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An X-ray Diffraction Study of the Structures of $KHCO_3$ and $KDCO_3$ at 298, 219 and 95 K

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The crystal structures of normal and deuterated potassium hydrogen carbonate, $KHCO_3$ and $KDCO_3$, have been studied at 298, 219 and 95K using three-dimensional single-crystal X-ray data collected on a semi-automatic Stoe–Philips Weissenberg diffractometer. Both unit cells are monoclinic, containing four formula units and having the centrosymmetric space group $P2_1/a$ (chosen to conform with previous work on $KHCO_3$). The cell dimensions at 298K for $KHCO_3$ are: $a=15·1725$ (11), $b=5·6283$ (5), $c=3·7110$ (4) Å, $\beta=104·631$ (6)°, $V=306·62$ Å^3; and for $KDCO_3$: $a=15·1948$ (9), $b=5·6307$ (3), $c=3·7107$ (3) Å, $\beta=104·567$ (5)°, $V=307·27$ Å^3. The $KHCO_3$ structure, comprising $(HCO_3)_2^{2-}$ dimers and K^+ ions, is isomorphous with its deuterated counterpart. The heavy atoms of each HCO_3^- ion within the centrosymmetric dimer are closely coplanar at all temperatures, the separation between these planes being ~0·22 Å. The two symmetry-related O–H···O hydrogen bonds within the dimer have lengths 2·585 (2), 2·592 (2) and 2·591 (2) Å at 298, 219 and 95K, respectively. The corresponding lengths in $KDCO_3$ are: 2·607 (2), 2·613 (2) and 2·606 (2) Å, implying length increases of 0·022, 0·021 and 0·015 Å on deuteration at the three temperatures. The final $R(F)$ values obtained for the refinements of $KHCO_3$ were 0·037, 0·028 and 0·031, respectively. The corresponding values for $KDCO_3$ were 0·034, 0·033 and 0·033.

Introduction

For several years this Institute has been engaged in the systematic study of the effect of deuteration on the crystal structures of simple hydrogen-bonded compounds, *e.g.* $NaHC_2O_4.H_2O$ (Tellgren & Olovsson, 1971), $H_2SO_4.H_2O$ (Kjällman & Olovsson, 1972), $LiHC_2O_4.H_2O$ (Thomas, 1972), $N_2H_5HC_2O_4$ (Thomas, 1973). It has been suggested (Thomas, 1972) that whereas isotopic substitution would appear to affect directly only O···O hydrogen bonds of length $\lesssim 2·6$ Å, secondary structural rearrangements can result in substantial changes in considerably longer bonds. The classic example of such a situation would be in α-oxalic acid dihydrate (Delaplane & Ibers, 1969), in which O–H···O hydrogen bonds of lengths 2·512, 2·864 and 2·883 Å all experience length increases of the order of 0·020 Å on deuteration.

In an effort, therefore, to isolate better the effect of isotopic substitution within an individual hydrogen bond, we have here investigated a simpler hydrogen-bond situation – the $(HCO_3)_2^{2-}$ dimer in potassium hydrogen carbonate (Nitta, Tomiie & Koo, 1952, 1954; Pedersen, 1968). It is unfortunate that even here we have *two*, albeit crystallographically equivalent, O–H···O bonds constituting the dimeric bridge. The ideal situation of a single, structurally independent hydrogen bond in a relatively simple structure would appear to be a rare phenomenon in nature. A further aspect of particular theoretical significance is the temperature dependence of the isotope effect. Although the desirability of experimental measurement of the isotope effect at several temperatures has long been recognized, little work of any real value has been done. Earlier investigations based on cell parameter measurements alone (see the review by Gallagher, 1959) have since proved unreliable and can generally be ignored.

The amount of work which an investigation of this type involves has limited the present study to only three temperatures: 298, 219 and 95K. The thermal expansion occurring in both compounds over this temperature range has also been examined.

Crystal data

Potassium hydrogen carbonate, $KHCO_3$. F.W. 100·12. Monoclinic. Cell dimensions are given in Table 1. Space group: $P2_1/a$ [equivalent to $P2_1/c$, No. 14 in *International Tables for X-ray Crystallography* (1952)]. General position coordinates: $\pm(x,y,z;\ \frac{1}{2}+x,\frac{1}{2}-y,z)$. $Z=4$. μ_{calc} (Cu $K\alpha$) = 134·2 cm^{-1}. Deutero-potassium hydrogen carbonate, $KDCO_3$. F.W. 101·13. Monoclinic. Space group: $P2_1/a$, $Z=4$. μ_{calc} (Cu $K\alpha$) = 134·0 cm^{-1}.

Experimental

Crystals of $KHCO_3$ were obtained by recrystallization from a slightly warm, concentrated water solution of analytical grade $KHCO_3$. Clear lath-like crystals formed on cooling. The two crystals used for data collection measured 0·30 × 0·15 × 0·10 mm (298 K data) and 0·34 × 0·14 × 0·09 mm (219 and 95K data). Crystals of $KDCO_3$, having the same general morphology as $KHCO_3$, were obtained by first drying analytical grade K_2CO_3 by heating at 190C for four days. Dried CO_2 was then bubbled through a concentrated solution of K_2CO_3 in D_2O (>99·9%), whilst warming continuously at 80–90°C. Crystals formed on allowing the solution to cool while still maintaining the passage of dried CO_2. The degree of deuteration achieved was estimated to be of the order of 95% by comparing the peak heights of the O–H and O–D stretching modes in the IR spectrum from the $KDCO_3$ prepared. A rod-shaped crystal (length: 0·45 mm, cross section: 0·014 mm^2) was selected for data collection and quickly sealed in a thin-walled glass capillary to preserve the level of deuteration. This crystal was used at all three temperatures.

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The room-temperature cell parameters for both compounds were measured using a Guinier-Hägg powder camera calibrated with silicon [a = 5·43054Å, λ(Cu $K\alpha_1$) = 1·54051 Å]. The least-squares refinement used 52 and 53 observed θ values for $KHCO_3$ and $KDCO_3$, respectively. Low-temperature cell parameters were obtained by superposing room and low temperature Weissenberg exposures, and using the room-temperature cell parameters as calibration standard (Thomas, 1974). The final $KHCO_3$ refinements at 227 and 110K each involved 58 observed θ values. The corresponding numbers for $KDCO_3$ were 67 and 64. Cell parameters appropriate to the temperatures at which X-ray data were collected (219 and 95K) were obtained by interpolation (Table 1).

The general suitability of the crystals chosen was checked and the validity of the $P2_1/a$ space group assignment confirmed using standard X-ray photographic techniques. The adoption of a non-conventional space group was made to correspond with the choice made in earlier published works, especially in view of the possible confusion between the a axis and the [102] direction (Nitta *et al.*, 1954). The data collection then proceeded in the order 95, 219 and 298K, the cooling being achieved using a cooled nitrogen gas-stream technique (Olovsson, 1960). The low temperatures were determined by placing the junction of a fine-gauge thermocouple at the crystal position. A semi-automatic Stoe–Philips Weissenberg diffractometer was used for the data collection, its geometry being particularly amenable to low-temperature work. The room housing the diffractometer was humidity controlled (~40%) to reduce risk of frosting.

