Crystal Structures of Some Acid Salts of Monobasic Acids. Part 18.[1] Potassium Hydrogen Bisphenylacetate, redetermined by Neutron Diffraction

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The crystal structure of the title compound, $KH[C_8H_7O_2]_2$, has been redetermined by neutron diffraction and refined to R 2.8% for 991 reflections. The short, and formally symmetrical, hydrogen bond has $O \cdots H \cdots O$ 2.454(3) Å, and the estimated relative vibrational motion of the proton has its maximum nearly parallel to the bond, with root-mean-square amplitude 0.18 Å. The vibrations of the other atoms are discussed, with their interpretation by various rigid-body models. The most satisfactory model is probably that which treats the ten heavier atoms of each phenylacetate residue as an independent rigid body. A small error in the monoclinic β angle affects earlier work on this structure, though its effects on derived molecular geometry are marginally significant only on the results of the 1 968 X-ray work. Amended cell dimensions are: $a = 28.449(6)$, $b = 4.480(1)$, $c = 11.887(2)$ Å, $\beta = 89.60(2)°$. Geometric results of the X-ray analysis have been recalculated with these parameters and the agreement with neutron-diffraction results is satisfactory.

POTASSIUM HYDROGEN BISPHENYLACETATE, KHX_2 (where $HX = Ph \cdot CH_2 \cdot CO_2H$), was the first compound in which a crystallographically symmetrical OHO bond was recognised, the analysis (1948) having been based on two-dimensional X-ray work.[2] It has attracted wide attention, particularly in connection with its anomalous i.r. spectrum,[3] and with the related question whether the ' very short ' hydrogen bonds $(O \cdots O <2.45$ Å$)$, in this crystal and also in the many other Type A structures now known,[4] are genuinely symmetrical.[5] Two-dimensional neutron-diffraction (ND) work was reported by Bacon and Curry (BC) at room temperature [6] as well as at lower temperatures.[7] Subsequently a three-dimensional analysis was based on X-ray data collected on a linear diffractometer by Manojlović and Speakman (MS) in 1968.[8] We now report a precise ND study.[9a]

EXPERIMENTAL

Amended Cell Dimensions.—The system is monoclinic, though pseudo-orthorhombic with the β angle near to 90°. From the 1948 work the sign of cos β was realised to be uncertain, but at that stage this was unimportant; interatomic distances derived from the atomic co-ordinates were not significantly affected. During the 1968 work the cell parameters were redetermined photographically, but unfortunately the error in the sign of cos β was not recognised. As the co-ordinates were now measured with better precision, this error affects the published molecular geometry to a small, but just significant, degree. *A fortiori* it was important to have precise cell dimensions for the present ND analysis. We have therefore redetermined the parameters by two independent methods. (1) By measuring the setting-angles, on a four-circle diffractometer, for *ca.* 40 reflections. These angles were used in least-squares

procedures to refine the cell parameters and results are given in Table 3. In this case calibration depends on attributing wavelengths of 0.710 69 Å to Mo-K_α radiation, or 0.709 25 Å to $K_{\alpha 1}$. (2) By taking Weissenberg photographs of the $h0l$ net, and superposing on it powder lines due to aluminium. The small distances between high-order X-ray spots and neighbouring (α_1) lines were measured, and the results used in a least-squares routine for determining a, c, and β. Here calibration depends on the cell parameter for Al, which was taken to be 4.049 07 Å.[9b] These results are also given in Table 1. The agreement

TABLE 1

Unit cell parameters re-determined with X-rays

	a	b	c	β
(1)	28.445(5)	4.480 6(7)	11.886 2(11) Å	89.610(13)°
(2)	28.457(6)		11.887(2)	89.56(2)°
(3)	28.434	4.489	11.915	(90.39°)

between (1) and (2) is good. Also in agreement are independent measurements (3) by Wölfel,[10] whose β angle is obtuse because he adopted the alternative scheme of indexing $hkl/\bar{h}kl$ reflections. We have assessed the following crystal data.

