An *X*-Ray Study of the *p*-n-Alkoxybenzoic Acids. Part III.[1] Crystal Structure of *p*-Ethoxybenzoic Acid

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The crystal structure of the title compound has been determined from 740 reflections measured by diffractometer. Crystals are monoclinic, $a = 27.148(4)$, $b = 4.013(1)$, $c = 21.787(3)$ Å, $\beta = 135.97(1)$°, space group $C2/c$, $Z = 8$. The structure was solved by a fit of the weighted reciprocal lattice to the calculated Fourier transform for the molecule, and refined by block-diagonal least-squares to R 0.053.

The carboxy-group seems to be disordered by 180° rotation about the C–C bond joining it to the phenyl ring. The structure, including small deviations from overall planarity, is similar to that of *p*-methoxybenzoic acid. Molecules exist as centrosymmetric hydrogen-bonded dimers [O $\cdots$ O 2.600(3) Å] the packing being similar to that of anisic acid, but significantly different from that of higher homologues.

As part of our studies of relationships between the liquid-crystalline properties[2] of the *p*-n-alkoxybenzoic acids and their crystal structures[2–4] we have determined the crystal structure of *p*-ethoxybenzoic acid.

RESULTS AND DISCUSSION

Final atomic positional and thermal parameters are in Table 1; Figure 1 shows a view of the molecule together with the atom numbering scheme. Bond lengths and angles are in Table 2, and details of least-squares mean planes through selected atoms in Table 3.

In its overall molecular geometry, and in its observed thermal behaviour, the molecule closely resembles anisic acid. It occurs in the crystal as hydrogen-bonded centrosymmetric dimers, O $\cdots$ O 2.600(3) Å, packed as near-planar units in a layer-type structure (Figure 2). As with one of the two crystallographically independent molecules found in the asymmetric unit of *p*-n-butoxybenzoic acid,[4] there is evidence suggesting disorder of the carboxy-group in the crystal. Thus, although the two C–O bond lengths in the carboxy-group are significantly different [1.256 and 1.287(4) Å] the difference is less than expected. Sutton[5] gives mean values of 1.233 and 1.312(5) Å for such bonds, and in anisic acid the corresponding distances are 1.233 and 1.290(5) Å, and in the ordered molecule of *p*-n-butoxybenzoic acid 1.236 and 1.293(3) Å. In addition, the hydrogen atom of the carboxy-group is located by a difference synthesis almost

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[1] Part II, R. F. Bryan, *J. Chem. Soc.* (*B*), 1967, 1311.

[2] A. E. Bradfield and B. Jones, *J. Chem. Soc.*, 1929, 2260; B. Jones, *ibid.*, 1935, 1874; G. M. Bennett and B. Jones, *ibid.*, 1939, 420.

[3] Part I, R. F. Bryan, *J. Chem. Soc.*, 1960, 2517.

[4] Part IV, R. F. Bryan and L. Fallon, III, following paper.

[5] *Chem. Soc. Special Publ.*, No. 18, 1965, pp. S20—21.

TABLE 1

Positional parameters, as fractions of the unit cell edges (× 10^4, H × 10^3), and with respect to a space-group centre of symmetry as origin, and anisotropic thermal parameters (× 10^4).* Estimated standard deviations are in parentheses and applicable to the least significant figures quoted

