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2,3-Dimethoxybenzoic Acid. A Redetermination

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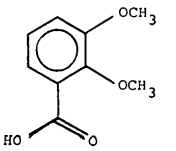
Abstract. $C_9H_{10}O_4$, monoclinic, $P2_1/n$, $a = 15{\cdot}538$ (5), $b = 6{\cdot}922$ (3), $c = 8{\cdot}196$ (3) Å, $\beta = 97{\cdot}96$ (2)° ($\lambda = 1{\cdot}5418$ Å), $U = 873{\cdot}0$ Å^3, $M_r = 182{\cdot}17$, $Z = 4$, $D_x = 1{\cdot}386$, $D_m = 1{\cdot}387$ (4) g cm^{-3} (flotation in aqueous KI), $F(000) = 384$, μ(Cu $K\alpha$) = 9·4 cm^{-1}. The structure was solved, independently of earlier work, by the multisolution tangent-formula method. Refinement by least squares gave $R = 0{\cdot}030$ for 1034 independent significant reflections. The molecules are present in the crystal as non-planar centrosymmetric hydrogen-bonded dimers [O—H···O 2·631 (2) Å]. The plane of the carboxy group is inclined at 36·3° to that of the phenyl ring. The plane of the 3-methoxy group makes an angle of 2·3° with that of the phenyl ring, but the plane of the 2-methoxy group is inclined to the phenyl plane at an angle of 74·2°, with O(1) on the same side of the ring as C(8).

Introduction. Swaminathan, Sarangapani & Lessinger (1977) (SSL) have reported the structure of the title compound (I) as determined from visually estimated photographic intensity data. We are interested in accurate information on packing modes of alkoxy-substituted benzoic acids (Bryan & Hartley, 1980) and felt it worthwhile to redetermine this structure using more accurate diffractometer intensity data.



(I)

A suitable crystal was obtained by recrystallization of a commercial sample of the acid (Aldrich Chemical Co.) from 95% ethanol. The unit-cell dimensions were derived from a least-squares fit to the observed diffractometer values of $\pm 2\theta$ for 24 strong general reflections. Systematic absences in $h0l$ with $h + l$ odd, and in $0k0$ with k odd uniquely define the space group as $P2_1/n$, a non-standard setting of $P2_1/c$, the space group identified by SSL. The cell given by SSL is

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related to that given here by: $\mathbf{a}_S^* = \mathbf{a}_B^* - \mathbf{c}_B^*$; $\mathbf{b}_S^* = \mathbf{b}_B^*$; $\mathbf{c}_S^* = \mathbf{a}_B^*$, where the subscripts S and B denote the original and this work, respectively. Our unit-cell volume is considerably smaller than that reported by SSL (918·3 Å^3), and our measured density is considerably higher than that which they report (1·29 g cm^{-3}).

Intensity measurements were made from a single-crystal prism 0·25 mm on each side. A Picker diffractometer was used with Cu $K\alpha$ radiation (graphite monochromator) in the $\theta/2\theta$ scan mode with a scan range of 3° in 2θ and a scan speed of 2° min^{-1}. The reflections in a single quadrant of reciprocal space ($2\theta < 120°$) were measured and intensity significantly above background was measured by scintillation counting with pulse-height analysis at 1034 of the 1227 independent locations accessible to the instrument [84·3%, $I > 3\sigma(I)$]. This may be compared to the 1260 observable reflections measured by SSL. No absorption corrections were made.

The structure was solved by routine application of the program *MULTAN* in its 1974 version (Germain, Main & Woolfson, 1971). H atoms were located from general-plane difference electron density maps. The carboxy proton was found as a single peak midway between the hydrogen-bonded O atoms. Block-diagonal least-squares refinement of all parameters, minimizing the function $\sum w(|F_o| - |F_c|)^2$, gave at convergence $R = 0{\cdot}030$ and $R_w = 0{\cdot}035$ for the 1034 data used.†

The maximum shift-to-error ratio in the final cycle of refinement was 0·21 and the average ratio was 0·04. Anisotropic thermal parameters were used for O and C, and individual isotropic B values were refined for H. The scattering functions used were those of Cromer & Waber (1974) for O and C, and of Stewart, Davidson & Simpson (1965) for H. A final difference electron density map showed the only structurally significant density to be concentrated around the midpoints of the various bonds.