Crystal Data.—$C_{16}H_{15}KO_4$, $M = 310.4$. Monoclinic, $a = 28.449(6)$, $b = 4.480(1)$, $c = 11.887(2)$ Å, $\beta = 89.60(2)°$, $U = 1 515.0$ Å³, $D_m = 1.33-1.34$, $Z = 4$, $D_c = 1.361$ g cm⁻³. Space group $I2/a$ (No. 15).

Bond lengths and angles calculated from the X-ray co-ordinates of MS, but using amended cell parameters, are given later.

Neutron Diffraction.—The crystals were prepared from a solution of KOH and phenylacetic acid in ethanol. There appear laths elongated on the b axis with prominent (100) faces. By seeding a slightly supersaturated solution with a small crystal it was possible to develop the laths into plates *ca.* 2 mm thick, from which suitable specimens could be cut. A crystal of dimensions 4.08 × 3.50 × 2.15 mm

[1] Part XVII, M. J. Barrow, M. Currie, K. W. Muir, J. C. Speakman, and D. N. J. White, *J.C.S. Perkin II*, 1975, 15.

[2] J. C. Speakman, *Nature*, 1948, **162**, 695; Part I, *J. Chem. Soc.*, 1949, 3357.

[3] See *e.g.* M. Davies and J. O. Thomas, *J. Chem. Soc.*, 1952, 2858; N. Albert and R. M. Badger, *J. Chem. Phys.*, 1958, **29**, 1193; A. Novak, *Structure and Bonding*, 1974, **18**, 177; D. Hadži and S. Bratos, in ' The Hydrogen Bond,' eds. P. Schuster, G. Zundel, and C. Sandorfy, North-Holland, Amsterdam, 1976, chap. 12.

[4] J. C. Speakman, *Structure and Bonding*, 1972, **12**, 141; A. L. Macdonald, J. C. Speakman, and D. Hadži, *J.C.S. Perkin II*, 1972, 2289.

[5] For the contrary case see M. Catti and G. Ferraris, *Acta Cryst.*, 1976, **B32**, 2754.

[6] G. E. Bacon and N. A. Curry, *Acta Cryst.*, 1957, **10**, 524.

[7] G. E. Bacon and N. A. Curry, *Acta Cryst.*, 1960, **13**, 717.

[8] Lj. Manojlovic and J. C. Speakman, *Acta Cryst.*, 1968, **B24**, 323.

[9] (*a*) C. R. Walker, Ph.D. Thesis, University of Sheffield, 1975; (*b*) International Tables for X-ray Crystallography, Vol. III, Kynoch Press, Birmingham, 1962.

[10] E. R. Wölfel, ' Theorie und Praxis der Röntgenstrukturanalyse,' Braunschweig, Vieweg, 1975.

and of mass 37.4 mg was chosen after some preliminary examination of rocking-curves in a monochromatic neutron beam and the rejection of some evidently twinned specimens.

Two different diffractometers were used for the intensity measurements, namely a Mk. VI diffractometer with $\lambda = 1.180$ Å at the DIDO reactor (at the A.E.R.E., Harwell) and a Hilger and Watts diffractometer with $\lambda = 1.134$ Å at the PLUTO reactor. Throughout data collection, the 020 reflection was used as a standard and its intensity measured after every 15 ordinary reflections, i.e. ca. 3 times a day. Reflections were measured in three quadrants of the reciprocal lattice, $(hkl, \bar{h}kl)$, $(hkl, h\bar{k}l)$, and $(hkl, hk\bar{l})$, and, after correcting for absorption, any whose intensities I were $<3\sigma(I)$ were rejected. Averaging the three independent sets then produced 991 independent reflections. The absorption coefficient was measured experimentally as $1.90(4)$ cm^{-1}, and corrections were applied using the ABSORB program from the X-Ray '74 System; correction factors ranged from 1.400 0 to 1.968 5, these extremes being for the 039 and $\bar{4}00$ reflections, respectively.