The diffractometer, operating in an equi-inclination geometry and in its ω–2θ scan mode, was steered by a pre-generated control tape carrying setting angles and scan specification for successive reflexions within a given layer. The appropriate μ-angle was adjusted manually and a new control tape supplied for each layer and at each temperature. Conveniently, the short cell-edge c lay parallel to the longest crystal edges. The choice of c as oscillation axis thus limited the number of accessible layers to four ($hk0 \rightarrow hk3$) when using Cu $K\alpha$ radiation (Ni filtered). Two standard reflexions were selected in each layer and these were monitored every 30 reflexions measured during data collection. A bank of three 50% attenuators lay in the path of the incident beam. Automatic pre-selection of these (0, 1, 2 or 3) and step-time (×1, ×2, ×4, ×8 or ×16) resulted in a possible absolute internal scale factor for a given reflexion of up to 128.

Sets of $\pm h,k,l$ reflexions were collected for $l = 0 \rightarrow 3$ and for detector arm deflexion angles of up to 140°. Systematically absent reflexions of the type $0k0$ for $k = 2n+1$ and $h0l$ for $h = 2n+1$ were not measured.

The integrated peak intensities were corrected for background and assigned standard deviations $\sigma_c(I)$ based on Poisson counting statistics as described by Jönsson & Liminga (1971). Random deviations from the mean of up to $5\sigma_c(I)$ were observed in the intensities of the standard reflexions; the average random fluctuations taken over the 8 standard reflexions were ±2·8, ±1·0 and ±1·0$\sigma_c(I)$ for $KHCO_3$, and ±2·0, ±0·9 and ±0·8$\sigma_c(I)$ for $KDCO_3$. (*Note*: here and henceforth when three values appear they refer to the temperatures 298, 219 and 95K, respectively). The integrated intensities were corrected for Lorentz, polarization and absorption effects, resulting in six sets

Table 1. *Cell dimensions in* $KHCO_3$ *and* $KDCO_3$; *the values at* 219 *and* 95 K *are interpolated*

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

(a) $KHCO_3$

T	a	b	c	β	V	D_x (g cm^{-3})
298K	15·1725 (11) Å	5·6283 (5) Å	3·7110 (4) Å	104·631 (6)°	306·62 Å^3	2·169
227	15·1562 (18)	5·6197 (8)	3·6891 (6)	104·382 (11)	304·36	2·185
219	15·1538 (20)	5·6186 (10)	3·6868 (10)	104·356 (20)	304·10	2·187
110	15·1193 (18)	5·6057 (8)	3·6630 (6)	104·014 (11)	301·21	2·207
95	15·1150 (20)	5·6044 (10)	3·6609 (10)	103·980 (20)	300·93	2·210

(b) $KDCO_3$

T	a	b	c	β	V	D_x (g cm^{-3})
298K	15·1948 (9) Å	5·6307 (3) Å	3·7107 (3) Å	104·567 (5)°	307·27 Å^3	2·186
227	15·1722 (17)	5·6194 (6)	3·6905 (6)	104·326 (12)	304·86	2·203
219	15·1700 (20)	5·6183 (10)	3·6885 (10)	104·297 (20)	304·62	2·205
110	15·1367 (19)	5·6064 (7)	3·6661 (7)	103·983 (14)	301·89	2·225
95	15·1311 (20)	5·6054 (10)	3·6644 (10)	103·953 (20)	301·63	2·227

of F_o^2 and $\sigma_c(F_o^2)$ values. In all cases the crystals were described explicitly in terms of their six rational boundary planes. Transmission factors for $KHCO_3$ were in the range 0·146–0·359 for the 298K data-set and 0·157–0·385 for the 219 and 95K data-sets. The transmission factors for $KDCO_3$ at all three temperatures were in the range 0·184–0·336. The calculated mean path lengths within the crystals were saved for each reflexion for use in subsequent corrections for extinction effects. The F_o^2 values and path lengths were averaged for reflexions for the type $hk0$ and $\bar{h}k0$. Each data-set contained ~560 independent reflexions of which 540, 554 and 555 for $KHCO_3$ and 528, 536 and 540 for $KDCO_3$ had F_o^2 values in excess of $2\sigma_c(F_o^2)$ and were used in the subsequent least-squares refinements.

Refinements

$KHCO_3$

A series of full-matrix least-squares refinements were performed in which the function minimized was $\sum w(|F_o|-|F_c|)^2$, where $w=1/\sigma^2(F)$. The $\sigma(F)$ values were derived assuming the relation: $\sigma(F)=\sigma(F^2)/2F$. In the final refinements the weighting schemes were modified by the substitution: $\sigma^2(F^2)=\sigma_c^2(F^2)+(0{\cdot}05\,F^2)^2$; the intention being to weight down stronger reflexions, *i.e.* those most affected by random errors. That this had been achieved was checked by weight analyses following the final refinements. The agreement values quoted in Table 2 were calculated from the expressions:

$$R(F)=\sum \big||F_o|-|F_c|\big|/\sum|F_o|$$

and

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

Table 2. *Agreement values after the final refinements*

$R(F)$ and $R_w(F)$ are defined in the text.

		$R(F)$	$R_w(F)$
$KHCO_3$	298K	0·037	0·052
	219	0·028	0·040
	95	0·031	0·051
$KDCO_3$	298K	0·034	0·044
	219	0·033	0·043
	95	0·033	0·044

The room-temperature refinement was made first, taking as starting values the heavy-atom positional parameters given by Pedersen (1968), the H atom position was obtained unambiguously from a Fourier difference synthesis. The 219 and 95K refinements were then made in that order, using the final parameters from the 295 and 219K refinements respectively as starting values. Inspection of F_o and F_c values following refinements using only a single overall scale-factor gave no indication that individual scale-factors for each layer were called for. Consequently, only a single overall scale-factor was assumed to apply throughout. In the final refinements it was found necessary to remove from the data-sets 14, 15 and 19 reflexions showing serious disagreement. These groups contained both strong and weak reflexions but had two features in common: all reflexions had low θ angles (~10°) and, with two exceptions, lay on the second and third layers. These reflexions suffer presumably from the well-known distortion affecting low θ, high μ-angle reflexions measured using an equi-inclination Weissenberg geometry system. Such a distortion can affect the measured intensities by varying amounts depending upon the crystal-, μ- and detector-angle settings.

The final refinements also included an isotropic extinction parameter g (Coppens & Hamilton, 1970). All data-sets were found to be seriously extinction-affected as evidenced by the high g values refined: 9640 (690), 5810 (340) and 3530 (310).

Table 3. *Heavy-atom coordinates* (× 10⁵) *and hydrogen and deuterium atom coordinates* (× 10³)

For each atom the three rows are, from the top, the coordinates at 298, 219 and 95K.

(*a*) $KHCO_3$

	x	y	z
K	16533 (3)	2177 (10)	29533 (13)
	16561 (2)	3227 (7)	29500 (9)
	16595 (3)	3487 (8)	29497 (11)
H	11 (2)	682 (11)	−465 (9)
	16 (2)	694 (6)	−451 (7)
	25 (2)	704 (6)	−437 (9)
C	11967 (14)	51500 (30)	−14363 (68)
	11977 (10)	52253 (25)	−14404 (48)
	11972 (14)	52447 (32)	−14471 (64)
O(1)	19329 (11)	52915 (27)	9482 (55)
	19336 (7)	54280 (18)	9426 (35)
	19339 (10)	54594 (21)	9602 (45)
O(2)	8221 (9)	31998 (31)	−27353 (42)
	8305 (7)	32869 (21)	−27406 (28)
	8305 (9)	32975 (28)	−27538 (37)
O(3)	7761 (9)	71772 (27)	−27448 (43)
	7657 (7)	72763 (19)	−27523 (26)
	7652 (8)	73126 (23)	27632 (34)

