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Acta Cryst. (1994). C**50**, 1485–1487

Methyl (3a*R*,4*R*,7*S*,7a*S*)-1,3-Dioxo-7-phenyl-1,3,3a,4,7,7a-hexahydro-4-isobenzofurancarboxylate

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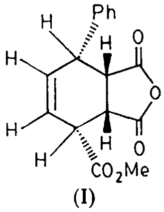
(*Received* 23 *November* 1993; *accepted* 22 *February* 1994)

Abstract

The structure of the title compound, $C_{16}H_{14}O_5$, has been determined by X-ray diffraction. The molecule contains four chiral centres; both enantiomers are present in the crystal as a result of the centrosymmetric space group. As expected for a Diels–Alder adduct, the ring-junction H atoms display a *cis* relationship. The conformation of the six-membered ring is an ideal boat, whereas the five-membered ring is significantly flattened.

Comment

The Diels–Alder reaction has played an important role in the development of synthetic, mechanistic and theoretical organic chemistry. The remarkable stereo- and regioselectivities associated with cycloaddition provide various polyfunctionalized molecules containing multiple chiral centres which are of potential use in protein catalysis (Suckling, Tedford, Bence, Irvine & Stimson, 1993; Braisted & Schultz, 1990; Hilvert, Hill, Nared & Auditor, 1989). In order to construct a hierarchy and unambiguously assign the stereochemistry of the four contiguous chiral centres, the crystal structure determination of methyl (3a*R*,4*R*,7*S*,7a*S*)-1,3-dioxo-7-phenyl-1,3,3a,4,7,7a-hexahydro-4-isobenzofurancarboxylate (I) was undertaken. The compound is the Diels–Alder adduct of (*E*,*E*)-1-methoxycarbonyl-4-phenyl-1,3-butadiene with maleic anhydride and was prepared by heating the reactants in a xylene solution.



(I)

The results of the present structure analysis are in agreement with those of the structure determinations of (1*R*,6*R*,10*S*)-10-[(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)oxy]bicyclo[4.4.0]decane-2,5,8-trione (Gupta, Raynor, Stoodley, Slawin & Williams, 1988) and (2*Z*,4*E*)-1,3,6-triacetoxyhexa-2,4-diene (Areces, Roman, Pozo & Serrano, 1993), based on X-ray, spectral and chemical evidence. The *ORTEP*II (Johnson, 1976) view (Fig. 1) shows that the molecule consists of a bicyclic core (*AB*) with a *cis* relationship between the H atoms [H1—C1—C2—H2 torsion angle −3.8°]. There are four chiral centres [configurations *S*(C1), *R*(C2), *R*(C3), *S*(C6)]; the enantiomorph is also present since the space group is centrosymmetric. The bond distances [C—C bond lengths range from 1.492 (3) to 1.558 (3) Å] and angles quoted in Table 2 are as expected. Ring *A* is in an almost ideal boat conformation, with C3 and C6 displaced by 0.588 (2) and 0.579 (2) Å, respectively, in the same direction from the least-squares plane through the remaining endocyclic atoms. For this ring, the Q and θ puckering parameters (Cremer & Pople, 1975) are 0.675 (3) Å and 89.8 (2)°, respectively. The five-membered ring *B* is significantly flattened (the sum of absolute values of torsion angles is 16.7°), with a maximum deviation of 0.030 (3) Å at C1, and is nearly

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ISSN 0108-2701 ©1994

orthogonal to ring *A*; the dihedral angle between the least-squares planes through ring *B* and the planar part of ring *A* (C1, C2, C4, C5) is 96.1 (1)°. The phenyl ring and the methoxycarbonyl moiety [O4—C15—O5—C16 torsion angle 0.7 (4)°] are essentially planar and inclined to ring *A* by 47.6 (1) and 25.8 (2)°, respectively. The molecular packing is determined only by van der Waals contacts.

