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Acta Cryst. (1997). C**53**, 1721–1723

(3a*R**,4*S**,5*S**,7a*R**)-4-Nitrobenzoic Acid 5-Methyl-1,3,3a,4,5,7a-hexahydroisobenzofuran-4-yl Ester

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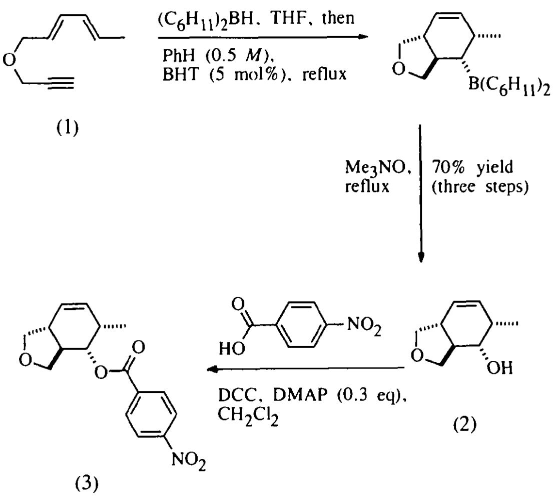
(Received 2 April 1997; accepted 12 May 1997)

Abstract

The crystal structure determination of the title compound, $C_{16}H_{17}NO_5$, establishes the relative stereochemistry. The molecule contains a furanyl ring with a twist conformation fused to an unsaturated six-membered ring with a twist-chair conformation. There are weak intermolecular C—H···O interactions, with distances C···O$(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$ 3.254 (2) and H···O$(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$ 2.41 Å.

Comment

Recent studies have identified alkenylboranes as reactive dienophiles in Diels–Alder reactions (Matteson, 1995). The potential to control the relative stereochemistry of at least three new stereocentres in the intramolecular variant, and the synthetic utility of the C—B bond in the cycloadducts have prompted us to examine this reaction. During the course of our studies, the first example of this strategy to form bicyclo[4.4.0]decenes was reported (Singleton & Lee, 1995). In contrast, our research has focused on the formation of hydrindene-type structures, using a 'one-pot' procedure (Batey, Lin, Hayhoe & Wong, 1997). Thus, an alkenylborane, generated *in situ* by selective hydroboration of a dienyne, undergoes an intramolecular Diels–Alder reaction, after which the C—B bond in the cycloadduct is transformed. In an intramolecular reaction, two modes of cycloaddition (*endo*/*exo*) are possible. In the case of the dienyne (1) (see reaction scheme below), a single diastereomer, (2), formed as a viscous oil, was derived as the crystalline *p*-nitrobenzoate ester, (3), in order to determine the relative stereochemistry about the six-membered ring.



DMAP = dimethylaminopyridine
DCC = dicylohexylcarbodiimide
BHT = butylated hydroxytoluene

The crystal structure determination establishes the diastereomer as the product of *endo* addition in the intramolecular Diels–Alder reaction. A search of the Cambridge Structural Database (Allen *et al.*, 1979) revealed that there are only three other structures (refcodes: DAHDUL, FUMZIW and JEWRUY) containing similar *trans*-fused six- and five-membered rings as in (3), but (3) is the first compound reported that contains an unsubstituted furanyl group fused to a cyclohexene ring system.

The five-membered furanyl ring is in a twist conformation. C6 is 0.412 (3) Å above and C7 is 0.301 (3) Å below the plane formed by the three atoms C8, C9 and O3. The twist conformation of the furanyl group in (3) is consistent with the conformation of the molecule of tetrahydrofuran that was determined at 103 and 148 K by Luger & Buschmann (1983). The furanyl group in (3) has similar bond lengths and angles to those in tetrahydrofuran; the only exceptions are the magnitudes of the angles C7—C8—O3 and C6—C9—O3 in (3), which are 104.63 (9) and 104.32 (9)°, respectively, compared with 107.4 (4)° at 103 K and 106.7 (4)° at 148 K for tetrahydrofuran (the tetrahydrofuran molecule has crystallographic twofold symmetry).

The six-membered ring of the fused ring system in (3) has a twist-chair conformation. Atoms C3, C4, C5 and C6 form a least-squares plane [with maximum deviation of 0.008 (1) Å for C4] and C7 is 0.644 (2) Å below the plane, while C2 is 0.139 (2) Å above the plane. The six- and five-membered rings are *trans*-fused along the C6—C7 bond (see Fig. 1).