Discussion. Final atomic positional parameters and equivalent isotropic B values are given in Table 1, and bond lengths and bond angles (not involving H) are given in Fig. 1. Given the lower accuracy of the original determination, there are no significant differences in molecular geometry to be noted, although our analysis is, of course, considerably more accurate. Our bond-length and bond-angle e.s.d.'s of 0·002 Å and 0·15° may be compared to those of SSL, 0·01 Å and 1·1 – 1·9°.

The two carboxy C—O bond lengths are equivalent, within the limits of error, indicating a disorder of this group of a type common in aromatic carboxylic acids.

† Lists of structure factors, anisotropic thermal parameters and details of least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36468 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* (×10^4, *for* H ×10^3) *and isotropic B values* (Å^2)

Hydrogen atoms have been labelled to correspond to the atom of attachment. For non-hydrogen atoms $B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}\,\mathbf{a}_i\cdot\mathbf{a}_j$.

	x	y	z	B_{eq}/B
O(1)	66 (1)	8756 (2)	1839 (2)	4·27 (6)
O(2)	785 (1)	8342 (2)	−296 (2)	4·26 (7)
O(3)	1229 (1)	7563 (2)	4569 (1)	3·48 (6)
O(4)	1856 (1)	4266 (2)	5940 (2)	4·50 (7)
C(1)	1048 (1)	6114 (2)	1887 (2)	2·77 (8)
C(2)	1283 (1)	5971 (2)	3582 (2)	2·80 (8)
C(3)	1646 (1)	4252 (2)	4268 (2)	3·21 (8)
C(4)	1771 (1)	2716 (3)	3257 (2)	3·78 (9)
C(5)	1554 (1)	2882 (3)	1561 (2)	3·79 (9)
C(6)	1200 (1)	4567 (3)	873 (2)	3·47 (9)
C(7)	616 (1)	7858 (2)	1111 (2)	3·02 (8)
C(8)	539 (1)	7497 (3)	5562 (3)	4·79 (9)
C(9)	2186 (1)	2525 (3)	6736 (3)	5·04 (10)
H(O)	−32 (2)	1026 (5)	99 (3)	15·7 (11)
H(4)	200 (1)	154 (2)	370 (2)	4·4 (4)
H(5)	167 (1)	179 (3)	83 (2)	5·2 (5)
H(6)	105 (1)	474 (2)	−34 (2)	4·8 (4)
H(8*a*)	−4 (2)	746 (3)	484 (3)	8·1 (6)
H(8*b*)	55 (2)	879 (3)	609 (3)	9·6 (7)
H(8*c*)	61 (2)	640 (3)	637 (3)	8·4 (8)
H(9*a*)	176 (1)	146 (3)	645 (2)	6·8 (5)
H(9*b*)	225 (1)	285 (3)	788 (2)	7·7 (6)
H(9*c*)	272 (1)	210 (3)	633 (2)	7·1 (5)

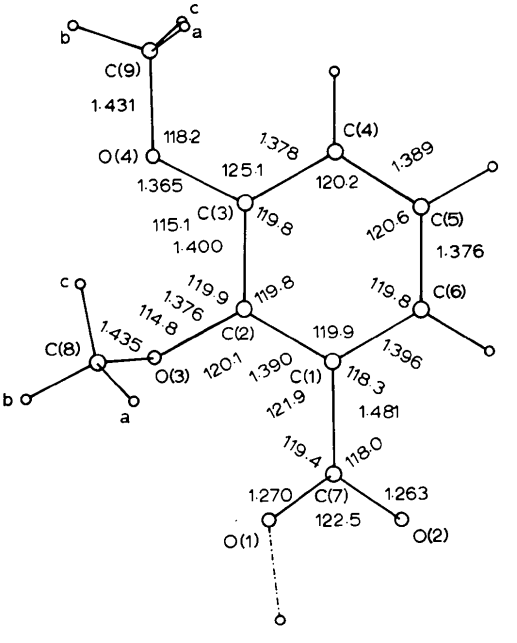

Fig. 1. Projection of the molecule onto the plane of the phenyl ring showing bond lengths (Å) and bond angles (°). E.s.d.'s are 0·002 Å and 0·15°.