(*b*) $KDCO_3$

	x	y	z
K	16540 (3)	2850 (9)	29583 (14)
	16564 (3)	3511 (9)	29554 (13)
	16597 (3)	3652 (8)	29521 (13)
D	21 (3)	691 (9)	−449 (10)
	21 (3)	691 (9)	−436 (10)
	20 (3)	698 (8)	−440 (10)
C	12005 (15)	51990 (37)	−14296 (66)
	11998 (15)	52409 (38)	−14324 (65)
	11996 (15)	52529 (38)	−14310 (69)
O(1)	19350 (11)	53839 (31)	9399 (54)
	19366 (11)	54640 (29)	9394 (50)
	19359 (10)	54843 (26)	9574 (50)
O(2)	8330 (10)	32577 (30)	−27233 (47)
	8384 (10)	33107 (30)	−27292 (43)
	8350 (10)	33109 (29)	−27406 (44)
O(3)	7721 (11)	72337 (29)	−27330 (47)
	7660 (10)	72990 (28)	−27377 (43)
	7649 (10)	73230 (27)	−27458 (42)

$KDCO_3$

An exactly similar refinement procedure was employed here as for $KHCO_3$ (see Table 2), except that the positional starting parameters were taken directly from the final room-temperature $KHCO_3$ refinement. Poor agreement in certain low-θ, high μ-angle reflexions was also found in $KDCO_3$ data-sets: 5, 3 and 13 reflexions were removed from the final refinements. An isotropic extinction parameter g was again included in the refinements, resulting here in the values 6390 (420), 7300 (420) and 5470 (340).

The final positional and thermal parameters for the $KHCO_3$ and $KDCO_3$ refinements are given in Tables 3 and 4, and the corresponding observed and calculated structure factors (along with extinction coefficients) in Table 5. In all refinements the atomic scattering factors as well as the real ($\Delta F'$) and imaginary ($\Delta F''$) anomalous dispersion terms for K were taken from *International Tables for X-ray Crystallography* (1962). The atomic scattering factors for C and O were those given by Hanson, Herman, Lea & Skillman (1964); while the spherical scattering factors for H (and D) were those proposed by Stewart, Davidson & Simpson (1965).

Computer programs

The following is a summary of the more important programs used in the course of this investigation. The first three were run on the departmental IBM 1800 computer and the remainder on an IBM 370/155.

THEXP:	Calculation and plotting of thermal expansion diagrams; written by J.O. Thomas.
WITAK:	Preparation of control tapes for a Stoe–Philips Weissenberg diffractometer; adapted by Å. Kvick.
INTAK:	Reduction of primary intensity data from a Stoe–Philips Weissenberg diffractometer; adapted by Å. Kvick.

Table 4. *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. The parameters appropriate to 298, 219 and 95K appear as in Table 3.

(*a*) $KHCO_3$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B	R_1	R_2	R_3
K	26 (1)	163 (3)	412 (9)	2 (1)	15 (1)	2 (1)		158 (1)	162 (1)	177 (1)
	16 (1)	100 (2)	260 (6)	1 (1)	6 (1)	−1 (1)		123 (1)	126 (1)	145 (1)
	6 (1)	37 (3)	179 (8)	1 (1)	−1 (1)	2 (1)		74 (3)	78 (3)	115 (2)
H							7·8 (1·1)			
							4·1 (0·5)			
							2·5 (0·5)			
C	19 (1)	144 (7)	384 (24)	0 (1)	26 (3)	5 (6)		140 (3)	152 (3)	159 (5)
	13 (1)	103 (5)	237 (17)	0 (1)	20 (2)	−1 (5)		110 (3)	127 (4)	129 (3)
	6 (1)	43 (6)	157 (22)	0 (1)	12 (3)	−16 (6)		75 (6)	83 (5)	104 (6)
O(1)	21 (1)	220 (6)	576 (18)	1 (1)	0 (3)	−8 (6)		146 (3)	187 (3)	209 (3)
	13 (1)	141 (5)	380 (13)	1 (1)	−3 (2)	−10 (4)		115 (2)	150 (2)	171 (2)
	5 (1)	60 (6)	274 (17)	1 (1)	−6 (2)	3 (5)		67 (5)	98 (5)	142 (4)
O(2)	26 (1)	143 (5)	554 (15)	2 (1)	−1 (2)	−13 (5)		151 (3)	157 (2)	211 (2)
	18 (1)	84 (4)	361 (11)	1 (1)	−3 (2)	−12 (4)		116 (3)	127 (2)	173 (2)
	7 (1)	35 (5)	249 (14)	1 (1)	−4 (2)	−10 (5)		75 (5)	84 (4)	137 (3)
O(3)	25 (1)	140 (5)	618 (16)	−3 (1)	−2 (1)	8 (6)		149 (3)	157 (2)	219 (2)
	17 (1)	80 (4)	411 (12)	−1 (2)	−6 (2)	7 (4)		113 (3)	125 (2)	182 (2)
	6 (1)	31 (5)	268 (16)	−1 (1)	−11 (2)	11 (6)		70 (6)	71 (5)	147 (3)

(*b*) $KDCO_3$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B	R_1	R_2	R_3
K	26 (1)	129 (2)	463 (7)	2 (1)	6 (1)	−1 (2)		144 (1)	157 (1)	192 (1)
	18 (1)	82 (3)	364 (7)	2 (1)	4 (1)	−2 (1)		114 (2)	132 (1)	166 (1)
	8 (1)	28 (3)	279 (7)	1 (1)	0 (1)	1 (1)		66 (3)	91 (2)	141 (2)
D							5·9 (1·0)			
							4·8 (0·9)			
							3·3 (0·8)			
C	19 (1)	125 (7)	385 (23)	−1 (2)	16 (3)	−2 (7)		141 (4)	145 (4)	162 (4)
	14 (1)	89 (7)	315 (23)	0 (2)	16 (3)	−4 (7)		119 (5)	124 (4)	144 (5)
	7 (1)	38 (7)	271 (23)	0 (2)	13 (3)	−7 (7)		77 (7)	88 (6)	132 (6)
O(1)	21 (1)	198 (6)	588 (18)	1 (2)	−12 (3)	−14 (6)		140 (3)	178 (3)	219 (3)
	15 (1)	134 (6)	439 (17)	−1 (1)	−11 (3)	−11 (6)		117 (4)	146 (3)	189 (3)
	8 (1)	54 (6)	317 (17)	1 (1)	−4 (3)	−6 (5)		88 (4)	93 (5)	153 (4)
O(2)	27 (1)	110 (5)	611 (16)	1 (1)	−5 (3)	−11 (6)		132 (3)	158 (3)	222 (3)
	19 (1)	68 (5)	466 (15)	1 (1)	−2 (2)	−11 (6)		104 (4)	136 (3)	190 (3)
	10 (1)	24 (5)	361 (15)	−1 (1)	0 (2)	−8 (5)		61 (7)	101 (4)	160 (3)
O(3)	25 (1)	104 (5)	666 (16)	−3 (1)	−12 (3)	0 (6)		129 (3)	153 (3)	232 (3)
	18 (1)	63 (5)	517 (16)	−1 (1)	−10 (2)	8 (6)		100 (4)	130 (3)	202 (3)
	9 (1)	21 (5)	370 (16)	0 (1)	−6 (2)	11 (6)		58 (7)	95 (4)	166 (3)

DATAPW: Corrections for Lorentz, polarization and absorption effects for data collected using a Weissenberg geometry. Mean path-lengths were calculated for use in a subsequent isotropic extinction correction; written by Coppens, Leiserowitz & Rabinovich (1965) and modified for local use by J.O. Thomas.

UPALS: Full-matrix least-squares refinement program; written by J.-O. Lundgren (1972).

DRF: Fourier calculation program: rewritten by R. Liminga.

ORFFE: Crystallographic function and error program; written by Busing, Martin & Levy (1964); modified for local use by Å. Kvick.