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	206(1)	1 169(8)	937(2)	20(1)	1 055(27)	39(1)	35(4)	20(1)	1(5)
O(2)	833(1)	−1 382(8)	776(2)	24(1)	1 122(28)	31(1)	28(4)	20(1)	−11(5)
O(3)	3 134(1)	−285(7)	4 936(1)	20(1)	735(23)	28(1)	10(4)	15(1)	−7(4)
C(1)	1 389(2)	−323(9)	2 224(2)	19(1)	453(30)	30(2)	−7(5)	18(1)	4(6)
C(2)	2 015(2)	−1 852(10)	2 594(2)	21(1)	488(31)	35(2)	−3(5)	20(1)	−5(6)
C(3)	2 607(2)	−1 917(10)	3 494(2)	19(1)	512(30)	29(2)	−2(5)	17(1)	2(6)
C(4)	2 577(2)	−436(9)	4 043(2)	20(1)	459(30)	26(3)	−13(5)	16(1)	−2(6)
C(5)	1 952(2)	1 057(10)	3 688(2)	22(1)	581(33)	37(2)	−1(5)	21(1)	−8(7)
C(6)	1 363(2)	1 110(10)	2 788(2)	19(1)	599(32)	32(2)	6(5)	18(1)	−2(6)
C(7)	780(2)	−210(10)	1 261(2)	20(1)	589(32)	36(2)	−3(5)	20(1)	−2(6)
C(8)	3 800(2)	−1 745(11)	5 340(2)	19(1)	641(35)	34(2)	13(5)	15(1)	10(7)
C(9)	4 320(2)	−1 136(12)	6 316(3)	23(1)	773(40)	31(2)	5(6)	14(1)	3(8)
H(2)	204	−310	217	4.0 †					
H(3)	309	−312	377	5.0					
H(5)	194	221	413	5.0					
H(6)	87	229	252	4.0					
H(8a)	372	−445	520	7.0					
H(8b)	398	−64	507	7.0					
H(9a)	415	−240	657	9.0					
H(9b)	437	141	644	9.0					
H(9c)	483	−218	664	9.0					
H(0)	−110	−10	25	5.0					

* In the form -$[h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{13} + 2kl\beta_{23}]$.
† Isotropic thermal parameters for hydrogen as B (Å^2).

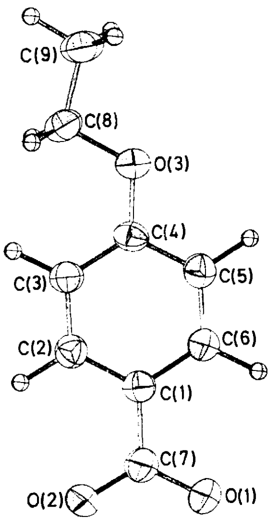

FIGURE 1 View of the molecule as found in the crystal, showing the numbering scheme adopted. Hydrogen atoms are numbered to correspond to the atom of attachment. Thermal ellipsoids for C and O atoms are drawn to the 50% probability level as boundary surface, and hydrogen atoms are represented by spheres of arbitrary radius in calculated positions

midway between the two hydrogen-bonded oxygen atoms with O–H 1.27 and 1.35 Å. These distances are unacceptable in an ordered arrangement, but are compatible with a disorder of the carboxy-group by 180° rotation about C(1)–C(7). This type of disorder has been invoked [6] to explain similar observations in the crystal structure of aspirin [7] and in the oxalate residues in ammonium and potassium tetraoxalates.[8] Hayashi and Unemura [9] describe changes in the solid-phase i.r. spectrum of benzoic acid at low temperatures, and attribute these to the coexistence in the crystal of two distinct equilibrium configurations of the dimers.

TABLE 2

Molecular geometry, with estimated standard deviations in parentheses *

(*a*) Bond lengths (Å)

O(1)–C(7)	1.287(4)	C(3)–C(4)	1.389(4)
O(2)–C(7)	1.256(4)	C(4)–C(5)	1.396(4)
C(1)–C(7)	1.467(4)	C(5)–C(6)	1.377(4)
C(1)–C(2)	1.395(4)	C(4)–O(3)	1.358(3)
C(1)–C(6)	1.401(4)	C(8)–O(3)	1.450(4)
C(2)–C(3)	1.377(4)	C(8)–C(9)	1.502(5)

(*b*) Bond angles (deg.)

O(1)–C(7)–O(2)	121.9(3)	C(2)–C(3)–C(4)	119.1(3)
O(1)–C(7)–C(1)	118.1(3)	C(3)–C(4)–C(5)	120.4(3)
O(2)–C(7)–C(1)	120.0(3)	C(3)–C(4)–O(3)	124.0(3)
C(7)–C(1)–C(2)	119.4(3)	C(4)–C(5)–C(6)	120.0(3)
C(7)–C(1)–C(6)	121.8(3)	C(4)–O(3)–C(8)	118.0(3)
C(1)–C(2)–C(3)	121.4(3)	C(5)–C(4)–O(3)	115.6(3)
C(1)–C(6)–C(5)	120.3(3)	O(3)–C(8)–C(9)	106.6(3)
C(2)–C(1)–C(6)	118.7(3)		

* Estimated standard deviations include allowance for the effects of the cell parameter errors and correlations between the parameters of an individual atom. Bond lengths are uncorrected for the effects of thermal motion.

