position vectors are rationally dependent, has precisely one homometric mate, its enantiomorph.

We wish to express our appreciation to Mr Peter O'Hara of the National Bureau of Standards for performing the calculations contained in this paper. He has programmed the calculation of equation (2·2) for the digital computer, SEAC, thus making a high-speed computer available for the computation of phases.

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A Neutron-Diffraction Study of Potassium Hydrogen Bis-Phenylacetate

BY G. E. BACON AND N. A. CURRY
Atomic Energy Research Establishment, Harwell, Berks, England

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Fourier projections derived from single-crystal intensity data give the positions and thermal vibrations of all the atoms in the structure. The mean length of the C–H bonds to the benzene ring is 1·13 Å. The acidic hydrogen atom at the centre of symmetry shows no measurable anisotropy but it is very diffuse, with a r.m.s. amplitude of displacement of 0·29 Å.

Introduction

In two earlier papers (Bacon & Curry, 1956*a*, *b*) we have shown how neutron-diffraction data can supplement existing knowledge of the molecular structure derived using X-rays in the cases of sodium sesquicarbonate and α-resorcinol. In each instance the supplementary information depended on the detection of hydrogen atoms. In the former substance we were able to provide detailed information about the hydrogen bond across a symmetry centre, which links two carbonate groups, and also about the hydrogen atoms within the molecules of water of crystallization; in resorcinol we were able to show detail both for the intermolecular hydrogen bonds and for the C–H bonds to the benzene ring. The present study is a natural sequel to these two earlier ones. Potassium hydrogen bis-phenylacetate, $(C_6H_5CH_2COO)_2KH$, is an acid salt of phenylacetic acid and its structure was studied, using X-ray diffraction methods, by Speakman (1949). This X-ray work showed that phenylacetate residues in the structure were related by a centre of symmetry in such a way that the O–O distance between their carboxyl groups was 2·55 Å, suggesting a short hydrogen bond in which the hydrogen atom was either centrally located at the centre of symmetry or statistically distributed between two possible positions, one on each side of the centre. These two possible structures may usefully be considered in relation to the structure of KHF_2, of which $(C_6H_5CH_2COO)_2KH$ might be regarded as an aromatic analogue, where there is a very short F–H–F bond, of length only 2·26 Å, and a variety of physical evidence that the hydrogen atom is indeed centrally located (Peterson & Levy, 1952).

Experimental details

Potassium hydrogen bis-phenylacetate has monoclinic symmetry with space group $C2/c$ and

$$a = 28{\cdot}4,\ b = 4{\cdot}50,\ c = 11{\cdot}97\ \text{Å},\ \beta = 90{\cdot}4^\circ.$$

It was prepared as described by Speakman and recrystallized from ethyl alcohol, from which it develops as laths elongated along the b axis. This habit is of the desired type, since the aim of the experimental work is to produce a projection on the (010) plane of the neutron-scattering density, but it was found very difficult to grow crystals sufficiently large to give adequately intense diffracted beams. As a very exceptional occurrence, a crystal measuring 3·7 × 0·7 × 0·3 cm. was produced and from this was cut a very suitable crystal of dimensions 3·7 × 0·3 × 0·3 cm., which was used for most of the work, together with two smaller specimens. The crystal was mounted with the b axis vertical, and 118 ($h0l$) reflexions were measured using a monochromatic neutron beam of wavelength 1·09 Å. About 100 of these reflexions were first measured with the small simple spectrometer designed for single-crystal work and described by Bacon & Dyer (1955). Subsequent checks of the intensities were car-