Refinement was done with the program CRYLSQ of the X-Ray '70 System, and started from the co-ordinates of MS with isotropic temperature factors B 4.0 Å^2 for hydrogen atoms and 2.5 Å for all others. The neutron-scattering amplitudes were taken to be: hydrogen -0.374, carbon 0.665, oxygen 0.580, and potassium 0.37×10^{-12} cm. The initial R factor was 25%. Five cycles reduced it to 12.6%; and at this stage transfer to anisotropic temperature factors, making a total of 165 variables, led to R 2.9% after five more cycles. This was achieved without allowance for secondary extinction, and it was evident that only a few of the strongest reflections might be affected. (Thus the extinction factor, $|F_0| - |F_c|/|F_c|$ was no more than 6.5% and 6.9% for $\bar{4}02$ and $\bar{2}11$.) In fact, two further cycles, with down-weighting of both weak and very strong reflections, gave no more than a token improvement to R 2.8%. The least-squares weighting scheme was $w = 1/(\sigma_0^2)$, where $\sigma_0^2 = \sigma^2(F) + (0.01F)^2$. Here $\sigma^2(F)$ is the statistical variance of observation of F, and the term $0.01F$ is introduced to allow for errors such as machine inadequacies or inadequate absorption or extinction corrections. It is not surprising that these crystals, which are soft in texture, should have a wide mosaic spread and be largely free from extinction. Observed structure amplitudes and calculated structure factors have been deposited in Supplementary Publication No. SUP 21940 (9 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Table 2 gives the final fractional co-ordinates, together with their standard deviations estimated from the least-squares refinement. Thermal parameters are in Table 3. The nomenclature is such that the Debye–Waller amplitude factor in the structure-amplitude factor, i.e. $\exp(-B \sin^2\theta/\lambda^2)$, is equal to $\exp\{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{23}kl + b_{31}lh)\} = \exp\{-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{23}b^*c^*kl + 2U_{31}c^*a^*lh)\}$, where U_{ij} represents the averaged atomic displacement U_i along axis i multiplied by that along axis j, U_j. The numbering of atoms is the same as that used in the earlier analyses, and is shown in Figure 1, a

projection on the (010) plane, which also shows the relationship between neighbouring molecules. Symmetry-related units needed in the description of the structure are coded as follows: CCU x, y, z; I $-x, -y, -z$; II $-x, y, \frac{1}{2} - z$; III $x, -y, \frac{1}{2} + z$; IV $x, 1 - y, \frac{1}{2} + z$; V $-x, 1 - y, -z$.

TABLE 2

Fractional co-ordinates ($\times 10^5$), with standard deviations in parentheses

	x	y	z
K	0	21 132(69)	25 000
O(1)	4 300(6)	28 104(34)	-14 692(10)
O(2)	2 870(5)	18 397(31)	3 315(9)
C(1)	5 050(4)	32 143(24)	-4 672(8)
C(2)	8 762(5)	54 010(28)	-787(11)
C(3)	12 871(4)	38 238(25)	4 473(9)
C(4)	13 599(5)	39 704(35)	15 979(11)
C(5)	17 394(6)	25 178(41)	20 782(14)
C(6)	20 464(7)	8 753(40)	14 044(18)
C(7)	19 742(6)	7 245(39)	2 506(17)
C(8)	15 963(5)	21 975(32)	-2 161(11)
H(1)	0	0	0
H(2)	7 173(12)	69 049(70)	5 266(30)
H(3)	9 927(12)	67 100(75)	-7 996(29)
H(4)	11 239(14)	52 722(98)	21 127(26)
H(5)	17 968(18)	26 710(130)	29 705(32)
H(6)	23 441(17)	-2 740(120)	17 780(48)
H(7)	22 155(15)	-5 390(120)	-2 749(47)
H(8)	15 396(13)	20 871(96)	-11 122(26)