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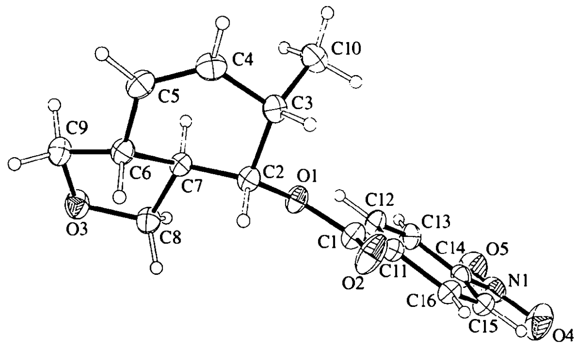

Fig. 1. View of the molecule with the atomic labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are drawn as small spheres.

In the nitrobenzoate ester group, the benzene ring atoms, C11–C16, form a least-squares plane [with maximum deviation 0.006 (1) Å for C11]. The atoms of the $-NO_2$ substituent and the –COO ester group are close to the plane of the benzene ring, the largest deviation being 0.135 (2) Å for O1. The fused ring system is rotated out of the plane of the nitrobenzoate ester group by an angle of 58.0 (1)°.

In (3), furanyl O atoms are involved in intermolecular close contacts of the type C—H···O. These interactions occur between molecules related by 2_1 screw axes to form infinite chains of molecules. The relevant distances are given in Table 2.

Experimental

Alcohol (2) (see scheme above) was derived as the *p*-nitrobenzoate ester by stirring the alcohol (53 mg, 0.34 mmol) with dicyclohexylcarbodiimide (DCC; 112 mg, 0.54 mmol), dimethylaminopyridine (DMAP; 12 mg, 0.098 mmol) and *p*-nitrobenzoic acid (80 mg, 0.48 mmol) in CH_2Cl_2 (3.0 ml). After stirring overnight, H_2O (5 ml) was added and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 ml). The organic layer was then washed with brine (10 ml), dried with anhydrous $MgSO_4$ and concentrated *in vacuo*. Flash column chromatography provided the title compound as a pale yellow solid (85 mg, 82%). Pale yellow crystals grew from a solution of ether–pentane (3:2) over 3 d at 295 K.

Crystal data

$C_{16}H_{17}NO_5$	Mo $K\alpha$ radiation
$M_r = 303.31$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 43 reflections
$P2_1/c$	$\theta = 5.25$–$25.00°$
$a = 8.0485 (9)$ Å	$\mu = 0.099$ mm^{-1}
$b = 14.301 (2)$ Å	$T = 213 (2)$ K
$c = 13.2703 (14)$ Å	Flat needle
$\beta = 91.769 (7)°$	0.49 × 0.45 × 0.36 mm
$V = 1526.7 (3)$ Å^3	Pale yellow
$Z = 4$	
$D_x = 1.320$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens *P*4 diffractometer	$\theta_{max} = 30°$
ω scans	$h = 0 \rightarrow 11$
Absorption correction: none	$k = 0 \rightarrow 20$
4686 measured reflections	$l = -18 \rightarrow 18$
4405 independent reflections	3 standard reflections every 97 reflections
3182 reflections with $I > 2\sigma(I)$	intensity decay: <2%
$R_{int} = 0.020$	

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.251$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.043$	$\Delta\rho_{min} = -0.219$ e Å^{-3}
$wR(F^2) = 0.129$	Extinction correction: *SHELXTL/PC* (Sheldrick, 1994)
$S = 1.045$	
4405 reflections	
201 parameters	Extinction coefficient: 0.0027 (14)
H atoms riding	Scattering factors from *International Tables for Crystallography* (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.071P)^2 + 0.0556P]$ where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{max} = 0.001$	

Table 1. *Selected geometric parameters (Å, °)*

O3—C9	1.4430 (15)	C4—C5	1.326 (2)
O3—C8	1.4500 (15)	C5—C6	1.497 (2)
C2—C7	1.5027 (14)	C6—C9	1.517 (2)
C2—C3	1.546 (2)	C6—C7	1.5266 (14)
C3—C4	1.515 (2)	C7—C8	1.516 (2)
C9—O3—C8	109.78 (9)	C9—C6—C7	100.63 (9)
C7—C2—C3	109.97 (9)	C2—C7—C8	120.39 (9)
C4—C3—C2	111.13 (9)	C2—C7—C6	107.91 (8)
C5—C4—C3	125.83 (11)	C8—C7—C6	100.88 (9)
C4—C5—C6	119.71 (11)	O3—C8—C7	104.63 (9)
C5—C6—C9	121.68 (10)	O3—C9—C6	104.32 (9)
C5—C6—C7	110.27 (9)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C13—H13*A*···O3^{i}	0.94	2.41	3.254 (2)	149