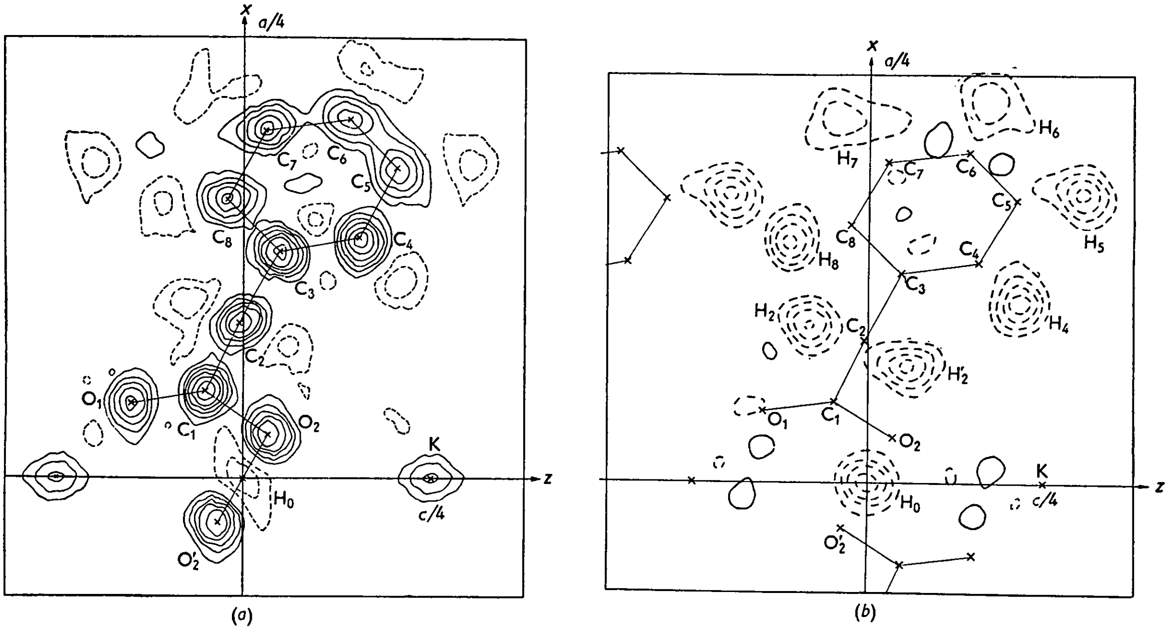

Fig. 1. (a) Projection of the neutron-scattering density on the (010) plane. (b) Projection on the (010) plane of the neutron-scattering density due to hydrogen atoms only, derived by synthesis of $F_o - F_{\mathrm{KCO}}$.
Full lines are positive contours; broken lines are negative.

ried out both with this instrument and with our larger conventional type of 'powder spectrometer'. We emphasize that a small simple instrument is entirely satisfactory for single-crystal studies of this kind. A typical recording of the ($h00$) reflexions of potassium hydrogen bis-phenylacetate has already been published in the paper to which we have just referred.

All our measurements were made at room temperature.

Analysis of results

The intensity data were analysed along the lines described in our earlier papers. The initial Fourier synthesis, for which the signs of the amplitudes F_o were computed from the structural information given by Speakman's X-ray work and approximate estimates of the hydrogen positions, is shown in Fig. 1(a). The structure is projected on the (010) plane and is to be compared with the structure as determined by X-rays, which is given in Fig. 2 of Speakman's (1949) paper. The neutron projection shows a rather better resolution. A very similar range of reflexions was covered in the two cases, with the Fourier series terminated at $d \approx 0{\cdot}9$ Å, but the scattering amplitudes of all the atoms in the molecule are more closely similar for neutrons in comparison with the predominating effect of the potassium ions for X-rays. The hydrogen atoms in the molecule are all clearly visible in our Fig. 1(a) but their detailed contours are very irregular, on account of the large diffraction ripples from the neighbouring carbon and oxygen atoms. At this preliminary stage in the analysis the 'reliability index' $\Sigma|F_o - F_c| \div \Sigma|F_o|$ was 23·4%.

The peak amplitudes of the various atoms in the projection of Fig. 1(a) were used to estimate the Debye factors B, in the correction term $\exp(-B \sin^2 \theta/\lambda^2)$ for the effect of thermal vibrations, in the manner described in our earlier papers. Using these values of B and slightly modified co-ordinates for one or two of the carbon and oxygen atoms, a Fourier synthesis of $(F_o - F_{\mathrm{KCO}})$ was made, where F_{KCO} is the calculated contribution to each structure factor F_{hkl} which is due to potassium, carbon and oxygen atoms, i.e. the calculated contribution from all atoms other than hydrogen. The result is a projection of the scattering density due to the hydrogen atoms alone, with the details now unobscured by the diffraction ripples from the other atoms. This projection still contains false detail due to any errors in the assumed positions of these other atoms (for which the parameters determined by X-ray diffraction have been used so far) and to errors in our first approximations to the values of the individual temperature factors B. By using a process of successive refinement which we have described earlier (Bacon & Curry, 1956a) we arrive at Fig. 1(b), which is the fourth in a series of difference syntheses. At this stage of the analysis the reliability index has fallen to 13·0%, which we can compare with the 14% achieved by Speakman for the (010) projection given by X-ray diffraction data. We may regard this as indicating roughly that we have located the hydrogen atoms with the same accuracy as the X-ray investigation succeeded in locating the heavier atoms. Table 1 compares the atomic co-ordinates as found with X-rays and neutrons, and lists the values of B which we have ascribed to each atom.

