C6*A*—C5*A*—C4*A*	117.7 (4)	C4*B*—C5*B*—C8*B*	114.6 (4)
C6*A*—C5*A*—C8*A*	128.1 (4)	C5*B*—C6*B*—N1*B*	123.0 (4)
C4*A*—C5*A*—C8*A*	113.9 (3)	C4*B*—N4*B*—O4*B*1	112.1 (4)
C5*A*—C6*A*—N1*A*	123.9 (4)	C4*B*—N4*B*—O4*B*2	114.2 (4)
C4*A*—N4*A*—O4*A*	111.3 (3)	C7*B*1—O4*B*1—N4*B*	122.1 (5)
C7*A*—O4*A*—N4*A*	113.2 (3)	O4*B*1—C7*B*1—C8*B*	122.7 (6)
O4*A*—C7*A*—C8*A*	114.9 (4)	C7*B*2—O4*B*2—N4*B*	112.3 (5)
C7*A*—C8*A*—C5*A*	105.9 (3)	O4*B*2—C7*B*2—C8*B*	123.8 (6)
C6*B*—N1*B*—C2*B*	120.8 (3)	C7*B*1—C8*B*—C5*B*	114.6 (4)
C6*B*—N1*B*—C1′*B*	119.5 (3)	C7*B*2—C8*B*—C5*B*	101.7 (5)

The low number of observed reflections, as a result of poor crystal quality, made it necessary to apply similarity restraints for the 1,2 and 1,3 distances in the two molecules, and similar U_{ij} restraints for atoms closer than 1.7 Å. During refinement, the behaviour of the oxazino ring in residue *B* indicated local disorder. Two alternative conformations (with site-occupancy factors 0.5) for atoms O4 and C7 (O4*B*1 and O4*B*2, and C7*B*1 and C7*B*2) were used to describe this disorder.

The H atoms were placed at calculated positions (C—H = 0.98 Å for tertiary C—H, C—H = 0.97 Å for secondary CH_2, C—H = 0.93 Å for C_{sp2}—H, C—H = 0.96 Å for an idealized methyl group and N—H = 0.90 Å, $U = 1.2U_{eq}$ of the parent atom) and refined in the riding mode or rotating mode (methyl groups).

Absorption coefficients were taken from *International Tables for Crystallography* (1992, Vol. C, Table 4.2.4.2).

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: Siemens *REDUCE*. Program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1102). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(±)-*threo*-3-Hydroxy-2,3-diphenylpropanoic Acid Methyl Ester

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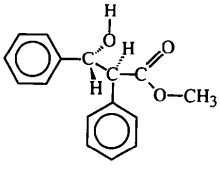
Abstract

The crystal structure of methyl (±)-*threo*-3-hydroxy-2,3-diphenylpropanoate, $C_{16}H_{16}O_3$, has been determined. In the crystal, the phenyl group at the chiral α-C atom and the hydroxy group at the chiral β-C atom are in the energetically preferred *trans* conformation. The torsion angle $O—C_\beta—C_\alpha—C_{phenyl}$ is 175.8 (2)°. The H atoms at the chiral C atoms are also in an antiperiplanar arrangement. Pairs of molecules are linked *via* a pair of weak intermolecular hydrogen bonds between hydroxyl H and carbonyl O atoms. The IR spectrum verifies the presence of this hydrogen bond. The dihedral angle between the least-squares planes through the phenyl rings is 53.0 (1)°. The distance between the α and β chiral C atoms is 1.530 (3) Å. The bond distances and angles of the molecule are as expected.

Comment

We are interested in the effects which different substituents have on the stereochemistry of substituted diphenylethanes possessing two chiral C atoms. This work is part of a project involving the structural investigation of substituted chiral and diastereoisomeric diphenylethanes. This structural information is significant because the diphenylethane skeleton is present in some natural products and affects fundamental stereochemical reactions (Hayashi, Matsumoto, Kiyoi, Ito, Kohira, Tominaga & Hosomi, 1988; Gong & Streitwieser, 1990; Reetz, 1984). In order to compare the conformational results derived from circular dichroism measurements in solution with those in the solid state, a crystal structure determination of the title compound, (I), was undertaken.



(I)

The OH stretching band is relatively downshifted but is very sharp. The reason for this could be that hydrogen bonds only link pairs of molecules instead of being involved in an infinite hydrogen-bonding system.