ORTEP2: Thermal-ellipsoid plot program for stereoscopic illustration of crystal structures, with an added facility for avoiding overlaps; written and later augmented by C.K. Johnson (1965); modified for local use by P.-G. Jönsson.

Description of the room-temperature structures

General

As found by Nitta, Tomiie & Koo (1952), the $KHCO_3$ structure comprises distinct K^+ ions and $(HCO_3)_2^{2-}$ dimers, the K^+ ions having eight oxygen-atom neighbours. Both structures are closely isomorphous; a general view of $KHCO_3$ is given in Fig. 1. Relevant distances and angles are listed in Table 6, and illustrated in Figs. 2 and 3. The standard deviations quoted have been calculated using the variance-covariance matrices after the last cycles of refinement; cell-parameter errors are also taken into account.

The K^+ *ion*

The immediate environment of the K^+ ion in $KHCO_3$

Table 5. *Observed and calculated structure factors for* (*a*) $KHCO_3$ *and* (*b*) $KDCO_3$ *at* 298, 219 *and* 95K

The 11 columns are, in order: k, l, $(100|F_o|$, $100|F_c|$, $100\,E)$ at 298K, $(100|F_o|$, $100|F_c|$, $100\,E)$ at 219K, and $(100|F_o|$, $100|F_c|$, $100\,E)$ at 95K. Asterisks mark reflexions not included in the final refinements; E is the extinction correction factor multiplying F_o.

(*a*) $KHCO_3$

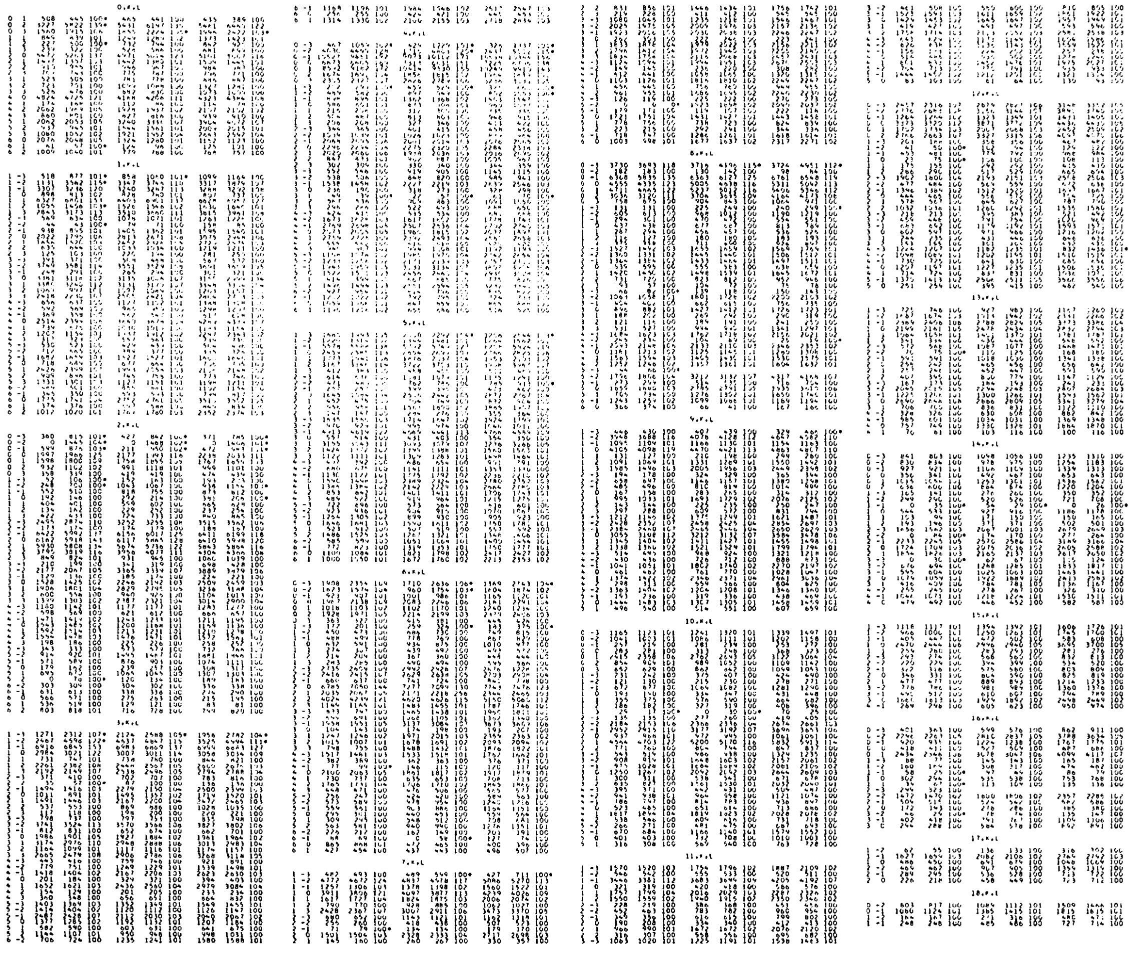


Table 5 (*cont.*)

(*b*) $KDCO_3$

0,K,L

0	1	609	484	100*	587	488	100	506	450	100
0	2	5741	5674	125	6117	5936	124	5898	6174	126
0	3	1359	1804	103*	1933	2007	104	2177	2182	104
1	1	1103	1119	102	1355	1400	103	1438	1460	103
1	2	678	652	100	882	836	100	954	918	100
1	3	418	421	100	589	588	100	711	695	100
2	0	4561	5090	130	4630	4944	132	4973	4962	129
2	1	1305	1302	102	1307	1305	102	1366	1381	102
2	2	895	899	100	891	876	100	913	906	100
2	3	747	714	100	731	731	100	728	740	100
3	1	633	671	100	831	845	100	870	923	100
3	2	884	900	100	1152	1166	101	1314	1338	101
3	3	602	598	100	820	815	100	477	469	100
4	0	4209	4356	114	3844	3472	114	4204	4188	112
4	1	179	96	100*	85	71	100*	122	70	100*
4	2	1850	1822	103	1803	1780	103	1976	1987	103
4	3	715	711	100	707	694	100	508	795	100
5	1	2789	2792	106	3043	3054	112	4248	4238	112
5	2	1219	1210	101	1639	1617	102	1990	2007	103
5	3	1311	1348	102	1405	1443	105	2530	2495	106
6	0	1541	1596	102	976	979	100	897	887	100
6	1	44	83	100*	113	94	100*	0	130	100*
6	2	832	855	100	609	622	100	637	639	100

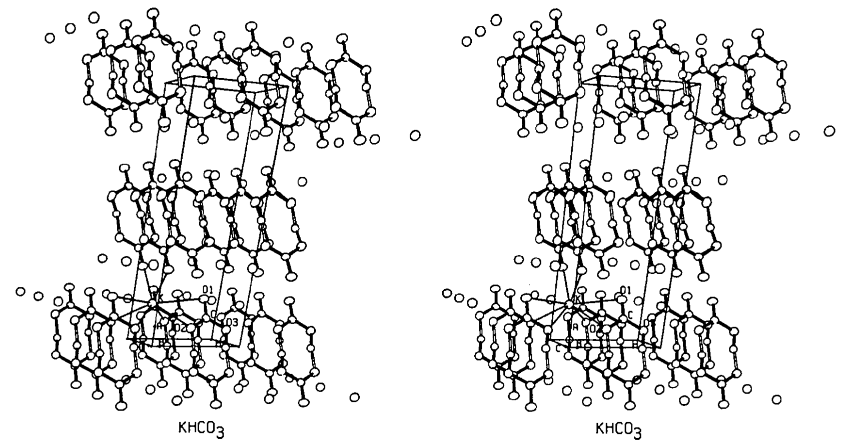


Fig. 1. A general stereoscopic illustration of the structure. The atoms of the asymmetric unit are labelled and the boundaries of the thermal vibration ellipsoids of all non-hydrogen atoms include 50% probability. Covalent bonds are filled, O···O hydrogen bonds are open and electrostatic K^+–O contacts are drawn as thin lines.

is illustrated in Fig. 2. The striking similarity between corresponding K–O distances in $KHCO_3$ and $KDCO_3$ (Table 6) indicates that the K^+ ion experiences only a very minor packing rearrangement as a result of the isotope effect occurring within the $(HCO_3)_2^{2-}$ dimers (see below).