Table 1. *Atomic parameters and temperature factors of individual atoms*

	x/a		y/b		z/c		B (10^{-16} cm.^{2})	
Atom	Neutron	X-ray	Least squares	X-ray	Neutron	X-ray	Neutron	X-ray
K	0	0	—	0·206	0·250	0·250	4·3	3·8
O_1	0·044	0·045	—	0·290	−0·148	−0·143	3·2	
O_2	0·028	0·028	—	0·200	0·036	0·035	1·6	
C_1	0·050	0·048	—	0·318	−0·048	−0·046	3·0	3·8
C_2	0·087	0·085	—	0·540	−0·006	−0·007	3·3	
C_3	0·129	0·130	0·375	0·373	0·048	0·047	2·9	
C_4	0·136	0·135	0·372	0·373	0·157	0·167	3·0	
C_5	0·174	0·174	0·216	0·218	0·210	0·207	4·3	
C_6	0·203	0·204	0·066	0·062	0·144	0·140	5·0	
C_7	0·198	0·198	0·058	0·062	0·027	0·021	5·2	
C_8	0·159	0·160	0·219	0·218	−0·021	−0·020	4·7	
H_0	0	—	—	—	0	—	6·6	—
H_2	0·098	—	(0·676)	—	−0·082	—	7·5	
H_2'	0·072	—	(0·684)	—	0·055	—	6·8	
H_4	0·111	—	0·502	—	0·214	—	6·8	
H_5	0·177	—	0·228	—	0·304	—	7·0	
H_6	0·235	—	−0·071	—	0·169	—	11·9	
H_7	0·224	—	−0·080	—	−0·036	—	13·0	
H_8	0·149	—	0·240	—	−0·110	—	6·8	

Table 2 lists the various bond lengths which we have deduced from our data. In arriving at these values we have had to supplement the information given by our neutron-diffraction projections with the knowledge of the y parameters deduced from the X-ray study.

Table 2. *Bond lengths*

	Neutron	X-ray		Neutron	X-ray
C_3–C_4	1·32 Å	1·44 Å	C_2–C_3	1·53 Å	1·57 Å
C_4–C_5	1·43	1·39	C_1–C_2	1·54	1·52
C_5–C_6	1·33	1·36			
C_6–C_7	1·41	1·43			
C_7–C_8	1·43	1·37			
C_8–C_3	1·39	1·38			
Mean	1·39	1·40			
C_1–O_1	1·22	1·18			
C_1–O_2	1·30	1·24			
O_2–H–O_2'	2·54	2·55			
C_4–H_4	1·15	—	C_2–H_2	1·14	—
C_5–H_5	1·13	—	C_2–H_2'	1·07	—
C_6–H_6	1·14	—			
C_7–H_7	1·24	—			
C_8–H_8	1·10	—			

It would, of course, have been more satisfactory if a neutron-diffraction projection could have been obtained on the (001) plane also, but we have not yet been able to grow a crystal of sufficient length in the direction of the c axis for this purpose. However, many of the bond lengths of interest make only small angles with the xz plane so that the absence of neutron information about the y parameters of the atoms is not of undue importance. In order to determine the y parameters of the hydrogen atoms we have assumed the benzene ring and the C–H bonds to be planar, and have represented this plane by an equation of the form $Z = Ax+By+C$. We have obtained the values of A, B, C by the method of least squares from the neutron values of x, z for the carbon atoms and their y parameters as known by X-ray data. The values obtained were $A = 16{\cdot}0$, $B = 3{\cdot}55$ and $C = -3{\cdot}35$ when x, y, z are expressed in fractional co-ordinates. The values of y then deduced are those listed in the least-squares column of Table 1.