The thermal motion is illustrated pictorially in Figure 2, which is a view along the y axis, showing the 50% probability thermal ellipsoids computed by the
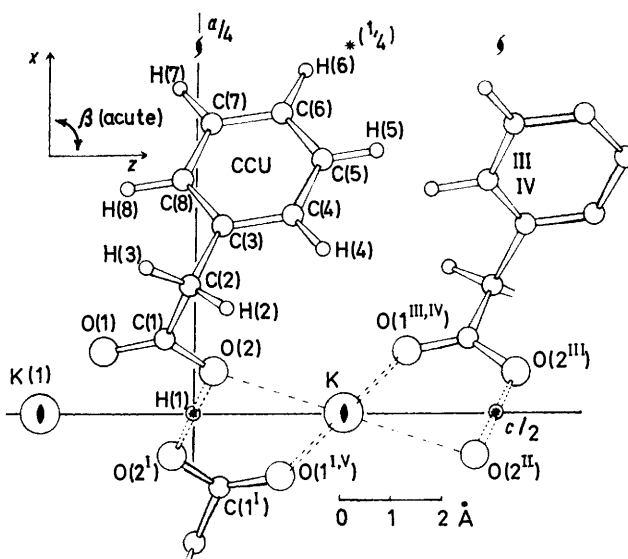

FIGURE 1   A projection on the 010 plane of a portion of the unit cell of potassium hydrogen bisphenylacetate, indicating in particular the relationship between neighbouring molecules, and emphasising the nature of the β (acute) angle. Centres of symmetry in the structure are indicated by asterisks

program ORTEP.[11] The principal axes of these ellipsoids, and their direction cosines relative to the crystal axes are deposited in the Supplementary Publication. Perhaps the most striking features of Figure 2 are the large anisotropic motions of C(5)—(7) and their

[11] C. K. Johnson, Oak Ridge National Laboratory Report. ORNL 3794, 1965.

associated hydrogen atoms, which recall BC's conclusion,[7] and the large motions of H(2) and H(3) which suggest some large oscillation of the methylene group.

We have attempted to associate the experimental values of U_{ij} with various models of motion in a rigid, or partially rigid, body. As a first, and least ambitious,

line, about the normal to the plane of the ring, and about a third, mutually perpendicular axis. This model involves 66 values of U_{ij}, and the root-mean-square deviation of their values from the unconstrained-analysis values of Table 2 was 0.003 1 $Å^2$. However, bearing in mind that some of the individual standard deviations

TABLE 3

Vibrational parameters ($Å^2 \times 10^4$), with standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K	755(24)	362(16)	222(11)	0	−49(12)	0
O(1)	569(9)	480(8)	290(6)	−69(7)	−9(5)	16(5)
O(2)	418(9)	375(7)	289(6)	−31(6)	−3(5)	1(5)
C(1)	346(7)	288(5)	302(5)	25(5)	−22(4)	4(4)
C(2)	457(8)	264(6)	542(7)	−22(6)	−96(5)	19(6)
C(3)	350(7)	333(6)	402(6)	−50(5)	−31(4)	0(4)
C(4)	517(9)	655(9)	414(7)	−67(7)	−78(6)	20(6)
C(5)	657(12)	844(12)	633(9)	−74(9)	−258(8)	170(8)
C(6)	495(11)	630(11)	1 180(14)	−33(8)	−346(10)	195(10)
C(7)	404(10)	607(10)	1 041(13)	83(8)	−68(8)	−80(9)
C(8)	425(9)	502(8)	582(8)	32(6)	6(6)	−96(6)
H(1)	539(23)	539(21)	380(14)	130(18)	44(14)	45(14)
H(2)	702(20)	500(16)	1 028(22)	109(14)	−174(17)	−291(17)
H(3)	776(22)	640(18)	930(21)	−214(16)	−190(16)	359(18)
H(4)	905(25)	1 132(28)	579(16)	92(23)	−2(16)	−182(19)
H(5)	1 329(39)	1 646(44)	739(23)	−41(35)	−456(24)	212(25)
H(6)	822(30)	1 166(35)	1 859(47)	180(27)	−640(29)	291(32)
H(7)	698(28)	1 207(35)	1 757(45)	408(26)	34(26)	−404(33)
H(8)	943(26)	1 121(28)	619(18)	220(22)	29(16)	−229(19)

assumption, we have postulated merely that the phenyl group moves as a rigid unit. Using the Schomaker–Trueblood theory [12] to analyse the U_{ij} of the carbon and hydrogen atoms, we concluded that the phenyl group is in libration about a point only 0.5 Å from C(3). The principal amplitudes of translation were found to be 0.19, 0.15, and 0.23 Å with the largest in the plane of the