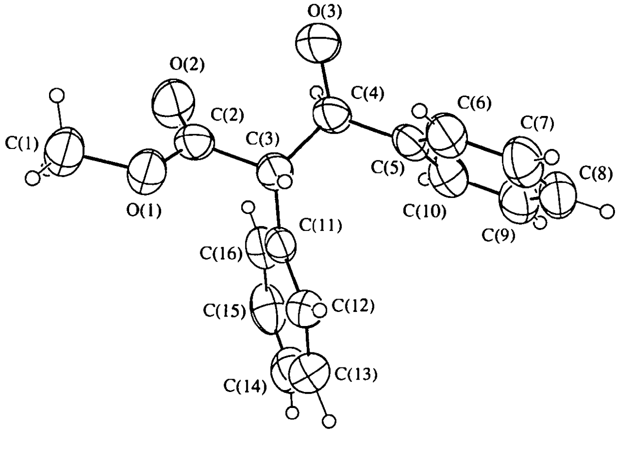


Fig. 1. General view (*SHELXTL-Plus*; Sheldrick, 1987) of the title molecule showing the atom-numbering scheme. Anisotropic displacement ellipsoids represent 50% probability boundaries. H atoms are represented as spheres of arbitrary radii and the H atom at O(3) is not shown.

Experimental

The title compound was synthesized according to the methods of Zimmerman & Traxler (1957) and Mladenova, Blagoev & Kurtev (1974) by Reformatsky reaction from the methyl ester of α-bromophenylacetic acid, Zn turnings and benzaldehyde in dimethoxyethane solution. The final product was obtained after acid hydrolysis followed by recrystallization from ethyl acetate–hexane solution. Suitable crystals were grown from ethanol (m.p. 447–448 K).

The IR spectrum of the title compound in the solid state (KBr pellet) shows a C=O stretching band at 1716 cm^{-1} and an O—H stretching band at 3465 cm^{-1}, with a Raman C=O band at 1719 cm^{-1}.

Crystal data

$C_{16}H_{16}O_3$
$M_r = 256.30$
Monoclinic
$P2_1/n$
$a = 15.988\ (4)$ Å
$b = 5.7150\ (10)$ Å
$c = 16.097\ (4)$ Å
$\beta = 112.88\ (2)°$
$V = 1355.1\ (5)$ Å^3
$Z = 4$
$D_x = 1.256$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 7.5–14.4°$
$\mu = 0.086$ mm^{-1}
$T = 293\ (2)$ K
Block
0.74 × 0.46 × 0.26 mm
Colourless

Data collection

Nicolet *R3m/V* diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4099 measured reflections
1786 independent reflections
1288 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0621$
$\theta_{\rm max} = 22.55°$
$h = -17 \rightarrow 17$
$k = 0 \rightarrow 6$
$l = -17 \rightarrow 17$
6 standard reflections frequency: 150 min intensity decay: not significant

Refinement

Refinement on F^2
$R(F) = 0.0409$
$wR(F^2) = 0.1202$
$S = 1.041$
1784 reflections
190 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0611P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.23$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
O1	0.70259 (10)	−0.0056 (3)	0.07067 (9)	0.0550 (5)
O2	0.65383 (12)	−0.3550 (3)	0.09335 (11)	0.0769 (6)
O3	0.47575 (12)	−0.2726 (4)	−0.06648 (12)	0.0665 (8)
O3*A* †	0.5556 (6)	−0.6070 (8)	−0.0812 (6)	0.041 (4)
C1	0.7424 (2)	0.0376 (5)	0.16630 (14)	0.0648 (7)
C2	0.65954 (14)	−0.2066 (4)	0.04264 (14)	0.0487 (6)
C3	0.62601 (14)	−0.2248 (4)	−0.05903 (13)	0.0454 (6)
C4	0.53875 (14)	−0.3683 (4)	−0.10031 (14)	0.0520 (6)
C5	0.50234 (13)	−0.3537 (4)	−0.20214 (14)	0.0471 (6)
C6	0.4563 (2)	−0.1559 (4)	−0.2461 (2)	0.0559 (6)
C7	0.4232 (2)	−0.1386 (5)	−0.3385 (2)	0.0645 (7)
C8	0.4358 (2)	−0.3168 (5)	−0.3886 (2)	0.0676 (8)
C9	0.4820 (2)	−0.5138 (5)	−0.3466 (2)	0.0684 (8)
C10	0.5152 (2)	−0.5320 (4)	−0.2538 (2)	0.0594 (7)
C11	0.70203 (13)	−0.3180 (3)	−0.08374 (12)	0.0421 (5)
C12	0.73144 (15)	−0.1939 (4)	−0.14058 (14)	0.0512 (6)
C13	0.8009 (2)	−0.2761 (6)	−0.1634 (2)	0.0688 (8)
C14	0.8421 (2)	−0.4822 (6)	−0.1299 (2)	0.0744 (8)
C15	0.8137 (2)	−0.6125 (5)	−0.0736 (2)	0.0697 (8)
C16	0.7433 (2)	−0.5319 (4)	−0.05049 (15)	0.0550 (7)

† Site occupancy of 0.134 (4).