Discussion

We are primarily interested in the information about the hydrogen atoms which is deduced from Figs. 1(*a*) and 1(*b*). As Table 1 shows, the thermal vibrations are large. The atoms H_2, H_2', which are part of the CH_2 group, and the three less remote atoms H_4, H_5, H_8, which are attached to the benzene ring, have an average B value of 7·0 Å^2, which is a little larger than the value of 6·2 Å^2 which we deduced for the ring atoms in resorcinol. On the other hand, the two hydrogen atoms H_6 and H_7, on the side of the benzene ring remote from the centre of symmetry of the unit cell, have much larger thermal vibrations. These seem to be due to two influences. First, it appears that the molecule as a whole undergoes a vibration about the origin of the projection or perhaps about a point near to C_3, for it is found that the thermal vibrations of the carbon atoms increases significantly as we pass from C_3 and C_4 to C_5 and C_8 and on to C_6 and C_7. Secondly, it would seem that the hydrogen atoms H_6 and H_7 vibrate anisotropically with their largest vibrations at right angles to the direction of the C–H bond. This type of vibration, which tends to maintain the C–H distance between the neighbouring carbon and hydrogen atoms at the expense of less rigid distances between more remote atoms, does not seem unreasonable when we consider the open nature of the *inter*molecular structure. We do not consider that our present experimental accuracy justifies a full quantitative assessment of the anisotropic molecular vibrations which we have described. The very large values of B obtained for H_6, H_7, in particular, must be regarded as purely empirical: the assumptions involved in the Debye treatment of thermal vibrations do not hold for such large apparent movements of the atoms.

It may be of interest to contrast the type of molecular vibration which we find here with that which we have previously reported in α-resorcinol. In the latter, where the molecules are interlinked by hydrogen bonds, we find *lines* of rigid atoms passing through the structure; in the phenylacetate the structure is based much more on rigid *points*, at the centres of symmetry between pairs of phenylacetate residues. It may be noticed from Table 1 that of the two oxygen atoms attached to C_1, the atom O_2, which takes part in the hydrogen bond across the origin, is more rigidly fixed than O_1. The same conclusion is reached from a comparison of the peak heights of O_1 and O_2 in Speakman's X-ray projection.

The lengths of the C–H bonds to the carbon atoms in the benzene ring have already been listed in Table 2. The standard deviations of the atomic co-ordinates are estimated by Cruickshank's (1949) method to be 0·011 Å for carbon and oxygen and 0·033 Å for hydrogen, except for the very diffuse hydrogen atoms H_6 and H_7. From these values it follows that the standard deviation of the C–H bonds to C_4, C_5 and C_8 is 0·035 Å, and is more than this for the bonds to C_6 and C_7. The mean length of all five of the C–H bonds to the benzene ring is 1·15 Å, and the mean length of those three whose determination is most accurate is 1·13 Å; we take this latter value as our estimate of the length of a C–H bond to the benzene ring in this compound. For comparison we note that the values in Table 2 for the two C–H bonds within the CH_2 group formed from C_2 are equal to 1·14 and 1·07 Å, if it is assumed that the environment of carbon C_2 is tetrahedral as a means of fixing the y parameters of H_2, H_2'. For the time being, until we have collected data by a neutron-diffraction study of other aromatic compounds, we can but record that these various values are not significantly different from that of 1·08±0·04 Å which we deduced in α-resorcinol.

It is interesting to compare the C–C bond lengths given by the X-ray and neutron studies in view of their approximately equal reliability indices of 0·14 and 0·13. Taking our calculated standard deviation for the C–C bonds as 0·016 Å, differences greater than 0·050 Å should be significant. Most of the differences between individual C–C lengths and the mean value are less than this for both X-rays and neutrons. On the other hand, for C_3–C_4 the neutron value is less than the mean of 1·39 Å by more than 0·05 Å and the X-ray value is greater than the mean by about this amount. This emphasizes that the reliability index and the standard deviations can only give an assessment of the *general* level of accuracy of an analysis.

Finally, we consider the contours of the hydrogen atom at the centre of symmetry. Fig. 1(*b*) shows no elongation along the O–O bond: in fact the lowest contour is remarkably circular and the higher contours show a slight elongation in the direction perpendicular to the O–O bond. The absence of elongation along the bond is quite striking when the shape of the atom in Fig. 1(*b*) is compared with its counterpart at the centre of symmetry in sodium sesquicarbonate (Bacon & Curry, 1956*a*). It seems, therefore, that a genuine symmetrical O–H–O bond cannot be ruled out in the case of potassium hydrogen bis-phenylacetate, and indeed Hadzi & Novak (1955) have concluded that there is positive evidence in favour of this from the infra-red spectrum. Moreover, the slight elongation of the atom at right angles to the bond is what might be expected if the equilibrium position is indeed central, since vibrations might be expected to take place more readily at right angles to the restraining force of the oxygen links. From the point of view of our own study, however, we emphasize that this apparently symmetrical bond has been attained at the expense of a very diffuse hydrogen atom. The Debye B value for this atom is $6{\cdot}6\times10^{-16}$ cm.^{2}, which corresponds to a r.m.s. amplitude of thermal displacement of 0·29 Å, and this displacement will take place, to a first approximation at least, both along and at right angles to the O–H–O bond.

