Acta Cryst. (1968). **B24**, 323

The Crystal Structure of, and Hydrogen Bond in, Potassium Hydrogen Bisphenylacetate: a Redetermination.

BY LJUBICA MANOJLOVIĆ AND J. C. SPEAKMAN

Chemistry Department, University of Glasgow, Glasgow, W.2, Scotland

(*Received* 15 *May* 1967)

The crystal structure of potassium hydrogen bisphenylacetate, $KH(C_8H_7O_2)_2$, determined in 1948 by two-dimensional X-ray methods, has been reinvestigated by three-dimensional analysis. The final value of R is 8·4 % for 1950 reflexions measured on a linear diffractometer. The length of the crystallographically symmetrical $O\cdots H\cdots O$ bond has been amended from 2·55 Å, previously reported, to 2·443 ± 0·004 Å. This may therefore be an example of a genuinely symmetrical OHO-bond.

The crystal structure of potassium hydrogen bisphenylacetate, KHX_2 (where HX = phenylacetic acid, $C_6H_5.CH_2.CO_2H$) was determined by Speakman (1948, 1949) using two-dimensional X-ray methods. The structure includes a short hydrogen bond lying across a crystallographic centre of inversion (Fig. 1). The apparent symmetry of this bond has attracted some interest: for instance, Blinc, Hadži & Novak (1960) discussed the anomalous infrared spectrum, whilst Bacon & Curry (1957, 1960) studied a projection of the structure by neutron diffraction. This compound is of importance as the first representative of a class of acid salts with 'very short' hydrogen bonds (Speakman, 1967). For this reason, and because the $O\cdots H\cdots O$ distance of 2·55 Å, reported in 1949, has often been cited – sometimes without regard to the limited accuracy of the original analysis – we have now redetermined the structure by three-dimensional methods.

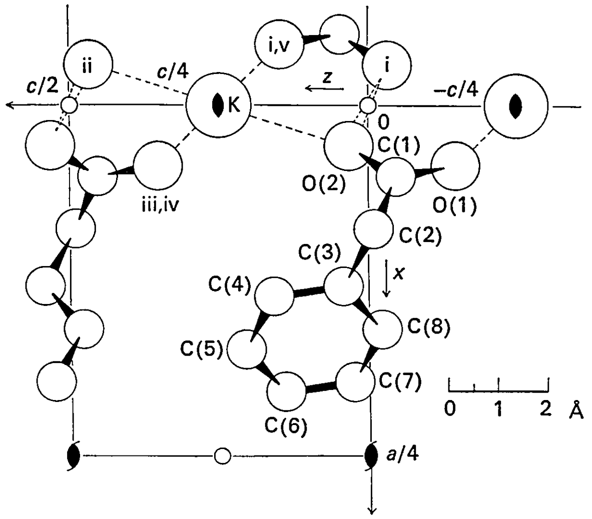

Fig. 1. The (010) projection of the structure, showing the numbering of atoms in the crystal-chemical unit. The significance of Roman numerals is the same as in Table 4.

Crystal data. $KH(C_8H_7O_2)_2$, F.W. 310·4. *Monoclinic*, $a=28{\cdot}40$ (2), $b=4{\cdot}49$ (1), $c=11{\cdot}90$ (2) Å, $\beta=90{\cdot}6$ (1)°, $V=1517$ Å^3, $d_m=1{\cdot}33$–$1{\cdot}34$ g.cm^{-3}, $Z=4$, $d_c=1{\cdot}359$ g.cm^{-3}, $F(000)=648$. [Cu $K\alpha_1$ taken to have $\lambda=1{\cdot}5405$ Å.] *Space group*, $I2/a$ (no. 15), with equivalent positions $\pm(x,y,z;\ x,\bar{y},\tfrac{1}{2}+z)+(0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})$.

The intensities of 1950 independent reflexions were measured on a Hilger–Watts linear diffractometer, Mo radiation being used in conjunction with balanced filters. After the Lp correction had been applied, the resulting observed structure amplitudes were on a scale slightly greater than absolute. All reflexions were included in the analysis; those with negative counts were allotted intensity of unity. Absorption was small (for Mo $K\alpha$ radiation, $\mu=3{\cdot}6$ cm^{-1}) and was neglected.