Symmetry code: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

This work was supported by the NSERC Canada and the University of Toronto.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1329). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1723–1725

(*E*)-2,2,5,5-Tetramethyl-3,4-diphenylhex-3-ene, $C_{22}H_{28}$

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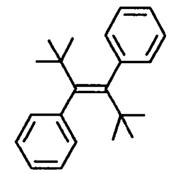
(*Received 26 November 1996; accepted 13 May 1997*)

Abstract

In the title compound, an unusually short central C═C bond observed at room temperature is shown to be an artifact by a measurement at low temperature. The phenyl planes are perpendicular to the plane of the double bond.

Comment

The structure of the title compound, (1), has prompted numerous investigations of this molecule and its derivatives (Bellucci, Chiappe, Bianchini, Lenoir & Herges, 1995; Gano & Gano, 1994; Gano, Jacob & Roesner, 1991; Gano, Jacob, Sekher, Subramaniam, Eriksson & Lenoir, 1996; Gano, Park, Pinkerton & Lenoir, 1990; Gano, Park, Subramaniam, Lenoir & Gleiter, 1991; Laali, Gano, Lenoir & Gundlach, 1994). Although a structure appeared for its *Z* isomer some time ago (Gano, Park, Pinkerton & Lenoir, 1991), difficulties preparing acceptable crystals, which are not unusual with (*E*)-stilbenes, limited reports, until now, to a disordered structure (Ermer, 1977; Pilati & Simonetta, 1982) and a highly brominated derivative (Gano, Kirschbaum & Sekher, 1996). Suitable crystals were obtained by slow evaporation of a methanol solution. The triclinic cell contains two independent molecules (Fig. 1) which are located on inversion centers.



(1)

Although (*E*)-stilbene is planar in its crystalline form or at very low temperatures (Waldeck, 1991), in (1), the phenyl groups rotate out of the molecular plane to avoid steric repulsion of the *tert*-butyl groups. As seen in Fig. 1, the rings are perpendicular to the plane defined by the central C═C bond and its attached atoms: C1′—C1—C6—C7 93.2 (2), C1′—C1—C6—C11 −89.3 (2), C12′—C12—C17—C18 −96.8 (2) and C12′—C12—C17—C22 87.5 (2)°; C1′ = C1($-x$, $-y$, $-z$) and C12′ = C12($1-x$, $1-y$, $1-z$)].

Rotation of the phenyl groups so they are not in conjugation with the C═C bond might be expected

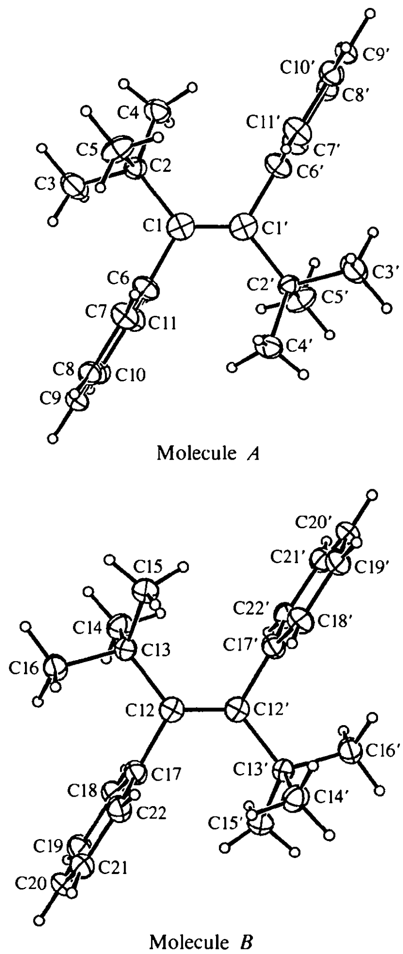


Fig. 1. *ORTEP* plots (50% probability) showing the two independent molecules of the title compound. Both molecules are viewed perpendicular to the plane defined by the atoms in the central C═C bond and its substituents.