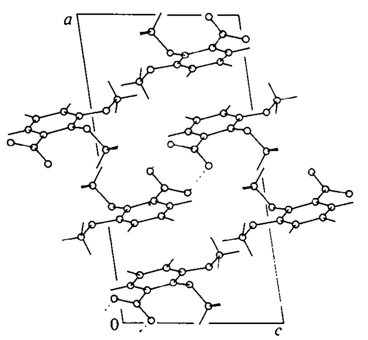

Fig. 2. Molecular packing seen in *b*-axis projection.

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.

This work was supported by a grant (DMR-78-19884) from the National Science Foundation, USA.

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2,6-Dimethoxybenzoic Acid

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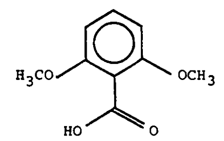
Abstract. $C_9H_{10}O_4$, orthorhombic, $P2_12_12_1$, a = 7·122 (3), b = 8·927 (6), c = 13·788 (8) Å (λ = 1·5418 Å), U = 876·6 Å^3, M_r = 182·17, Z = 4, D_x = 1·381, D_m = 1·365 (15) g cm^{-3} (flotation in aqueous KI), F(000) = 384, μ(Cu $K\alpha$) = 9·4 cm^{-1}. The structure was solved by the multisolution 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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chosen the longest axis to be *c* rather than *b*. The molar volume, 219·2 Å^3, may be compared with the 218·3 Å^3 found (Bryan & White, 1982) for the isomeric 2,3-dimethoxybenzoic acid.

Intensity measurements were made from a single-crystal needle 0·7 × 0·25 × 0·15 mm. A Picker diffractometer was used, with Cu $K\alpha$ radiation (graphite monochromator) in the $\theta/2\theta$ mode with a scan range of 4° and a scan speed of 2° min^{-1}. The reflections in two octants of reciprocal space ($2\theta <$ 120°) were measured by scintillation counting with pulse-height analysis, and the results for the two averaged. Intensity significantly above background was found at 708 of the 775 independent locations accessible to the instrument [91·4%, $I > 3\sigma(I)$].

The structure was solved by routine application of the program *MULTAN* in its 1974 version (Germain, Main & Woolfson, 1971). H atoms were found from general-plane difference electron density maps. Block-diagonal least-squares refinement of all parameters, minimizing the function $\sum w(|F_o| - |F_c|)^2$, gave, at convergence, $R = 0·035$ and $R_w = 0·033$ for the 708 data used.*

The maximum shift-to-error ratio in the final cycle of refinement was 0·25 and the average ratio was 0·11. Anisotropic thermal parameters were used for O and C, and individual isotropic *B* values were refined for H. The scattering factors 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 largest remaining density to be concentrated around the centers of the various bonds.

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1. Bond lengths and bond angles are given in Fig. 1, which also shows the numbering scheme adopted. The presence of the methoxy substituents at C(2) and C(6) forces the carboxy group out of coplanarity with the plane of the phenyl ring, with which it makes an angle of 56·2°. This angle may be compared to the 36·3° tilt present in the isomeric 2,3-dimethoxybenzoic acid (Bryan & White, 1982). The increase in tilt angle results from the characteristic deformation of the exocyclic valence angles at C(2) and C(6) caused by interactions of the methyl groups with H(3) and H(5). This deformation is absent at C(2) in the 2,3 isomer. The deformation pushes the two ether O atoms closer to the C(1)—C(7) axis, and the limiting intramolecular contacts O(1)···O(4) (2·861 Å) and O(2)···O(3) (2·853 Å) require an increased tilt of the carboxy group.

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 $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	B_{eq}/B
O(1)	501 (3)	−528 (2)	2845 (1)	3·30 (10)
O(2)	482 (3)	1906 (3)	3016 (2)	3·68 (12)
O(3)	−3463 (3)	2086 (3)	2674 (1)	3·27 (9)
O(4)	1002 (3)	−385 (3)	788 (2)	3·82 (11)
C(1)	−1291 (4)	850 (3)	1692 (2)	2·13 (13)
C(2)	−3022 (5)	1572 (4)	1770 (2)	2·90 (16)
C(3)	−4229 (5)	1663 (4)	973 (2)	3·69 (18)
C(4)	−3661 (6)	1040 (4)	113 (2)	4·26 (19)
C(5)	−1945 (5)	325 (4)	11 (2)	3·76 (19)
C(6)	−755 (5)	231 (3)	802 (2)	2·83 (16)
C(7)	−54 (5)	689 (4)	2553 (2)	2·61 (14)
C(8)	−4868 (6)	3226 (5)	2733 (3)	5·03 (21)
C(9)	1661 (6)	−1054 (5)	−96 (3)	5·60 (22)
H(O2)	−18 (6)	282 (4)	286 (2)	9·5 (12)
H(3)	−550 (6)	208 (4)	109 (2)	5·5 (8)
H(4)	−459 (4)	130 (3)	−47 (2)	4·9 (8)
H(5)	−140 (5)	−18 (3)	−64 (2)	6·3 (9)
H(8*a*)	−632 (5)	270 (3)	256 (2)	6·2 (9)
H(8*b*)	−469 (4)	372 (4)	222 (2)	6·1 (9)
H(8*c*)	−505 (4)	335 (4)	336 (2)	5·9 (9)
H(9*a*)	299 (5)	−147 (4)	7 (3)	10·1 (13)
H(9*b*)	137 (6)	−32 (3)	−61 (3)	7·3 (10)
H(9*c*)	75 (6)	−200 (5)	−25 (3)	11·2 (14)