Table 2. *Selected geometric parameters* (Å, °)

O1—C2	1.325 (3)	C2—C3	1.515 (3)
O1—C1	1.440 (3)	C3—C11	1.515 (3)
O2—C2	1.205 (2)	C3—C4	1.530 (3)
O3—C4	1.427 (3)	C4—C5	1.514 (3)
C2—O1—C1	117.9 (2)	O3—C4—C3	106.8 (2)
O2—C2—O1	123.1 (2)	C5—C4—C3	110.0 (2)
O2—C2—C3	126.5 (2)	C10—C5—C4	121.8 (2)

O1—C2—C3	110.3 (2)	C6—C5—C4	120.2 (2)
C2—C3—C11	108.9 (2)	C12—C11—C3	120.6 (2)
C2—C3—C4	112.7 (2)	C16—C11—C3	121.1 (2)
C11—C3—C4	112.8 (2)	C14—C15—C16	120.2 (3)
O3—C4—C5	111.2 (2)		
C1—O1—C2—C3	−177.6 (2)	C11—C3—C4—C5	−63.4 (2)
O2—C2—C3—C11	−91.3 (3)	O3—C4—C5—C10	−140.9 (2)
O2—C2—C3—C4	34.7 (3)	C3—C4—C5—C10	101.0 (2)
C11—C3—C4—O3	175.8 (2)	C2—C3—C11—C12	−123.4 (2)
C2—C3—C4—C5	172.7 (2)		

The lattice parameters were determined from a symmetry-constrained least-squares fit. Difference Fourier maps showed a peak near atom C4 at a position and density which could not be an H-atom peak. An O atom was placed at this position and isotropically refined. The sum of the occupancies of this O atom [O3*A* 0.134 (4)] and of atom O3 [0.866 (4)] were constrained to equal 1.0 and the distance C4—O3*A* was constrained to 1.400 (3) Å. The H atoms, except those at O3 which were not located, were placed in calculated positions (C—H 0.96 Å) and a common isotropic displacement parameter was refined for these atoms. For the H atoms of the phenyl rings and the H atoms at atoms C3 and C4, a constrained refinement of C—H distances in the range 0.90 (3)–1.03 (3) Å was performed. Atom O3*A* represents the presence in the crystals of 13% of molecules enantiomorphic at C4.

Data collection: Nicolet *R3m/V* software. Cell refinement: Nicolet *R3m/V* software. Data reduction: Nicolet *R3m/V* software. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1987). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *PARST* (Nardelli, 1983), *PLATON* (Spek, 1982) and *MISSYM* (Le Page, 1987).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1137). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,7-Bis(éthoxycarbonyl)-3a-méthyl-4a-phényl-3,5-bis(*p*-nitrophényl)-3a,4,4a,5-tétrahydro-3*H*-bis[1,2,4]triazolo[4,3-*a*:3′,4′-*d*][1,5]benzodiazépine, $C_{36}H_{32}N_8O_8.CHCl_3$

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Abstract

Double condensation of *N*-*p*-nitrophenyl-*C*-ethoxycarbonylnitrilimine with 2-methyl-4-phenyl-1,5-benzodiazepine leads to two stereoisomers of the title compound, diethyl 3a-methyl-4a-phenyl-3,5-bis(*p*-nitrophenyl)-3a,4,4a,5-tetrahydro-3*H*-bis[1,2,4]triazolo[4,3-*a*:3′,4′-*d*][1,5]benzodiazepine-1,7-dicarboxylate trichloromethane solvate. The stereochemistry of the major derivative was established. The 3a-methyl and the 4a-phenyl groups are *trans*. The oxadiazoline rings are quite planar while the seven-membered benzodiazepine ring adopts a *C*2 barrier conformation.

Commentaire

La cycloaddition dipolaire-1,3 du *N*-paranitrophényl-*C*-éthoxycarbonylnitrilimine, issu du précurseur convenable (1) (Huisgen & Koch, 1955; Sharp & Hamilton, 1946), avec la 2-méthyl-4-phényl-1,5-benzodiazépine (2) (Barltrop, Richards, Russel & Ryback, 1959; Mannschreck, Rissmann, Vögtle & Wild, 1967) conduit, quand on utilise deux équivalents de dipôle, à deux stéréoisomères: les bis[1,2,4]triazolo[4,3-*a*:3′,4′-*d*][1,5]benzodiazépines [(3*a*) (65%) et (3*b*) (30%)]. Les cycloadduits obtenus résultent d'une double condensation régiosélective sur les deux sites dipolarophiles N1═C2 et C4═N5 de (2). Ce double résultat est en accord avec celui observé par Aversa, Bonaccorsi,

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