FIGURE 2 A view along the y axis showing 50% probability thermal ellipsoids computed by the program ORTEP for an unconstrained refinement

group and in a direction roughly perpendicular to the C(3) · · · C(6) line. The principal amplitudes of libration were 8.3, 5.9, and 6.6° respectively about the C(3) · · · C(6)

[12] V. Shomaker and K. N. Trublood, Acta Cryst., 1968, B24, 63.
[13] T. J. Koetzle, M. S. Lehmann, J. J. Verbist, and W. C. Hamilton, Acta Cryst., 1972, B28, 3207.

are large, we feel that this agreement may be deceptive; for the wagging motion of the H atoms will confuse the analysis. A more authentic model would be one that considered only the six carbon atoms of the ring, but we then have only 36 U_{ij} observations to determine 20 parameters, namely 6 each for the symmetric T and L tensors, and 8 components for the S tensor. Such a small ratio of observations to parameters is unsatisfactory. A more promising proposition is to extend the rigid-body model to include the whole of the C_8O_2 skeleton, though recognising that the motion of O(2) may well be restricted by the hydrogen bond. This gives us 60 observations for the 20 parameters. Dependence on the heavier atoms alone is in line with experience in the rigid-body treatment of ND results for many similar structures, such as those of lysine hydrochloride [13] and tyrosine.[14]

Our final assessment for a rigid C_8O_2 skeleton was made with a program, due to Dr. Shmueli, which transforms the atomic co-ordinates and U_{ij} to a set of inertial axes, and then computes the Schomaker–Trueblood tensors with respect to the same axes. The root-mean-square motions along the axes of the T tensor are 0.20, 0.17, and 0.15 Å, whilst the libration amplitudes about L_1, L_2, and L_3 are 7.4, 3.1, and 2.2° respectively. These axes are shown in Figure 3, which is derived from a photograph of a model of the anion. The view is almost along L_3, the axis of least libration, which is accordingly much foreshortened. It can be seen that C(1), O(1), and O(2) are much closer to L_1, the axis of maximum libration, than are C(6), and H(6) at the opposite end of the anion. This accounts for the false impression given by BC's (010) projection that the
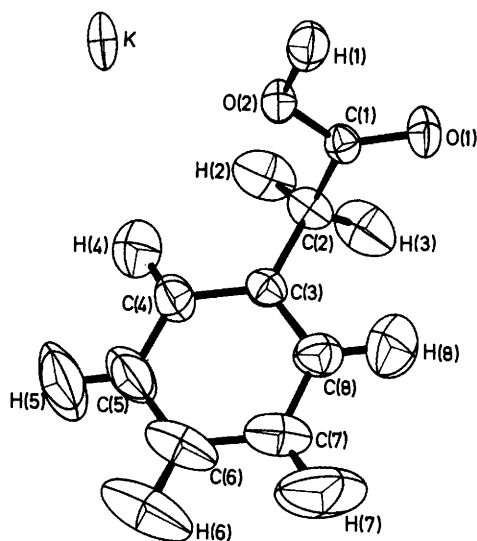
[14] M. N. Frey, T. F. Koetzle, M. S. Lehmann, and W. C. Hamilton, J. Chem. Phys., 1973, 58, 2547.

molecule was bending about C(3). (Root-mean-square. Δ for this assessment 0.003 2 Å².)

Interatomic distances and angles derived from the co-ordinates of Table 2 are given in column 2 of Table 4. For comparison the X-ray results, now recalculated with the amended cell parameters, are shown in column 3.