Refinement started from the positional parameters reported in 1949, and was by nine cycles of full-matrix, least-squares analysis, during which R fell from 31% to 8·4%, and R' from 6·4% to 0·78% ($R'=\Sigma w\Delta^2/\Sigma w|kF_o|^2$). The overall scale factor and the positional parameters of potassium, oxygen and carbon atoms were refined in all cycles. The vibrational parameters were refined as isotropic in the first three cycles, and as anisotropic in the remaining ones. After the sixth cycle of refinement, a difference synthesis was computed using terms with $(\sin\theta/\lambda)<0{\cdot}355$ Å^{-1}. This synthesis showed eight peaks, with heights in the range 0·26–0·32 e.Å^{-3}, corresponding to the eight hydrogen atoms in the asymmetric unit and no other peaks higher than 0·18 e.Å^{-3}; no region of the map was lower than −0·19 e.Å^{-3}. The hydrogen atoms were placed in calculated positions, acceptably related to the positions of the atoms to which they were bonded. In the remaining cycles, hydrogen atoms were included in the F_c calculations with the scattering function given by Stewart, Davidson & Simpson (1965), but their parameters were not refined. Scattering functions for K, O and C were taken from *International Tables for X-ray Crystallography*. The least-squares weighting scheme, due to Mr K.W. Muir, had $w=w_1\times w_2$, where $w_1=1$ if $(\sin\theta/\lambda)^2>0{\cdot}09$ else $w_1=(\sin\theta/\lambda)^2/0{\cdot}09$, and $w_2=1$

Table 1. *Analysis of the agreement of observed and calculated structure factors at the end of refinement*

Structure factors are on the absolute scale.

(*a*) as a function of the magnitude of observed structure factors

$\lvert F_o\rvert$ range	$\Sigma\lvert F_o\rvert$	$\Sigma\lvert F_c\rvert$	$\Sigma\lvert\Delta\rvert$	N*	R	$\Sigma\lvert\Delta\rvert/N$
0–5	2008·6	1960·3	847·2	777	0·422	1·09
5–10	3136·2	3086·9	412·4	436	0·131	0·95
10–15	3149·8	3116·5	215·6	258	0·068	0·84
15–20	2382·4	2364·5	117·3	137	0·049	0·85
20–30	3510·7	3476·5	119·9	144	0·034	0·83
30–50	5002·5	4992·7	142·8	133	0·029	1·07
50–100	3370·0	3337·5	111·8	52	0·033	2·15
100–180	1639·6	1608·5	64·7	13	0·039	4·98

(*b*) as a function of the layer line index

k	$\Sigma\lvert F_o\rvert$	$\Sigma\lvert F_c\rvert$	$\Sigma\lvert\Delta\rvert$	N*	R	$\Sigma\lvert\Delta\rvert/N$
0	4669·4	4708·3	238·0	186	0·051	1·28
1	6864·6	6778·8	445·5	374	0·065	1·19
2	5444·7	5377·9	350·0	367	0·064	0·95
3	3556·0	3588·8	289·4	355	0·081	0·82
4	2192·6	2204·4	341·8	349	0·156	0·98
5	1472·4	1285·2	367·0	319	0·249	1·15
all	24199·7	23943·4	2031·7	1950	0·084	1·04

* N = number of reflexions.

Table 2. *Final fractional coordinates and e.s.d.'s*

H(1) belongs to the carboxyl group, and H(2) and H(3) are bonded to C(2); the remaining hydrogen atoms are marked with the same numbers as the C atoms to which they are attached.

	x	y	z
K	0·00000	0·21169 (22)	0·25000
O(1)	0·04287 (8)	0·28069 (54)	−0·14693 (17)
O(2)	0·02864 (7)	0·18400 (47)	0·03306 (15)
C(1)	0·05023 (9)	0·32099 (60)	−0·04662 (22)
C(2)	0·08731 (10)	0·54135 (68)	−0·00738 (27)
C(3)	0·12862 (9)	0·38102 (65)	0·04499 (25)
C(4)	0·13589 (13)	0·39634 (97)	0·16007 (30)
C(5)	0·17400 (16)	0·25015 (116)	0·20696 (38)
C(6)	0·20422 (14)	0·08777 (111)	0·14018 (49)
C(7)	0·19731 (13)	0·07367 (104)	0·02594 (45)
C(8)	0·15957 (11)	0·22115 (84)	−0·02153 (32)
H(1)	0·0000	0·0000	0·0000
H(2)	0·0721	0·6918	0·0536
H(3)	0·0994	0·6709	−0·0789
H(4)	0·1116	0·5220	0·2122
H(5)	0·1802	0·2661	0·2975
H(6)	0·2341	−0·0297	0·1787
H(7)	0·2214	−0·0549	−0·0259
H(8)	0·1538	0·2128	−0·1125

if $|F_o| < 30$ else $w_2 = 30/|F_o|$. Refinement was ended when parameter shifts were smaller than 0·1 of their respective standard deviations. The ratio of the number of observed reflexions to the parameters refined is 20. A table of observed structure amplitudes and calculated structure factors is stored on magnetic tape at Glasgow University; a copy can be had by application to Dr J. G. Sime, quoting the reference number GL/1967/2. Table 1 provides evidence on the adequacy of data and refinement.