Apart from the anomalies in the geometry of the carboxy-group, the molecular dimensions found are in agreement with corresponding values for anisic acid and *p*-n-butoxybenzoic acid (see following paper for detailed comparisons). The bond angles at C(4) show the influence of steric repulsions involving H(3) and the methylene hydrogen atoms of C(8) with H · · · H 2.25 and 2.30 Å. While the molecule as a whole is closely

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[6] L. Manojlovic and J. C. Speakman, *J. Chem. Soc.* (*A*), 1967, 971.

[7] P. J. Wheatley, *J. Chem. Soc.*, 1964, 6036.

[8] M. Currie, J. C. Speakman, and N. A. Curry, *J. Chem. Soc.* (*A*), 1967, 1862.

[9] S. Hayashi and J. Unemura, *J. Chem. Phys.*, 1974, **60**, 2630.

planar (mean and maximum deviations from the twelve-atom least-squares mean plane 0.025 and 0.06 Å), a significant pattern of individual interrelated planar units is found which shows the molecule to be significantly non-planar. The phenyl ring is rigorously planar, but C(7) and O(3) are displaced to the same side of this plane by 0.06 and 0.04 Å. The rigorous plane through the four-atom carboxy-group includes the origin and makes an angle of 3.8° with the phenyl plane. As with the other acids [1-4] this is an inclination of two planes sharing a common point, C(1), and not a rotation about a common axis, C(1)–C(7). The three-atom plane O(3), C(8), C(9) is inclined at 3° to the ring plane and at 6.4° to that of the carboxy-group. As with the other acids, these distortions from planarity are attributed to steric interactions between the carboxy- and alkyl groups of neighbouring molecules.

TABLE 3

Equations of selected least-squares mean planes in the form $aX + bY + cZ = d$, where X, Y, and Z are in Å with respect to a Cartesian axial system having its origin coincident with the space-group origin and with $X = x + z\cos\beta$, $Y = y$, and $Z = z\sin\beta$

Plane	a	b	c	d
(1) Carboxy-group:	−0.4638	−0.8859	0.0041	−0.0006
(2) Alkoxy-group:	−0.4862	−0.8676	0.1047	0.5045
(3) Phenyl ring:	−0.4910	−0.8695	0.0535	0.1608

Deviations (Å) from plane (3), C(1)—(6): mean 0.005, max. 0.009, O(1) −0.05, O(2) −0.13, C(7) −0.06, O(3) −0.04, C(8) −0.08, C(9) −0.15

Molecular Packing.—The crystal packing is similar to anisic acid.[1] Both have layered structures with one short (*ca.* 4 Å) unit-cell axis. The perpendicular separation between phenyl rings along this axis is *ca.* 3.4 Å with inter-ring C · · · C contacts of 3.5—3.65 Å, and implies strong aromatic-aromatic interactions. By contrast, the lateral packing of molecules in the *ac* plane is fairly loose with H · · · H contacts > 2.6 Å, and with the closest intermolecular contact involving O(3) and H(5) of adjacent molecules (O · · · H 2.50 Å). However, as the high m.p.s of this acid (195 °C) and of anisic acid (184°) indicate, the packing arrangement is tighter in these two than in the higher homologues which have substantially lower m.p.s. Bennett and Jones [2] associated the failure of the two lowest members of the series to show liquid-crystalline behaviour with their high

TABLE 4

Shorter intermolecular contacts (Å)

$C(1) \cdots C(6^{I})$ $C(1^{II}) \cdots C(6)$	3.67	$H(6) \cdots H(9c^{IV})$ $H(6^{V}) \cdots H(9c)$	2.78
$C(2) \cdots C(1^{I})$ $C(2^{II}) \cdots C(1)$	3.62	$H(5) \cdots O(3^{VI})$ $H(5^{VI}) \cdots O(3)$	2.50
$C(3) \cdots C(4^{I})$ $C(3^{II}) \cdots C(4)$	3.64	$H(5) \cdots H(5^{VI})$ $H(5^{VI}) \cdots H(5)$	2.67
$C(5) \cdots C(3^{I})$ $C(5^{II}) \cdots C(3)$	3.52	$O(2) \cdots H(3^{VII})$ $O(2^{VIII}) \cdots H(3)$	2.66
$C(5) \cdots C(4^{I})$ $C(5^{II}) \cdots C(4)$	3.64	$H(2) \cdots H(2^{VII})$ $H(2^{VIII}) \cdots H(2)$	2.69
$C(6) \cdots C(2^{I})$ $C(6^{II}) \cdots C(2)$	3.52	$H(2) \cdots H(3^{VII})$ $H(2^{VIII}) \cdots H(3)$	2.70
$O(1) \cdots O(2)$ $O(1^{III}) \cdots O(2)$	2.60		