The bond C(3)—O(4), which forms part of the methoxy group almost coplanar with the ring, is significantly shorter (3·5σ) than the bond C(2)—O(3) where the plane of the methoxy group is inclined to the plane of the phenyl ring by 74·2°. The tilt of the carboxy plane

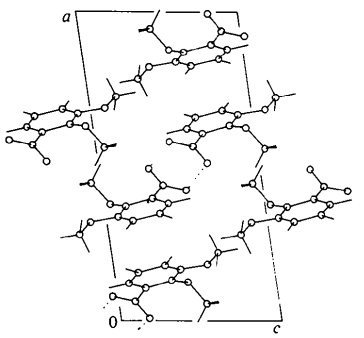

Fig. 2. Molecular packing seen in *b*-axis projection.

with respect to the ring, 36·3°, is dictated by the limiting intramolecular contact O(1)···O(3), 2·798 Å. C(8) is on the same side of the phenyl ring as O(1), and the contact O(1)···C(8), 3·160 Å, is also limiting.

A view of the molecular packing, in *b*-axis projection, is shown in Fig. 2. The non-planar centrosymmetric hydrogen-bonded dimers (O—H···O, 2·631 Å) form parallel stacks extended along **b**. The sterically least-bulky carboxy cores are surrounded by the sterically most-bulky methyl groups of neighbors. All interdimer contacts are of normal van der Waals type.

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2,6-Dimethoxybenzoic Acid

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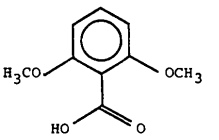
Abstract. $C_9H_{10}O_4$, orthorhombic, $P2_12_12_1$, a = 7·122 (3), b = 8·927 (6), c = 13·788 (8) Å (λ = 1·5418 Å), U = 876·6 Å^3, M_r = 182·17, Z = 4, D_x = 1·381, D_m = 1·365 (15) g cm^{-3} (flotation in aqueous KI), $F(000)$ = 384, μ(Cu $K\alpha$) = 9·4 cm^{-1}. The structure was solved by the multisolution tangent-formula method. Refinement by least squares gave R = 0·035 for 708 independent significant reflections. The molecules are linked, in the crystal, in infinite interlocking hydrogen-bonded ribbons extending parallel to **b** (O—H···O 2·673 Å) by the action of the corresponding space-group screw axis. The plane of the carboxy group is inclined to that of the phenyl ring by 56·2°. The C(2) and C(6) methoxy groups make angles of 21·6 and 2·8°, respectively, with the phenyl plane.

Introduction. We are interested in the influence upon molecular packing of differences in steric bulk between the aryl and alkoxy components of alkoxy-substituted benzoic acids (Bryan & Hartley, 1980), and have carried out a full three-dimensional structure determination of the title compound.



Swaminathan, Vimala & Lotter (1976) (SVL) have reported the solution of the *b*-axis projection of this compound, but the refinement was carried only to R = 0·15 and no atomic coordinates were given. This determination was carried out independently of the earlier work.

Crystals suitable for X-ray study were obtained by recrystallization of a commercial sample (Aldrich Chemical Co.) from 95% ethanol.

The space group was uniquely determined from the absence of all axial reflections of odd order on 25° precession photographs taken about each axis with Mo $K\alpha$ radiation. Our unit-cell dimensions are all smaller (0·5–1·3%) than those reported by SVL, and we have

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