The results of the analysis are embodied in Tables 2 to 5, and in Fig. 1. The dimensions of the phenylacetate residue are more regular than those found in the two-dimensional analysis; the O(1)–C(1)–O(2) angle is no longer anomalous, for instance. The C–C distances in the benzenoid ring ranged originally from 1·44 to 1·36 Å, and now only from 1·389 to 1·373 Å, with the mean and r.m.s. difference from the mean of $1·381 \pm 0·002_5$ Å. This value is significantly below the accepted mean for the C–C distance in benzenoid rings. We think that the difference is artificial and due to the

Table 3. *Vibration tensor components* (Å^2) *and e.s.d.'s*

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
K	0·0724 (7)	0·0460 (5)	0·0277 (5)	0·0000	−0·0047 (8)	0·0000
O(1)	0·0526 (12)	0·0601 (14)	0·0367 (11)	0·0029 (18)	0·0061 (18)	−0·0144 (20)
O(2)	0·0404 (10)	0·0484 (11)	0·0331 (10)	0·0015 (15)	0·0059 (15)	−0·0064 (16)
C(1)	0·0310 (12)	0·0398 (13)	0·0374 (14)	0·0014 (19)	0·0008 (19)	0·0112 (18)
C(2)	0·0431 (14)	0·0385 (14)	0·0589 (18)	0·0054 (24)	−0·0141 (25)	−0·0066 (22)
C(3)	0·0331 (12)	0·0423 (14)	0·0489 (16)	0·0011 (22)	−0·0024 (22)	−0·0165 (20)
C(4)	0·0551 (19)	0·0751 (24)	0·0507 (19)	0·0019 (33)	−0·0056 (29)	−0·0150 (34)
C(5)	0·0713 (25)	0·0897 (31)	0·0673 (25)	0·0363 (45)	−0·0437 (40)	−0·0238 (46)
C(6)	0·0471 (19)	0·0760 (27)	0·1210 (39)	0·0411 (53)	−0·0580 (45)	−0·0098 (37)
C(7)	0·0448 (18)	0·0695 (25)	0·1108 (35)	−0·0182 (47)	−0·0068 (40)	0·0095 (34)
C(8)	0·0442 (16)	0·0591 (20)	0·0655 (21)	−0·0124 (31)	0·0019 (29)	0·0014 (27)

The hydrogen atoms were assigned the isotropic thermal parameter, $U = 0·075$ Å^2.

effects of thermal motion. Correction is difficult since the phenylacetate residue is more firmly held, by electrovalency and the hydrogen bond, at one end than at the other (see Fig. 1). The simple model of a rigid body librating about its centre of mass is therefore inappropriate. In our experience, attempts empirically to place an effective centre of libration elsewhere have not usually given results that were quantitatively convincing. Nevertheless, 'wagging' of the phenyl group is qualitatively suggested by the high U_{ij} values for atoms C(5), C(6) and C(7).

Table 4. *Coordination octahedron around the potassium ion*

$K\cdots O(2)$	2·718 (2) Å
$K\cdots O(1^{i})$	2·801 (3)
$K\cdots O(1^{v})$	2·855 (3)
$O(2)\cdots K\cdots O(1^{i})$	71·4°
$O(2)\cdots K\cdots O(1^{iii})$	104·3
$O(2)\cdots K\cdots O(1^{iv})$	108·3
$O(2)\cdots K\cdots O(1^{v})$	76·1
$O(2)\cdots K\cdots O(2^{ii})$	174·8
$O(1^{i})\cdots K\cdots O(1^{iii})$	75·7
$O(1^{i})\cdots K\cdots O(1^{iv})$	179·2
$O(1^{i})\cdots K\cdots O(1^{v})$	105·1
$O(1^{v})\cdots K\cdots O(1^{iv})$	74·1

Superscripts refer to atoms at:

CCU	x, y, z	iii	$x, \bar{y}, \frac{1}{2}+z$
i	$\bar{x}, \bar{y}, \bar{z}$	iv	$x, 1-y, \frac{1}{2}+z$
ii	$\bar{x}, y, \frac{1}{2}-z$	v	$\bar{x}, 1-y, \bar{z}$