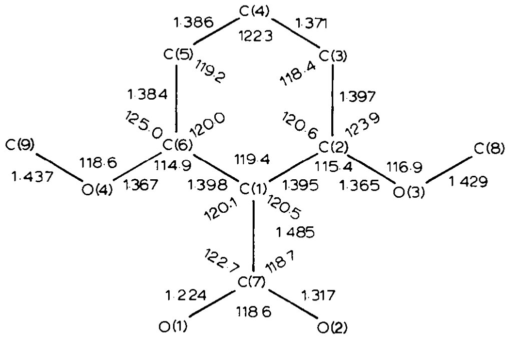

Fig. 1. Bond lengths (Å) and bond angles (°). E.s.d.'s are 0·004 Å and 0·3°.

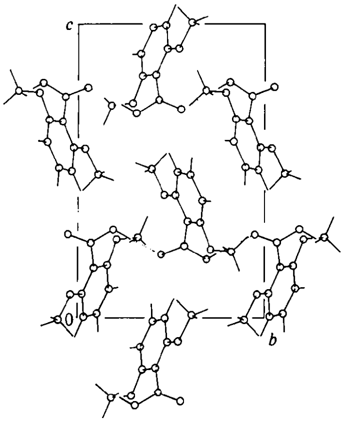

Fig. 2. Molecular packing seen in *a*-axis projection. Hydrogen bonds are indicated by dotted lines.

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* Lists of structure factors, anisotropic thermal parameters and information on selected least-squares mean planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36469 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The plane of the C(2) methoxy group is inclined at 24·4° to the plane of the phenyl ring, presumably an effect of crystal packing forces, whereas the C(6) methoxy group makes an angle of only 2·8° with the phenyl plane.

The molecules have an unusual hydrogen-bonding scheme, being linked through the carboxy groups into infinite, interlocking ribbons extending parallel to **b**. A view of the molecular packing, seen in *a*-axis projection, is given in Fig. 2.

This work was supported by a grant (DMR-78-19884) from the National Science Foundation, USA.

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trans–syn Cyclobutane-Type Photodimers of 1,3,3-Trimethyl-2,4(1*H*,3*H*)-pyridinedione and 1,3,3,6-Tetramethyl-2,4(1*H*,3*H*)-pyridinedione

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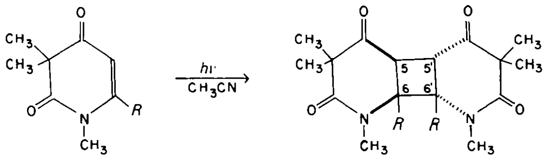
Abstract. (I) $C_{16}H_{22}N_2O_4$, monoclinic, $P2_1/c$, a = 6·370 (2), b = 13·989 (9), c = 17·598 (6) Å, β = 100·56 (2)°, Z = 4, M_r = 306·4, V = 1541·6 Å^3, D_x = 1·320 g cm^{-3}, R = 5·9% for 1901 observed reflections. (II) $C_{18}H_{26}N_2O_4$, monoclinic, $P2_1/a$, a = 12·245 (4), b = 11·929 (3), c = 12·467 (3) Å, β = 108·92 (2)°, Z = 4, M_r = 334·4, V = 1722·7 Å^3, D_x = 1·289 g cm^{-3}, R = 7·4% for 2180 observed reflections. Methylated analogues of uracil in which N(3) has been replaced by a tetrahedral C atom undergo photodimerization to form cyclobutane-type dimers. Unlike the pyrimidines, the most prevalent irradiation products of these pyridine analogues are the *trans–syn* dimers. Bond lengths and angles are very similar in the two dimers, except for the C(6)—C(6′) bond which is considerably longer in the dimer with methyl substituents on C(6) and C(6′).

Introduction. Irradiation of pyrimidines can produce cyclobutane-type dimers, formed by opening of the double bond at the C(5)—C(6) position. Four different types of dimers can be formed and each type has been characterized by crystal-structure analyses (Karle, 1976, and references therein). The *cis–syn* dimer is the most prevalent product both from irradiated DNA and from the irradiation of frozen thymine or uracil solutions. The dimer of methyl orotate had been the only example of a crystal-structure analysis of a *trans–syn* dimer (Birnbaum, 1972). Methyl orotate is resistant to dimerization in the frozen state but dimerizes efficiently in solution (Fisher & Johns, 1976).

In the present paper it is shown that the principal irradiation products of methylated analogues of uracil, in which N(3) has been replaced by a tetrahedral C atom, are the *trans–syn* cyclobutane-type dimers (compounds I and II):



(I) R = H m.p. 488–489 K
(II) R = CH_3 m.p. 528 K

Crystals of dimers (I) and (II) were supplied by Y. Kanaoka, Hokkaido University (Kanaoka, Hasebe & Sato, 1980; Hasebe, 1980).

Diffraction data were collected from clear, colorless prisms of (I) and (II), grown from ethyl acetate, on a Nicolet P3F diffractometer equipped with a graphite monochromator. The $\theta/2\theta$ scanning mode was used