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $x, 1 + y, z$	VI $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
II $x, y - 1, z$	VII $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
III $\bar{x}, \bar{y}, \bar{z}$	VIII $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$
IV $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$	
V $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$	

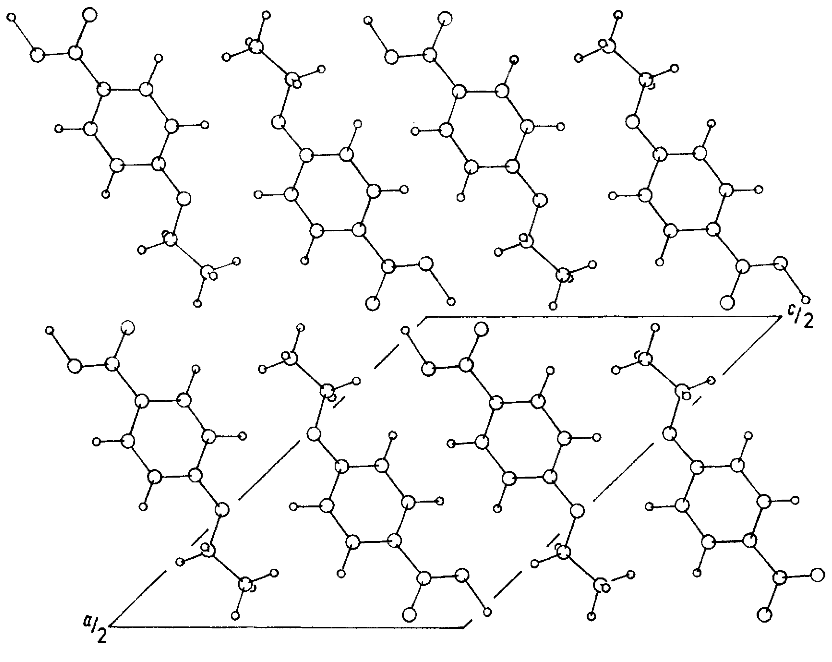

FIGURE 2 The molecular packing in the crystal viewed in projection down *b*. The outline of part of one unit cell has been drawn with the origin at the top left-hand corner of the outlined area

m.p.s, noting that 'a nematic liquid is at once produced when a mixture of the two acids is melted.' With the crystal structures of *p*-methoxy-, *p*-ethoxy-, and *p*-n-butoxybenzoic acids now known, the difference in m.p.s, and in crystal densities which fall progressively from *p*-methoxy to *p*-n-hexyloxybenzoic acid, may be unambiguously attributed to the adoption of layer structures, with strong aromatic–aromatic interactions, by the first two of these but not by the third and, presumably, the other higher homologues. With the identification of phenyl–phenyl interactions as the major contributors to the lattice energy, the suggestion [1] that tight interleaving of the alkyl and carboxy-groups of adjacent molecules arranged head-to-tail was responsible for the high m.p.s of the two lowest acids is seen to be incorrect. The same basic arrangement of these groups is found in all three acids studied. The variable factor is the extent of phenyl–phenyl overlap, which is much diminished in *p*-n-butoxybenzoic acid.

Thermal Analysis.—Root-mean-square amplitudes of vibration of the atoms along the principal axes of the thermal ellipsoids are given in Table 5. The pattern of vibration is similar to that for anisic acid.[1] The largest amplitudes of vibration are associated with the atoms of the carboxy- and the terminal atoms of the alkoxy-group. Each atom of the carboxy-group has its major axis of vibration near perpendicular to the molecular plane, while the major axis of vibration for the atoms of the alkyl group is, in each case, close to the molecular plane. The hydrogen bonding which links the molecules as centrosymmetric dimers thus does not dampen thermal vibration at the carboxy-group, and the molecule clearly does not vibrate as a rigid body. The pattern of vibrational amplitudes suggests an inertial centre close to the centre of mass of the monomeric unit. As with the vibrational pattern in anisic acid, the mutually perpendicular vibrations of carboxy- and terminal alkyl groups probably reflects the packing arrangement of these groups.