For comparison, the B value applicable to the room-temperature form of KH_2PO_4 (Bacon & Pease, 1953) is $2{\cdot}2\times10^{-16}$ cm.^{2} for vibrations at right angles to the O–H–O bond, corresponding to a r.m.s. amplitude of 0·16 Å. If for KH_2PO_4 we accept the hypothesis that there is a double potential well, with a disordered distribution of hydrogen atoms among the possible pairs of positions, we deduce that this r.m.s. amplitude of thermal displacement of 0·16 Å is applicable in all directions. Let us examine the implications of a double-potential-well picture for the phenylacetate. The O–O bond length is 2·54 Å, so that if the two hydrogen positions are at 1·07 Å from the two oxygen atoms then they will be at points ±0·20 Å from the centre of the O–O bond. This distance from the centre is a good deal smaller than our estimate of 0·29 Å for the r.m.s. amplitude of thermal vibration. In the face of such large vibrations the two discrete positions must lose most of their significance. Finally, returning to our neutron-diffraction projections, we have calculated the contours which we would expect on the two-position model. When allowance is made for the fact that the bond O_2–H_0–O_2' is inclined at about 45° to the plane of the projection, which reduces the effective off-centre distance of the two hydrogen atoms from ±0·20 Å to ±0·14 Å, we find that the half-width of the resultant atom measured along O_2–O_2' would be only 5% greater than for a single isotropic atom; it would be difficult to detect for certain such a small anisotropy as this. We conclude, therefore, that there is no conclusive evidence in favour of either a single- or two-position model and that with the large thermal vibrations any such distinction becomes rather meaningless. It would be of the greatest interest to re-examine this substance at a low temperature in order to determine whether the apparent isotropy of the central hydrogen atom is maintained.

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The Crystal Structure of *N,N′*-Hexamethylenebispropionamide

BY L. H. JENSEN

Department of Anatomy, University of Washington, Seattle, Washington, U.S.A.

SAMUEL KRIMM, ROBERT G. PARRISH* AND DARWIN L. WOOD†

Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan, U.S.A.

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The crystal structure of *N,N′*-hexamethylenebispropionamide has been determined by two-dimensional projections. The structure consists of molecules bound together by N–H ··· O bonds to form molecular ribbons. Relatively weak lateral forces operate to bind each molecular ribbon to its neighbors. Cutting properties of the crystals vary markedly with direction and correspond to the anisotropy of intermolecular forces.

Bond lengths and angles have been determined and are close to expected values, except for the appreciably short C–C bonds within the chain. A possible explanation for the apparent shortening is advanced.

Introduction

The molecular structure of simple compounds containing the peptide (–NHCO–) group is of considerable interest in connection with the structure of proteins. It is also important to know the structure of the peptide group for purposes of infra-red spectroscopic studies from which the location of transition moment directions with respect to the bond directions within the group may be determined. In this connection a study of the crystal structure of *N,N′*-hexamethylenebispropionamide (hereafter referred to as HMBPA) was undertaken.

Experimental

Unit-cell parameters were determined from rotating-crystal and precession photographs using Cu $K\alpha$ radiation:

$$a_0 = 18\cdot60,\ b_0 = 4\cdot96,\ c_0 = 7\cdot49\ \text{Å},\ \beta = 97°\ 15' .$$

The $h0l$ and $0k0$ reflections were extinguished for h odd and k odd respectively. Hence the space group was assumed to be $P2_1/a$. With two molecules per unit cell, $d_{\text{calc.}} = 1\cdot11$ g.cm.$^{-3}$.

Crystals of HMBPA in the form of needles or plates can be grown from chloroform solutions. From solutions using a mixed solvent of carbon tetrachloride and chloroform, well formed equilateral parallelopipeds are obtained.

The intermediate axis of the refractive index ellipsoid is coincident with the needle axis, the direction of

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* Now at the Textile Fibers Department, The E. I. DuPont DeNemours Company, Wilmington, Delaware, U.S.A.

† Now at Bell Telephone Laboratories, Inc., Murray Hill, New Jersey, U.S.A.