The $(HCO_3)_2^{2-}$ *dimers*

The internal geometry of the dimer is shown in Fig. 3, and its planarity is described in Table 7. The heavy atoms of *each* HCO_3^- ion are virtually coplanar, the carbon atom lying slightly (but consistently) out of the plane of the oxygen atoms. Contrary to earlier

Table 6. *Interatomic distances* (Å) *and angles* (°) *in* $KHCO_3$ *and* $KDCO_3$ *at* 298, 219 *and* 95K

Atoms not in the chosen asymmetric unit carry identifying subscripts: the first three digits refer to a lattice translation, *e.g.* 564 implies the operation $(x, y+1, z-1)$; the fourth digit specifies one of the symmetry operations:

1: $x, \; y, \; z$
2: $\frac{1}{2}+x, \; \frac{1}{2}-y, \; z$
3: $-x, \; -y, \; -z$
4: $\frac{1}{2}-x, \; \frac{1}{2}+y, \; -z$.

(*a*) K^+ ion

	KHCO$_3$			KDCO$_3$		
	298K	219K	95K	298K	219K	95K
K···O(1)	3·008 (2)	3·018 (1)	3·009 (1)	3·024 (2)	3·023 (2)	3·015 (2)
K···O(1)$_{5451}$	2·929 (2)	2·905 (1)	2·891 (1)	2·919 (2)	2·903 (2)	2·888 (2)
K···O(1)$_{5454}$	2·875 (2)	2·855 (1)	2·836 (2)	2·873 (2)	2·853 (2)	2·836 (2)
K···O(1)$_{5464}$	2·697 (2)	2·693 (1)	2·684 (2)	2·699 (2)	2·694 (2)	2·686 (2)
K···O(2)	2·742 (2)	2·727 (1)	2·720 (2)	2·735 (2)	2·723 (2)	2·717 (2)
K···O(2)$_{5561}$	2·826 (2)	2·802 (1)	2·780 (1)	2·816 (2)	2·796 (2)	2·779 (2)
K···O(3)$_{5451}$	2·784 (2)	2·786 (1)	2·780 (1)	2·790 (2)	2·788 (2)	2·782 (2)
K···O(3)$_{5461}$	2·885 (2)	2·885 (1)	2·865 (1)	2·895 (2)	2·890 (2)	2·873 (2)
$\overline{\mathrm{K\cdots O}}$	2·843	2·834	2·821	2·844	2·834	2·822
(*b*) CO$_3$ group						
C–O(1)	1·240 (3)	1·242 (2)	1·248 (3)	1·239 (3)	1·244 (3)	1·247 (3)
C–O(2)	1·274 (2)	1·262 (2)	1·264 (2)	1·266 (3)	1·255 (3)	1·262 (3)
C–O(3)	1·337 (2)	1·354 (2)	1·360 (2)	1·346 (3)	1·359 (3)	1·363 (2)
$\overline{\mathrm{C–O}}$	1·284	1·286	1·291	1·284	1·286	1·291
O(1)–C–O(2)	124·12 (17)	125·57 (14)	125·82 (17)	125·05 (20)	125·95 (20)	126·27 (20)
O(1)–C–O(3)	117·74 (16)	116·39 (13)	115·99 (15)	116·82 (19)	115·86 (19)	115·65 (18)
O(2)–C–O(3)	118·14 (18)	118·04 (14)	118·19 (18)	118·12 (20)	118·19 (19)	118·07 (19)

(*c*) Hydrogen bond

	KHCO$_3$			KDCO$_3$		
	298K	219K	95K	298K	219K	95K
O(3)···O(2)$_{5643}$	2·585 (2)	2·592 (2)	2·591 (2)	2·607 (2) [2·590]*	2·613 (2) [2·597]*	2·606 (2) [2·595]*
O(3)—H	1·09 (3)	1·00 (2)	0·87 (4)	0·96 (4)	0·93 (4)	0·95 (4)
H·····O(2)$_{5643}$	1·50 (3)	1·59 (2)	1·72 (4)	1·66 (4)	1·69 (4)	1·66 (4)
O(3)—H·····O(2)$_{5643}$	169·8 (5·7)	173·4 (2·9)	173·9 (3·2)	170·6 (4·4)	170·2 (4·6)	173·7 (4·2)
C——O(3)—H	110·8 (3·3)	110·7 (1·8)	111·5 (2·3)	110·6 (3·2)	107·9 (3·0)	109·9 (2·8)
C——O(3)···O(2)$_{5643}$	116·67 (12)	114·63 (9)	113·93 (11)	115·54 (13)	114·11 (13)	113·79 (13)
O(3)···O(2)$_{5643}$–C$_{5643}$	124·90 (12)	127·03 (10)	127·54 (12)	126·05 (14)	127·39 (14)	127·81 (14)
H·····O(2)$_{5643}$–C$_{5643}$	120·6 (2·4)	124·5 (1·1)	126·1 (1·2)	123·0 (1·8)	123·9 (1·6)	125·6 (1·6)

* Values in brackets result from combining positional parameters measured for $KHCO_3$ with the appropriate cell parameters for $KDCO_3$.

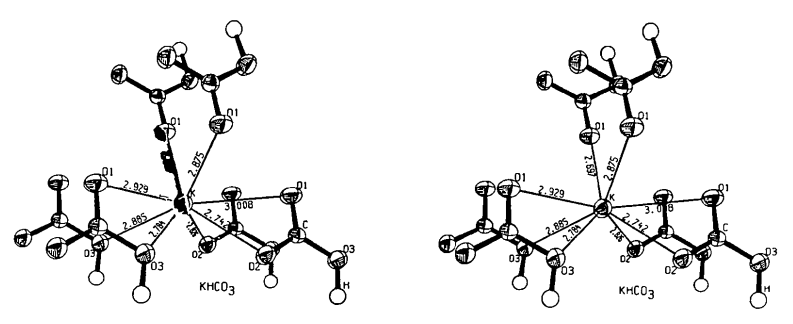


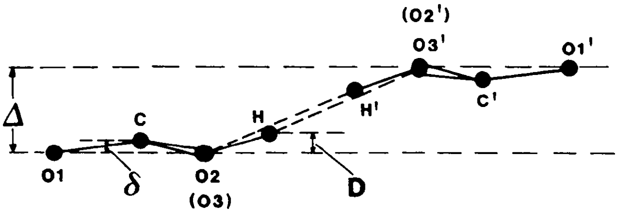
Fig. 2. The environment of the K^+ ion. The distances and thermal vibration ellipsoids (scaled to 50%) apply to $KHCO_3$ at 298K. A more specific definition of the oxygen atoms is given in Table 6.

belief, however, the dimer as a whole *deviates significantly* from planarity, so reconciling the earlier result of Pedersen (1968) (based on p.m.r. studies) that the H atoms lie out of the plane of an otherwise closely planar dimer. The displacement of the planes of the CO_3 groups observed here is by no means unusual for a carboxylic acid dimer configuration. The out-of-plane distortion of the HCO_3^- ion does not therefore need to imply (as argued by Pedersen) an intrinsic threat to the stability of the dimer. On the other hand, the suggested stabilizing effect of the lone-pair electrons of the carbonyl oxygens in a perfectly planar dimer configuration (Robertson, 1964) may be slightly diminished in the present case. It may be relevant to note that the more generally favourable linkage for HCO_3^- ions would appear to be either the one hydrogen-bond linked dimer as in $Na_2CO_3.NaHCO_3.2H_2O$ (Brown, Peiser & Turner-Jones, 1949), or the hydrogen-bonded linear chain as in $NaHCO_3$ (Sass & Scheuerman, 1962) and NH_4HCO_3 (Brooks & Alcock, 1950).

