

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71013 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1004]

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Structure of 1,4-Diethyl-3,5-dimethoxy-1,4-dihydrobenzoic Acid†

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Abstract

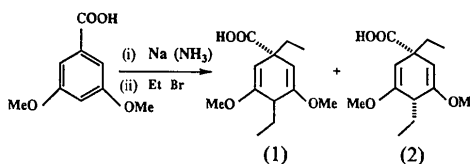
This X-ray diffraction study establishes the molecular structure of the major isomer resulting from the Birch reduction and dialkylation (with EtBr) of 3,5-dimethoxybenzoic acid, according to the procedure

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of Guzmán, Castanedo & Maldonado [*Synth. Commun.* (1991), **21**, 1001–1012]. The six-membered ring adopts a conformation intermediate between the envelope ¹E and the half-chair ¹H₆ conformations, defined by $\theta = 59.2(9)^\circ$, $\varphi = -12(9)^\circ$ and $Q = 0.024(3) \text{ \AA}$ [Cremer & Pople (1975). *J. Am. Chem. Soc.* **97**, 1354–1358; Boeyens (1978). *J. Crystallogr. Spectrosc. Res.* **8**, 317–320].

Comment

The Birch reduction and dialkylation reaction of aromatic carboxylic acids is a new reaction of current interest (Guzmán, Castanedo & Maldonado, 1991). The reaction, in its original version (excess of Na and alkyl halide in liquid NH₃) is poorly diastereoselective and thus from 3,5-dimethoxybenzoic acid and ethyl bromide, a 3:2 mixture of diastereoisomeric 1,4-reduced and diethylated acids, (1) and (2), is obtained in high yield, from which the major isomer can be isolated by fractional crystallization.



On the other hand, metallation of 1-ethyl-3,5-dimethoxy-1,4-dihydrobenzoic acid with ⁿBuLi in tetrahydrofuran, followed by ethylation (EtBr) is a completely diastereoselective alkylation process, affording as the only product a single isomer identified by this structure determination as (1), the major isomer of the above reaction.

The methoxy groups at C(3) and C(5) are nearly coplanar with the six-membered ring [dihedral angles of $-2.7(3)$ and $2.7(3)^\circ$, respectively], while the ethyl groups at C(1) and C(4) are *cis* to each other and perpendicular to the six-membered ring

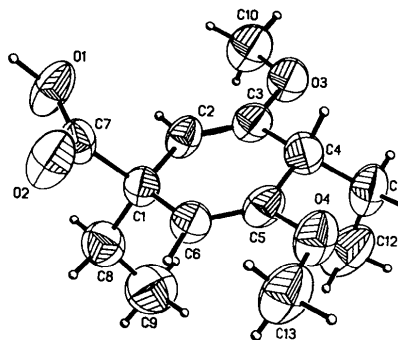


Fig. 1. The molecular structure of the title compound with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

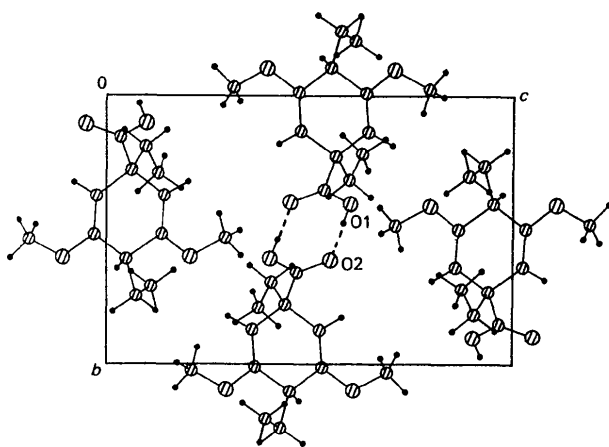


Fig. 2. Packing arrangement of the molecules as viewed along *a*. The dashed lines indicate hydrogen bonds.

[dihedral angles are 90.1 (2) and 90.5 (2)°, respectively]. In the crystal, the molecules of the title compound form centrosymmetric hydrogen-bonded dimers with O(1)⋯O(2) distance of 2.606 (5) Å and O(1)—H⋯O(2) angle of 175 (3)°. Two C—H⋯O intermolecular contacts are present: C(13)⋯O(1) (0.5 + *x*, −0.5 − *y*, 0.5 + *z*) 3.210 (5) Å and C(10)⋯O(2) (−0.5 + *x*, −0.5 − *y*, −0.5 + *z*) 3.203 (5) Å.