TABLE 4

Geometrical details of the phenylacetate residue; distances (Å) and angles (°), with standard deviations in parentheses. Both neutron and X-ray results embody the corrected cell parameters

	Neutron	X-Ray *	Neutron †
C(1)–O(1)	1.225(2)	1.225(3)	1.234
C(1)–O(2)	1.287(2)	1.282(3)	1.299
C(1)–C(2)	1.515(2)	1.521(4)	1.520
C(2)–C(3)	1.506(2)	1.515(4)	1.514
C(3)–C(4)	1.386(2)	1.387(2)	1.397
C(4)–C(5)	1.387(3)	1.387(5)	1.394
C(5)–C(6)	1.391(3)	1.374(7)	1.404
C(6)–C(7)	1.390(3)	1.375(8)	1.401
C(7)–C(8)	1.381(2)	1.384(5)	1.388
C(8)–C(3)	1.385(2)	1.380(5)	1.397
C(2)–H(2)	1.082(4)		
C(2)–H(3)	1.088(4)		
C(4)–H(4)	1.077(4)		
C(5)–H(5)	1.077(4)		
C(6)–H(6)	1.089(6)		
C(7)–H(7)	1.084(5)		
C(8)–H(8)	1.080(3)		
O(2) ··· O(2^I)	2.454(3)	2.451(4)	
K$^+$ ··· O(2)	2.701(1)	2.702(2)	
K$^+$ ··· O(1^I)	2.808(3)	2.806(3)	
K$^+$ ··· O(1^V)	2.862(1)	2.860(2)	
O(1)–C(1)–O(2)	124.1(1)	124.3(3)	
C(2)–C(1)–O(1)	121.2(1)	121.2(3)	
C(2)–C(1)–O(2)	114.7(1)	114.5(2)	
C(1)–C(2)–C(3)	111.6(1)	111.1(2)	
C(2)–C(3)–C(4)	120.6(1)	120.2(3)	
C(3)–C(4)–C(5)	120.4(2)	119.7(4)	
C(4)–C(5)–C(6)	119.9(2)	120.4(4)	
C(5)–C(6)–C(7)	119.8(2)	120.4(4)	
C(6)–C(7)–C(8)	119.6(2)	119.8(4)	
C(7)–C(8)–C(3)	121.1(1)	120.5(4)	
C(8)–C(3)–C(2)	120.2(1)	120.3(3)	
C(4)–C(3)–C(8)	119.2(1)	119.5(3)	
H(2)–C(2)–H(3)	108.2(3)		

* MS.   † Corrected for libration.

From the rigid-body analysis, co-ordinates may be corrected for the shrinkage effect, due to libration, discussed by Cruickshank (1956), and Busing and Levy.[15] Column 4 of Table 3 shows the effects on the ND results of this correction. (It is not expedient to apply such corrections to intermolecular distances.)

In general, the agreement between ND and X-ray results is close. The means, with their standard deviations, for the aromatic C–C distances are $1.381(2\frac{1}{2})$ (X-ray), 1.387(1) (ND), and 1.397 Å (ND corrected). The difference between the uncorrected values is only of possible significance, though it is in accord with

[15] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1964, **17**, 142.
[16] A. M. O'Connell, A. I. M. Rae, and E. N. Maslen, *Acta Cryst.*, 1966, **21**, 208.
[17] P. Coppens, Physical Chemistry, Ser. 2, vol. 11, ' Chemical Crystallography,' ed. J. M. Robertson, Butterworths, London, 1975, p. 25.

experience.[16] It may be attributed to the asphericity errors which affect straight X-ray analysis: ' carbon atoms are shifted . . . towards the centre of the ring in aromatic compounds.' [17] The ND corrected result agrees exactly with the spectroscopic measurements on benzene itself.