On the basis of the earlier observed C–O(2) and C–O(3) distances, 1·32 and 1·33 Å respectively (Nitta *et al.*, 1952), it has been suggested by Hamilton & Ibers (1968) that some degree of *statistical disorder* may be present in the orientation of the HCO_3^- ions in $KHCO_3$. Also, in a more general context, Currie, Speakman & Curry (1967) draw attention to the large range of differences found in C–O lengths in carboxylic groups (0·04–0·12 Å), raising the possibility that disorder is present in those cases where the difference is small. It is found here that the C–O(2) and C–O(3) distances [1·274(2) and 1·337(2) Å respectively] differ considerably more than in the earlier study. Neither has any evidence been found in the final difference maps obtained from this X-ray study (even at low temperatures) to substantiate the earlier disorder speculations. Nevertheless, to enable the reader to make a more complete appraisal of the present paper, it is essential that the preliminary results of a current room-temperature neutron-diffraction study of $KHCO_3$ and $KDCO_3$ (Thomas, Tellgren & Olovsson, 1974) be stated briefly here. Unequivocal evidence has been found in *both* compounds to suggest a 15–20% disordering effect of the type suggested earlier. The added

Table 7. *The planarity of the* $(HCO_3)_2^{2-}$ *dimer*

The two parallel planes through the oxygen atoms of each HCO_3^- ion are taken as references; the notation is defined as follows:



Perpendicular distances (Å)	KHCO₃			KDCO₃		
	298K	219K	95K	298K	219K	95K
Δ	0·222 (3)	0·223 (2)	0·241 (3)	0·219 (3)	0·219 (3)	0·230 (3)
D	0·09 (3)	0·07 (2)	0·03 (3)	0·03 (3)	0·06 (3)	0·06 (3)
δ	0·004 (3)	0·004 (2)	0·003 (3)	0·005 (3)	0·007 (3)	0·005 (3)

Table 8. *Nearest-neighbour interaction distances* (Å) *associated with the oxygen atoms in* $KHCO_3$ *and* $KDCO_3$ *at* 298, 219 *and* 95K

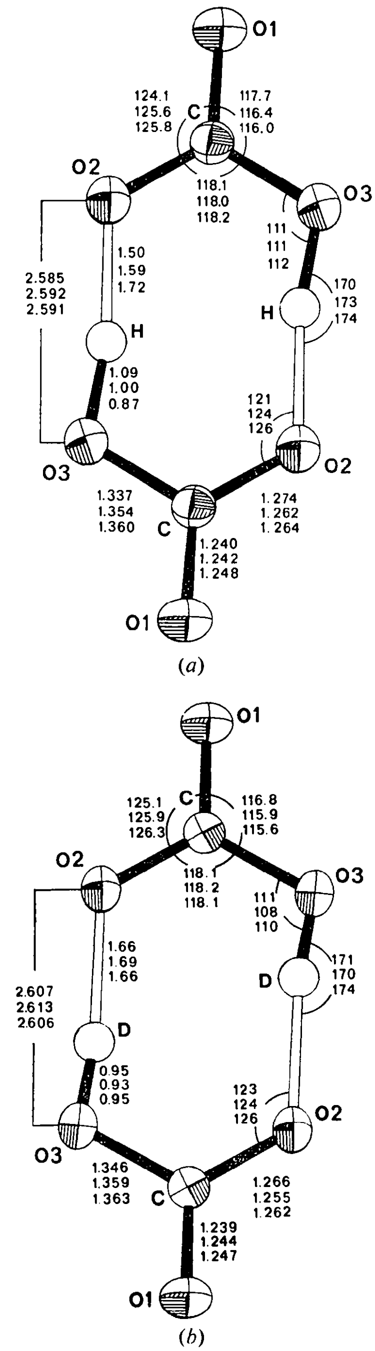
$\sum_n$ denotes the sum of the *n* interaction distances for a given oxygen atom.

	Interatomic contact	KHCO₃			KDCO₃		
		298K	219K	95K	298K	219K	95K
O(1)	O(1)···K	3·008	3·018	3·009	3·024	3·023	3·015
	O(1)···K	2·929	2·905	2·891	2·919	2·903	2·888
	O(1)···K	2·875	2·855	2·836	2·873	2·853	2·836
	O(1)···K	2·697	2·693	2·684	2·699	2·694	2·686
	O(1)—C	1·240	1·242	1·248	1·239	1·244	1·247
	$\sum_5$	12·749	12·713	12·668	12·754	12·717	12·672
O(2)	O(2)···K	2·742	2·727	2·720	2·735	2·723	2·717
	O(2)···K	2·826	2·802	2·780	2·816	2·796	2·779
	O(2)···O(3)	2·585	2·592	2·591	2·607	2·613	2·606
	O(2)—C	1·274	1·262	1·264	1·266	1·255	1·262
	$\sum_4$	9·427	9·383	9·355	9·424	9·387	9·364
O(3)	O(3)···K	2·784	2·786	2·780	2·790	2·788	2·782
	O(3)···K	2·885	2·885	2·865	2·895	2·890	2·873
	O(3)···O(2)	2·585	2·592	2·591	2·607	2·613	2·606
	O(3)—C	1·337	1·354	1·360	1·346	1·359	1·363
	$\sum_4$	9·591	9·617	9·596	9·638	9·650	9·624

complication which this discovery introduces into the discussion of the present results can readily be appreciated.

The room-temperature isotope effect

As seen from Fig. 3, the major isotope effect is the 0·022 Å lengthening of the symmetry-related pair of 2·585(2) Å hydrogen bonds O(3)–H···O(2) which link the HCO$_3^-$ ions. This result is supported by the current neutron study and is well in line with previous isotope effects observed in bonds of this length (Thomas, 1972), suggesting that the magnitude of the isotope effect occurring here is generally unaffected by its being in a dimeric bridge. The O···O bond-length change is seen to be accompanied by changes in the lengths of those C–O bonds within the HCO$_3^-$ ion which involve the hydrogen-bond donor and acceptor oxygen atoms. The C–O(2) distance in KHCO$_3$ shortens by 0·008 Å and the C–O(3) distance lengthens by 0·009 Å on deuteration. These effects can only be regarded as marginally significant, however.



(*a*)

(*b*)

Fig. 3. Distances and angles within the dimers in (*a*) KHCO$_3$ and (*b*) KDCO$_3$ at 298 (top), 219 and 95K. In both figures the thermal vibration ellipsoids (scaled to 50%) apply at 298K.

The effect of temperature on the structures

General

The relevant distances and angles found for the low-temperature structures of KHCO$_3$ and KDCO$_3$ are also given in Table 6. The K···O distances are seen to change considerably with temperature. On the other hand both the individual and the average K···O distances are again virtually identical in the two compounds at each temperature, suggesting the observed variations to be pure temperature effects independent of isotopic substitution.