The mean plane through C(2) and the six C atoms of the benzenoid ring is

$$0{\cdot}5637X'+0{\cdot}8166Y-0{\cdot}1241Z'=3{\cdot}3977\ \text{Å}\,,$$

where $X'=ax\sin\beta$, $Y=by$, $Z'=ax\cos\beta+cz$. The greatest deviations from this plane are for C(5), +0·006, and C(6), −0·006 Å, and the r.m.s. deviation is 0·004 Å. The mean plane through C(2) and the three atoms of the carboxyl group is

$$0{\cdot}6910X'-0{\cdot}7227Y-0{\cdot}0162Z'=-0{\cdot}0427\ \text{Å}\,;$$

the r.m.s. deviation here is 0·002 Å. The angle between these planes is 78·5°. Viewed along the C(2)–C(1) direction, bond C(2)–C(3) makes a dihedral angle of 110·5° clockwise from C(1)–O(1).

In a fully ionized carboxylate ion the C–O distances are equal, whilst in the neutral carboxyl group they differ by about 0·1 Å (Manojlović & Speakman, 1967). The difference of 0·068 Å between C–O and C–OH found in this compound therefore indicates the intermediate character of the carboxyl group; such a structural feature has also been observed in some other acid salts of monocarboxylic acids.

All non-bonded intramolecular contacts were calculated, as well as all intermolecular contacts shorter than 4·0 Å. None is anomalous.

The chief interest in this structure lies in the crystallographically symmetrical hydrogen bond $O(2)\cdots H(1)\cdots O(2^{i})$. The value of 113·9° for the $C(1)–O(2)\cdots O(2^{i})$ angle is such as to favour strong hydrogen bonding. The 1949 value of 2·55 Å for the $O(2)\cdots O(2^{i})$ distance compared with the value of about 2·45 Å, tentatively suggested by Coulson (1959) as the upper limit for the length of a truly symmetrical OHO-bond, led Rundle (1964) to question the results of infrared (Blinc, Hadži & Novak, 1960) and neutron diffraction (Bacon & Curry, 1957, 1960) studies of this compound, which favour the idea that the $O(2)\cdots O(2^{i})$ bond is not only crystallographically, but also genuinely, symmetrical. Our refinement leads to an $O(2)\cdots H(1)\cdots O(2^{i})$ distance of 2·443 ± 0·004 Å.

Whilst on leave of absence from the Institute of Nuclear Sciences 'Boris Kidrich', Vincha-Belgrade, Yugoslavia, one of us (Lj.M.) was supported by a grant from the Science Research Council. We made full use of the Glasgow series of KDF9 crystallographic programs developed by D.W.J. Cruickshank, J.G. Sime and others.

References

Bacon, G. E. & Curry, N. A. (1957). *Acta Cryst.* **10**, 524.
Bacon, G. E. & Curry, N. A. (1960). *Acta Cryst.* **13**, 717.
Blinc, R., Hadži, D. & Novak, A. (1960). *Z. Elektrochem.* **64**, 567.
Coulson, C. A. (1959). In *Hydrogen Bonding.* D. Hadži, editor. p. 339. London: Pergamon Press.
Manojlović, Lj. & Speakman, J. C. (1967). *J. Chem. Soc.* p. 971.
Rundle, R. E. (1964). *J. Physique*, **23**, 487.
Speakman, J. C. (1948). *Nature, Lond.* **162**, 695.
Speakman, J. C. (1949). *J. Chem. Soc.* p. 3357.
Speakman, J. C. (1967). *Chem. Comm.* p. 32.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

Table 5. *Bond lengths and angles with corresponding e.s.d.'s in phenylacetic acid residue*

Bonds			
O(1)–C(1)	1·223 (3) Å	C(4)–C(5)	1·379 (6) Å
O(2)–C(1)	1·291 (3)	C(5)–C(6)	1·384 (7)
C(1)–C(2)	1·515 (4)	C(6)–C(7)	1·373 (8)
C(2)–C(3)	1·506 (4)	C(7)–C(8)	1·376 (5)
C(3)–C(4)	1·389 (5)	C(8)–C(3)	1·389 (5)
Angles			
O(1)–C(1)–O(2)	124·7 (3)°	C(4)–C(3)–C(8)	120·1 (3)°
O(1)–C(1)–C(2)	120·6 (3)	C(3)–C(4)–C(5)	119·0 (4)
O(2)–C(1)–C(2)	114·8 (2)	C(4)–C(5)–C(6)	120·5 (4)
C(1)–C(2)–C(3)	110·6 (2)	C(5)–C(6)–C(7)	120·7 (4)
C(2)–C(3)–C(4)	119·5 (3)	C(6)–C(7)–C(8)	119·1 (4)
C(2)–C(3)–C(8)	120·4 (3)	C(7)–C(8)–C(3)	120·6 (4)