TABLE 5

Root-mean-square amplitudes of vibration (Å) of the atoms along the principal axes of the thermal ellipsoids

Atom	O(1)	O(2)	O(3)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)
Axis (1)	0.176	0.181	0.180	0.183	0.169	0.187	0.185	0.170	0.188	0.181	0.179	0.183
(2)	0.217	0.204	0.204	0.207	0.188	0.196	0.190	0.178	0.204	0.195	0.229	0.250
(3)	0.305	0.313	0.252	0.220	0.200	0.204	0.206	0.209	0.221	0.224	0.236	0.261

EXPERIMENTAL

Crystal Data.—$C_9H_{10}O_3$, $M = 166.2$. Monoclinic tabular, $a = 27.148(4)$, $b = 4.013(1)$, $c = 21.787(3)$ Å, $\beta = 135.97(1)°$, $U = 1\,650$ Å^3, D_m (by flotation) $= 1.323(5)$, $Z = 8$, $D_c = 1.338$, $F(000) = 724$. Systematic absences: hkl, $h + k$ odd; $h0l$, l odd; space group $C2/c$ or Cc, the former chosen and shown by the successful analysis to be correct. No molecular symmetry implied. Cu-K_α radiation, $\lambda = 1.5418$ Å, μ(Cu-K_α) $= 8.5$ cm^{-1}; single-crystal diffractometry.

The unit cell differs from that given in Part I in the choice of a axis. The relation between the new and old (primed) cell is given by $h = -h'$, $k = k'$, $l = l + h'$.

Intensity Data.—These were measured from a single crystal $0.35 \times 0.35 \times 0.15$ mm, mounted with a^* parallel to the ϕ-axis of a Picker four-circle diffractometer controlled by an XDS Sigma 2 computer. Scattered intensity significantly above background was measured at 740 of 940 independent reciprocal lattice points surveyed within a single quadrant ($2\theta < 56°$). The θ—2θ scan method was used with scintillation counting, pulse-height analysis, and monochromatic Cu-K_α radiation. Background measurements were taken from a carefully predetermined curve of background intensity as a function of scattering angle. For the separately measured and symmetrically related reflections $0kl$ and $0k\bar{l}$ the mean variation in corresponding structure amplitudes was 0.75%. A similar variation was noted in the structure amplitudes of two reference reflections used to measure the stability of the experimental conditions.

Structure Determination and Refinement.—The structure was originally solved from photographically measured intensities for the $h0l$ reflections, by a fit of the weighted reciprocal lattice for the zone to the calculated Fourier transform for a plane centrosymmetric dimer of the acid.[10] The long molecular axis was found to lie in the plane at $b = 0$, and the tilt of the molecular plane about this axis was found to be *ca.* 30°. Trial co-ordinates for the C and O atoms based on this model and the assumption of an overall isotropic B of 3.0 Å^2 gave R 0.31 for the complete set of three-dimensional data. Least-squares refinement by the block-diagonal approximation and with individual isotropic thermal parameters gave R 0.16; with anisotropic thermal parameters assumed R was 0.10 at convergence. All hydrogen atoms in the molecule, except for that associated with the carboxy-group, were clearly indicated in a three-dimensional difference electron-density map calculated at this stage, and were included in the refinement with fixed contributions based on geometrically assigned positions (C–H 1.08 Å) and realistic isotropic B values. The refinement was continued and at convergence gave R 0.056 with a Hughes type weighting scheme.[11] A $(\rho_o - \rho_c)$ map calculated in the plane of the carboxy-group now located the carboxy-hydrogen atom almost midway between the two hydrogen-bonded oxygen atoms. Inclusion of the hydrogen atom, in this basically improbable position, in a structure-factor calculation reduced R to 0.053, an apparently significant improvement.[12]

Atomic scattering factors for the neutral atoms were taken from ref. 13. Figure 1 was drawn by use of ORTEP

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[10] R. F. Bryan, 'The Crystal Structures of Some Organic Molecules,' Thesis, University of Glasgow, 1957

[11] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

[12] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

[13] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040; R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

II.[14] All calculations were carried out with local programs for the XDS Sigma 2 computer. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21310 (6 pp., 1 microfiche).*

We thank Dr. J. C. Speakman for drawing our attention to ref. 9.

[4/2471 *Received*, 26*th November*, 1974]

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

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