A similar conclusion is reached from an inspection of Table 8 in which the sums of the interaction distances (both covalent and electrostatic) are derived for each of the oxygen atoms. It is seen that for O(1) and O(2) this sum is invariant under deuteration at a given temperature; the inconsistency in the case of O(3) probably derives from the inclusion of the O(3)···O(2) hydrogen-bond distance in the sum instead of the poorly determined covalent O(3)–H distances. This invariance would appear to be related to the well established principle that the average distance for a given coordination is approximately constant. The same general degree of planarity is also found in the (HCO$_3$)$_2^{2-}$ and (DCO$_3$)$_2^{2-}$ dimers of the low-temperature structures (Table 7). The changes in the C–O lengths within the dimers, as illustrated in Fig. 3, are plotted in Fig. 4; no attempt is made to correct for the effects of thermal motion. Such corrections would require that some assumption be made as to the nature of the correlation expected in the thermal motion (*e.g.* Cruickshank, 1956; Schomaker & Trueblood, 1968). For the case of (HCO$_3$)$_2^{2-}$ dimers, however, it is highly uncertain as to what form this assumption should take. Neither rigidity of the dimer as a whole nor of the individual HCO$_3^-$ ions would seem realistic assumptions. Moreover, Johnson (1970) warns against the use of a TLS-type analysis when the 'rigid body' in question comprises only a small number of atoms. It was therefore felt prudent to leave the values uncorrected for thermal motion (also see below).

Nevertheless, a number of clearly suggestive points do emerge from inspection of Fig. 4:

(*a*) The variations in the three C–O distances with temperature are each very similar in $KHCO_3$ and $KDCO_3$.

(*b*) These variations are generally greater in the 298–219 K range.

(*c*) At all three temperatures, the C–O bond lengths involving the donor and acceptor oxygen atoms of the hydrogen bond undergo the more significant changes on deuteration.

(*d*) The average C–O distance at each temperature is identical in $KHCO_3$ and $KDCO_3$; this average increases slightly with decreasing temperature.

It is expected that the individual C–O distances of an HCO_3 group are mutually dependent, and moreover that the average C–O distance is the same in related compounds. In this case we notice that this average is indeed the same in $KHCO_3$ and $KDCO_3$ at a given temperature. However, the mutual dependence of the C–O bond lengths would appear only to affect the C–O(2) and C–O(3) bonds, *i.e.* those more directly involved in hydrogen bonding. The C–O(1) (and $\overline{C\text{–}O}$) distance is practically the same in $KHCO_3$ and $KDCO_3$ at a given temperature; the smaller changes observed with temperature are probably artifacts of thermal motion.

There is also some indication from Fig. 5 that the O···O distances tend *not* to vary with temperature in the same way in the two compounds; an observation which finds some support in thermal-expansion measurements made on $KHCO_3$ and $KDCO_3$.

Thermal expansion

Polar diagrams of the mean coefficients of linear thermal expansion as deduced from cell-parameter measurements at 298, 227 and 110K (Thomas, 1974) are given in Figs. 6 and 7. The figures are drawn using the program *THEXP*. It will be seen that the thermal expansion is highly anisotropic with a maximum occurring roughly in the direction perpendicular to the planes of the dimers, and a minimum (in fact, becoming *negative* in all of the cases shown) roughly in the direction of the hydrogen bond. This behaviour is in good general agreement with the predictions of Lonsdale (1959) as to the nature of the thermal expansion anisotropy in this type of system. It will also be noted that the thermal expansions in the two compounds exhibit certain differences, the most significant of these arising in a region of solid angle in the vicinity of the thermal expansion minima. These differences in thermal expansion behaviour reappear as differences in the response of the O···O hydrogen-bond distances in $KHCO_3$ and $KDCO_3$ to changes in temperature. This qualitative correspondence supports the dissimilarity found in the variations of the O···O distances in $KHCO_3$ and $KDCO_3$ with temperature as depicted in Fig. 5.

Temperature dependence of the isotope effect

One point must first be made in this connexion: the differences observed in a normal and a deuterated system are implicitly related to differences in the nature of the thermal motion of the two systems, *i.e.* different thermal corrections apply in the two cases. However, since the object of the present study is to observe the effect of temperature on the isotope effect, it is arguable whether it is relevant to make such corrections here.

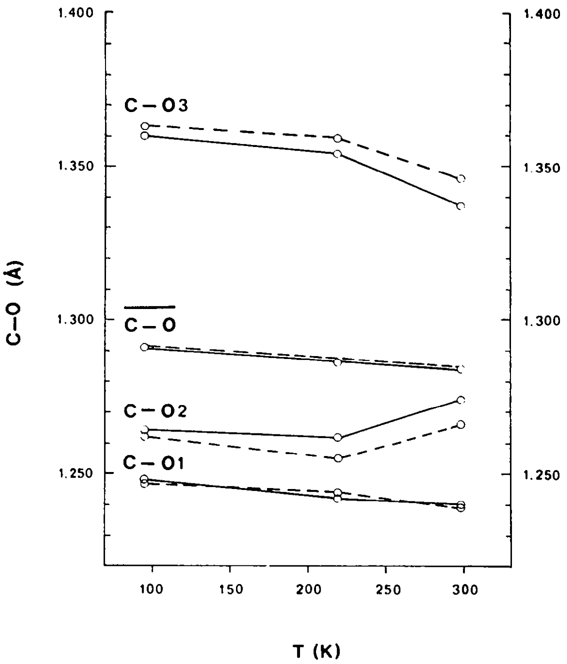


Fig. 4. The variation of C–O lengths with temperature in $KHCO_3$ (unbroken lines) and $KDCO_3$ (dashed lines).

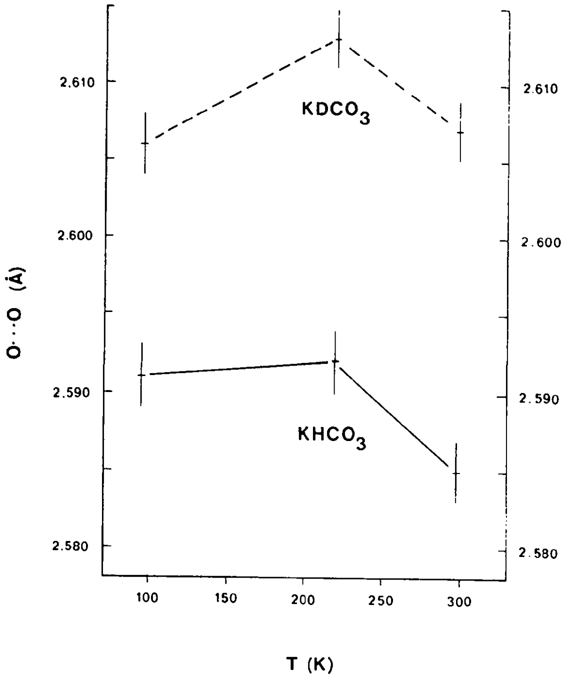


Fig. 5. The variation of O···O distance with temperature.

It will be seen from Table 6 that the O···O distances in $KDCO_3$ exceed those in $KHCO_3$ by 0·022, 0·021 and 0·015 Å; the differences between these values are hardly significant. Furthermore, the isotope effect at 95K can be expected to differ minimally from that at 0K (see Gallagher, 1959). This would imply that the isotope effect (though possibly diminishing slightly with temperature) does not tend to zero at absolute zero, so confirming the generally held view that isotope effect is essentially a zero-point-energy phenomenon. It must be noted, however, that this discussion has made the highly tenuous assumption that the fractional disordering effect has no influence on the isotope effect observed in the hydrogen bonds. The extent to which this assumption is justified will be discussed later in an analysis of the results of the neutron diffraction study.