Experimental

Crystal data

$C_{13}H_{20}O_4$	$D_x = 1.18 \text{ Mg m}^{-3}$
$M_r = 240.3$	Cu $K\alpha$ radiation
Monoclinic	$\lambda = 1.5418 \text{ \AA}$
$P2_1/n$	Cell parameters from 25 reflections
$a = 10.701 (5) \text{ \AA}$	$\theta = 9-27.1^\circ$
$b = 8.999 (4) \text{ \AA}$	$\mu = 0.676 \text{ mm}^{-1}$
$c = 14.970 (7) \text{ \AA}$	$T = 293 \text{ K}$
$\beta = 110.56 (4)^\circ$	$0.38 \times 0.24 \times 0.14 \text{ mm}$
$V = 1349 (1) \text{ \AA}^3$	Colourless
$Z = 4$	

Data collection

Nicolet P3/F diffractometer	$\theta_{\max} = 55.0^\circ$
$2\theta/\theta$ scans	$h = -10 \rightarrow 10$
Absorption correction: none	$k = 0 \rightarrow 9$
	$l = 0 \rightarrow 15$
2094 measured reflections	2 standard reflections
1954 independent reflections	monitored every 50 reflections
1448 observed reflections	intensity variation: 3%
$[I > 2.5\sigma(I)]$	
$R_{\text{int}} = 0.038$ (one equivalent only)	

Refinement

Refinement on F	$w = [\sigma^2(F_o) + 0.002(F_o)^2]^{-1}$
Final $R = 0.065$	$(\Delta/\sigma)_{\max} = 0.025$
$wR = 0.095$	$\Delta\rho_{\max} = 0.28 \text{ e \AA}^{-3}$
$S = 1.32$	$\Delta\rho_{\min} = -0.31 \text{ e \AA}^{-3}$

1448 reflections
158 parameters
Only coordinates of H atoms refined

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O(1)	−0.0032 (3)	−0.3973 (3)	0.4013 (2)	0.087 (1)
O(2)	0.1354 (2)	−0.3921 (3)	0.5493 (2)	0.083 (1)
O(3)	−0.0241 (2)	0.0950 (2)	0.2943 (2)	0.073 (1)
O(4)	0.2855 (2)	0.1002 (2)	0.6073 (1)	0.071 (1)
C(1)	0.1766 (3)	−0.2245 (3)	0.4379 (2)	0.052 (2)
C(2)	0.0830 (3)	−0.1338 (3)	0.3580 (2)	0.055 (1)
C(3)	0.0620 (3)	0.0099 (3)	0.3644 (2)	0.055 (1)
C(4)	0.1298 (3)	0.1036 (3)	0.4506 (2)	0.059 (1)
C(5)	0.2260 (3)	0.0122 (3)	0.5297 (2)	0.053 (1)
C(6)	0.2477 (3)	−0.1306 (3)	0.5236 (2)	0.055 (1)
C(7)	0.0970 (3)	−0.3454 (3)	0.4657 (2)	0.053 (1)
C(8)	0.2771 (3)	−0.3092 (4)	0.4037 (2)	0.073 (1)
C(9)	0.3667 (4)	−0.2130 (5)	0.3729 (3)	0.099 (2)
C(10)	−0.1020 (4)	0.0222 (4)	0.2090 (3)	0.086 (2)
C(11)	0.1976 (3)	0.2418 (4)	0.4271 (2)	0.078 (1)
C(12)	0.3079 (4)	0.2055 (5)	0.3908 (3)	0.102 (2)
C(13)	0.3740 (4)	0.0305 (4)	0.6899 (2)	0.081 (2)

Table 2. Geometric parameters (\AA , $^\circ$)

O(1)—C(7)	1.254 (4)	O(2)—C(7)	1.244 (3)
O(3)—C(3)	1.363 (3)	O(3)—C(10)	1.416 (4)
O(4)—C(5)	1.365 (3)	O(4)—C(13)	1.413 (4)
C(1)—C(2)	1.502 (3)	C(1)—C(6)	1.500 (4)
C(1)—C(7)	1.526 (4)	C(1)—C(8)	1.544 (5)
C(2)—C(3)	1.320 (4)	C(3)—C(4)	1.498 (4)
C(4)—C(5)	1.510 (4)	C(4)—C(11)	1.541 (5)
C(5)—C(6)	1.313 (4)	C(8)—C(9)	1.480 (6)
C(11)—C(12)	1.499 (6)		
C(3)—O(3)—C(10)	117.3 (2)	C(5)—O(4)—C(13)	117.2 (2)
C(2)—C(1)—C(6)	111.8 (2)	C(2)—C(1)—C(7)	108.9 (2)
C(6)—C(1)—C(7)	109.4 (2)	C(2)—C(1)—C(8)	110.5 (3)
C(6)—C(1)—C(8)	111.0 (2)	C(7)—C(1)—C(8)	105.1 (2)
C(1)—C(2)—C(3)	123.8 (2)	O(3)—C(3)—C(2)	125.4 (2)
O(3)—C(3)—C(4)	109.8 (2)	C(2)—C(3)—C(4)	124.7 (2)
C(3)—C(4)—C(5)	111.1 (2)	C(3)—C(4)—C(11)	112.4 (3)
C(5)—C(4)—C(11)	111.8 (2)	O(4)—C(5)—C(4)	109.7 (2)
O(4)—C(5)—C(6)	125.8 (2)	C(4)—C(5)—C(6)	124.5 (2)
C(1)—C(6)—C(5)	124.1 (2)	O(1)—C(7)—O(2)	122.6 (3)
O(1)—C(7)—C(1)	117.6 (3)	O(2)—C(7)—C(1)	119.7 (2)
C(1)—C(8)—C(9)	114.7 (3)	C(4)—C(11)—C(12)	113.7 (3)