The mean plane of the atoms of the benzenoid ring, C(3)—(8), is described by the equation: $-0.564\,07\,X' - 0.815\,40\,Y + 0.130\,22\,Z' = -3.395\,27$ (Å), where X', Y, and Z' are absolute orthogonal co-ordinates. None of the atoms deviates significantly from this plane. (χ^2 is 9.8 for three degrees of freedom.) The methylenic C(2)
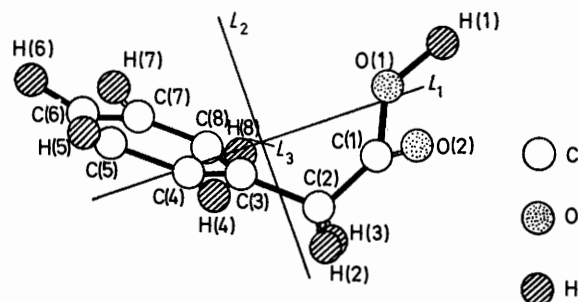

FIGURE 3   A perspective view of the libration axes L_1, L_2, L_3 in relation to the molecule, assuming a rigid C_8O_2 skeleton

atom is 0.004 Å from the plane. The four atoms associated with the carboxy-group, O(1), O(2), C(1), and C(2), have a mean plane equation of $0.686\,57\,X' - 0.726\,73\,Y - 0.022\,03\,Z' = -0.046\,55$; the central atom is 0.004 Å out of plane. The angle between the two mean planes is 78°. The dihedral angles C(1)–C(2)–C(3)–C(4) and O(1)–C(1)–C(2)–C(3) are $-108.5(4)$ and $-111.0(1)°$.

The three independent K$^+$ ··· O distances are included in Table 3. The results for the 12 O ··· K$^+$ ··· O angles do not differ materially from the X-ray results.

The Hydrogen Bond.—The relative vibrational motions of the hydrogen atom in the (non-linear) system C–O–H can be analysed into stretching (S) of O–H, bending (B) of C–O–H, and torsion (T) about C–O. When the hydrogen atom is not engaged in hydrogen bonding, the respective frequencies are in the order $S \gg B > T$. The amplitudes are in the reverse order: an ellipsoid representing the relative motion of the proton would have its minimum axis approximately in the O–H direction. This is still true when the hydroxy-group is involved in weak, or even moderately strong, hydrogen bonding. The shape of the ellipsoid can be independently assessed from good ND work, and it agrees with the principles stated.[18]

However, when the bonding is very strong (O ··· O $< ca.$ 2.5 Å), the ellipsoid is inverted: maximum amplitude, with greatly reduced frequency, lies on, or near, the bond axis.[18,19] The ND results for potassium hydrogen bisphenylacetate illustrate this principle. The amended cell dimensions raise the overall length of OHO

[18] See e.g. J. C. Speakman, *Chem. Soc. Specialist Reports*, ' Molecular Structure by Diffraction Methods,' vol. 3, 1975, p. 88.
[19] J.-O. Lundgren and R. Telgren, *Acta Cryst.*, 1974, **B30**, 1937.

a little, though it is still ' very short ' [O $\cdots$ O 2.454(3) Å]. Following a procedure used by McGaw and Ibers,[20] we find the mean-square amplitudes of the proton relative to its neighbouring oxygen atoms have the components $U_{\parallel}$ 0.032 2, and $U_{\perp}$ 0.007 5, —0.001 9 Å². (The negative value of one of the perpendicular values is, of course, physically unacceptable; it may be attributed either to experimental error affecting small differences or to imperfections in our model.) The root-mean-square motion of the proton along the bond amounts to 0.18 Å, sufficient to carry it across the intervening potential-energy barrier, if we were to suppose there to be a double-minimum potential of not unreasonable separation. This accords with the view that the proton may be vibrating anharmonically in a shallow, and effectively single-minimum, potential, which will have its minimum at the centre when the total environment is symmetrical, as it is in Type A structures.[21]

[20] B. L. McGaw and J. A. Ibers, *J. Chem. Phys.*, 1963, **39**, 2677.
[21] A. Sequeira, C. A. Berkebile, and W. C. Hamilton, *J. Mol. Structure*, 1967—8, **1**, 293; ref. 18, vol. 2, 1974, p. 53.