A final comment

This paper serves as yet another warning of the inherent inadequacies of even an accurately carried out X-ray diffraction investigation of a hydrogen-bonded

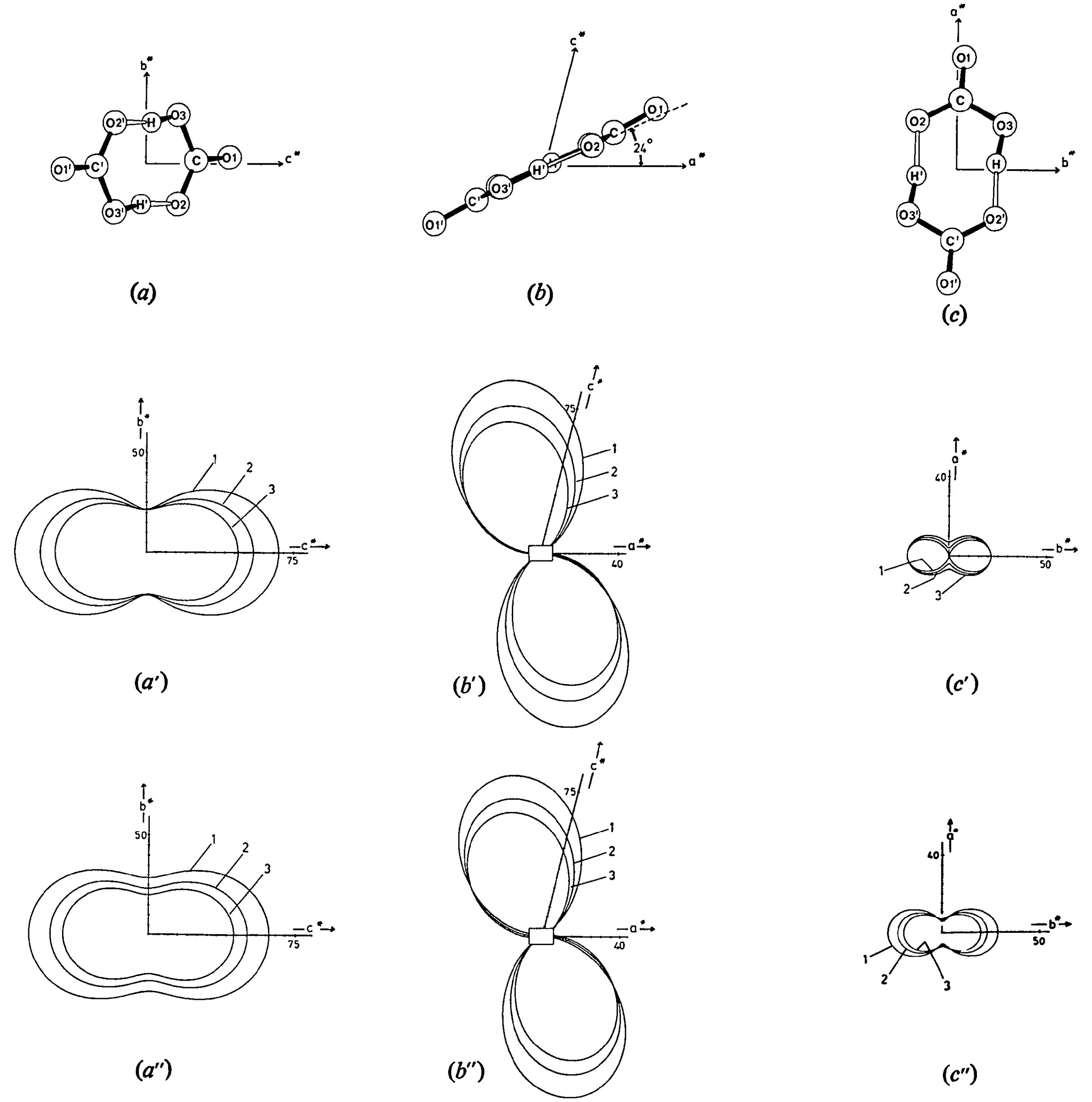
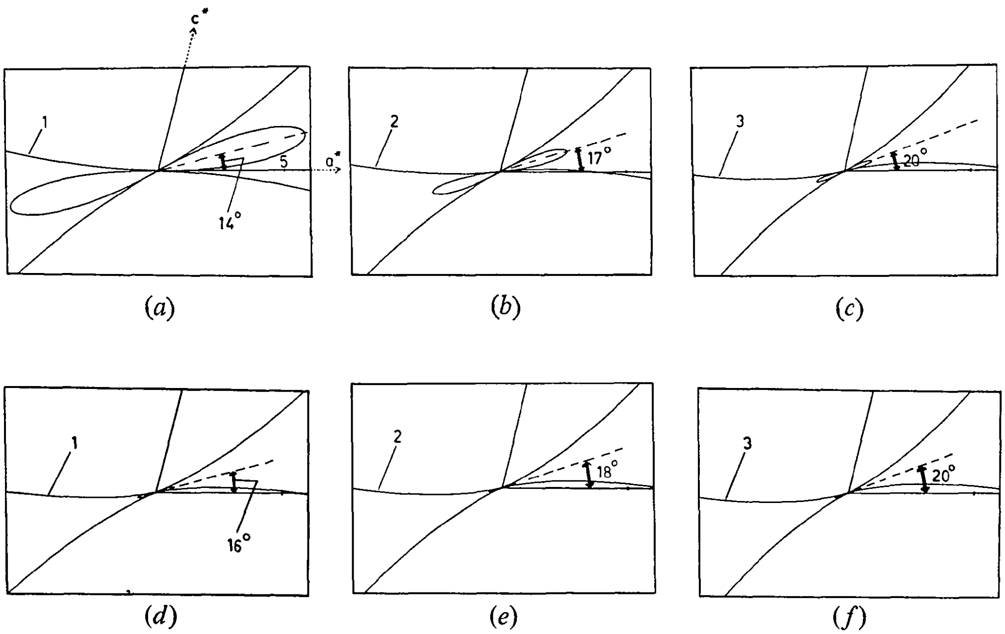


Fig. 6. Polar diagrams of the mean coefficient of linear thermal expansion ($\bar{\alpha}$) in the (*a*) (0*kl*), (*b*) (*h*0*l*) and (*c*) (*hk*0) planes. The dimer containing part of the chosen asymmetric unit is shown in projection along the *a*, *b*, and *c* axes in parts (*a*), (*b*) and (*c*). Parts (*a*')-(*c*') show the thermal expansion in $KHCO_3$, and parts (*a*'')-(*c*'') the thermal expansion in $KDCO_3$. The curves labelled 1, 2 and 3 refer to the temperature ranges 227–298K, 110–298K and 110–227K, respectively. All curves are reproduced on the same scale which is defined by the axial scale [$\times 10^{-6}(°)^{-1}$].



(*a*) (*b*) (*c*)

(*d*) (*e*) (*f*)

Fig. 7. An enlargement (× 14) of the detail near the origin in Fig. 6(*b*′) and 6(*b*″). Note here that the curves for the different temperature ranges no longer overlap but are given separately: (*a*)–(*c*) for $KHCO_3$ and (*d*)–(*f*) for $KDCO_3$.

system. The subsequent discovery of a fractional disorder effect in both $KHCO_3$ and $KDCO_3$ draws into question the full meaningfulness of some of the present findings and, to say the least, exposes $KHCO_3$ as a slightly unfortunate choice as subject for a study of this type.

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