The structure was solved by direct methods (*SHELXTL*; Sheldrick, 1985). The H atoms of the CH, CH₂ and CH₃ groups were placed in calculated positions. Non-H atoms were refined anisotropically. The H atoms were assigned a fixed isotropic displacement parameter of 0.060 Å² and the coordinates of the H atom bonded to O were refined.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55986 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1030]

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The Asymmetric Michael Process Involving Chiral Imines: Structure of (±)-*p*-Nitrobenzyl 2-(2,2-Dimethyl-1-phenylpropylamino)-1-cyclopentene-1-carboxylate

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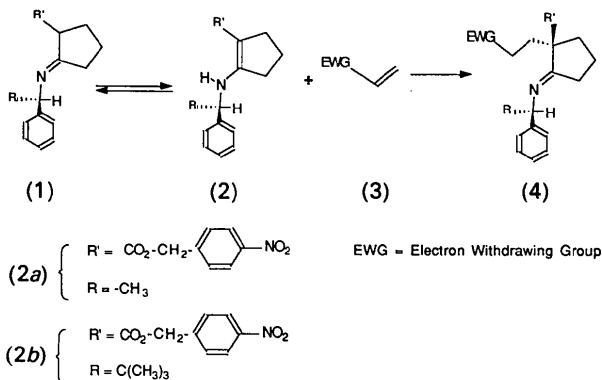
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Abstract

The enantioselective synthesis of quaternary carbon centres through Michael-type alkylation of chiral imines proceeds with high enantiomeric excess with 1-phenylethylamine as auxiliary, while 2,2-dimethyl-1-phenylpropylamine was found to be completely inactive. The crystal structure of a non-reactive imine based on the latter auxiliary reveals a conformation identical with that of the reactive and highly selective 1-phenylethylamine. The phenyl ring is almost perpendicular to the enamino ester plane (torsion angle C—N—C—Ph 71.8°). The enamino ester group is planar and is stabilized by a hydrogen bond between the imine group and the carbonyl group of the ester.

Comment

The enantioselective synthesis of quaternary carbon centres through Michael-type alkylation of chiral imines (1) was introduced in 1985 (Pfau, Reviel, Guingant & d'Angelo, 1985) and reviewed in 1992 (d'Angelo, Desmaele, Dumas & Guingant, 1992). The influence of the nature of the chiral imine on the diastereofacial differentiation has been discussed (d'Angelo, Reviel, Guingant, Riche & Chiaroni, 1989). The presence of an aromatic nucleus in the chiral auxiliary amine group appears crucial to ensure a good diastereofacial differentiation. The enantiomeric excess decreases from 90% with a phenyl group to 45% with a cyclohexyl group. Extension of this methodology to chiral enamino ester (2) ($R' = \text{CO}_2\text{CH}_3$) has been reported (Guingant & Hammami, 1991) and shown to proceed with high enantiomeric excess. The X-ray structure of (2a) (d'Angelo, Reviel, Guingant, Riche & Chiaroni, 1989) revealed that the phenyl group is nearly perpendicular to the plane of the enamino ester. As the upper face of the enamino group is sterically



hindered by the bulky aromatic group, the attack on the opposite face should greatly predominate. Compound (2) ($R' = \text{alkyl}$), where a *tert*-butyl group is substituted for the methyl group in the auxiliary amine, was found to be completely inactive (at least toward the electrophilic olefins which were used). An examination of the Dreiding models suggests that the two bulky substituents could bisect

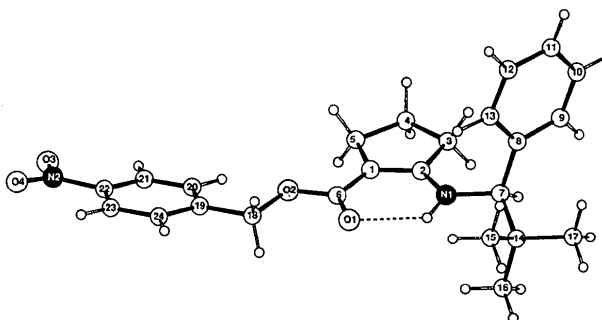


Fig. 1. General view of structure (2b) with atom-labelling scheme.