however.

It is generally agreed that earlier determinations of the isotope effect based on changes in cell parameter alone on deuteration are unacceptable, except in a few special cases. This is illustrated in the right-hand column of Table 6, in which the predicted isotope effects in the hydrogen bonds have been calculated from the fractional coordinates of the normal structure and the lattice parameters of the normal and deuterated cells. It is seen that the changes in cell parameters are inadequate in predicting the full extent of the isotope effect present. On the other hand, the signs and relative magnitudes of the effects in the different bonds of a compound are correctly given to a reasonable degree of consistency.

It should finally be stressed that a systematic treatment of the isotope effect should strictly involve consideration of the more detailed geometry of the individual bonds concerned. This essentially requires accurate neutron diffraction data. The more naive approach employed here is clearly an over-simplification. An essential requirement for an ideally rigorous experimental treatment would also be that the systems studied contain only one independent species of hydrogen bond. The possibility of cooperative effects of the type suggested above would then be largely avoided.

References

ABDEL HADY, S., NAHRINGBAUER, I. & OLOVSSON, I. (1969). *Acta Chem. Scand.* **23**, 2764.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A**26**, 71.

COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035.

DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* B**25**, 2423.

FOLLNER, H. (1970). *Z. anorg. allgem. Chem.* **373**, 198.

HAAS, D. J. (1964). *Acta Cryst.* **17**, 1511.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.

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

JOHNSON, C. K. (1965). ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

KJÄLLMAN, T. & OLOVSSON, I. (1972). *Acta Cryst.* B**28**, 1692.

PEDERSEN, B. F. (1968). *Acta Chem. Scand.* **22**, 2953.

ROBERTSON, J. M. & UBBELOHDE, A. R. (1939). *Proc. Roy. Soc.* A**170**, 222.

RUNDLE, R. E. (1964). *J. Phys. Radium,* **25**, 487.

SEQUEIRA, A., SRIKANTA, S. & CHIDAMBARAM, R. (1970). *Acta Cryst.* B**26**, 77.

SINGH, T. R. & WOOD, J. L. (1969). *J. Chem. Phys.* **50**, 3572.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

TELLGREN, R. & OLOVSSON, I. (1971). *J. Chem. Phys.* **54**, 127.