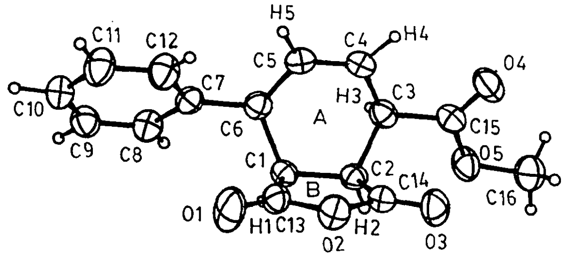

Fig. 1. *ORTEP*II (Johnson, 1976) view of the molecule showing the atom-labelling and ring-numbering scheme.

Experimental

Crystal data

$C_{16}H_{14}O_5$
$M_r = 286.27$
Monoclinic
$C2/c$
$a = 19.819$ (3) Å
$b = 10.364$ (2) Å
$c = 13.706$ (3) Å
$\beta = 104.600$ (10)°
$V = 2724.4$ (9) Å^3
$Z = 8$
$D_x = 1.396$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 20 reflections
$\theta = 10$–15°
$\mu = 0.871$ mm^{-1}
$T = 293$ (2) K
Prismatic
0.45 × 0.38 × 0.36 mm
Colourless

Data collection

Rigaku AFC-5 diffractometer
ω-2θ scans
Absorption correction: empirical
$T_{\min} = 0.907$, $T_{\max} = 1.000$
2037 measured reflections
2037 independent reflections

1744 observed reflections [$I > 2\sigma(I)$]
$\theta_{\max} = 59.99°$
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 11$
$l = -15 \rightarrow 14$
3 standard reflections monitored every 150 reflections
intensity variation: 7.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0512$
$wR(F^2) = 0.1288$
$S = 1.130$
1989 reflections
246 parameters
H atoms refined isotropically
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0680P)^2 + 1.3963P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.169$
$\Delta\rho_{\max} = 0.195$ e Å^{-3}
$\Delta\rho_{\min} = -0.162$ e Å^{-3}
Extinction correction: none
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)

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

	x	y	z	$U_{\rm eq}$
O1	−0.04250 (9)	0.2216 (3)	0.08026 (14)	0.0922 (8)
O2	−0.14922 (8)	0.1416 (2)	0.03541 (11)	0.0593 (5)
O3	−0.25832 (9)	0.0925 (2)	−0.04306 (13)	0.0676 (5)
O4	−0.30124 (9)	0.0078 (2)	−0.2832 (2)	0.0795 (6)
O5	−0.32575 (8)	0.2124 (2)	−0.26116 (13)	0.0645 (5)
C1	−0.11589 (11)	0.2713 (2)	−0.0868 (2)	0.0440 (5)
C2	−0.19183 (11)	0.2340 (2)	−0.1258 (2)	0.0419 (5)
C3	−0.20768 (12)	0.1592 (2)	−0.2274 (2)	0.0491 (6)
C4	−0.15443 (13)	0.0555 (2)	−0.2199 (2)	0.0569 (6)
C5	−0.08828 (13)	0.0840 (2)	−0.1839 (2)	0.0566 (6)
C6	−0.06860 (11)	0.2223 (2)	−0.1542 (2)	0.0487 (6)
C7	0.00772 (11)	0.2515 (2)	−0.1118 (2)	0.0479 (5)
C8	0.03054 (13)	0.3786 (2)	−0.1144 (2)	0.0544 (6)
C9	0.09963 (13)	0.4108 (3)	−0.0796 (2)	0.0597 (6)
C10	0.14820 (14)	0.3177 (3)	−0.0409 (2)	0.0640 (7)
C11	0.12670 (14)	0.1928 (3)	−0.0376 (2)	0.0722 (8)
C12	0.05723 (13)	0.1606 (3)	−0.0717 (2)	0.0638 (7)
C13	−0.09522 (12)	0.2134 (3)	0.0173 (2)	0.0549 (6)
C14	−0.20673 (11)	0.1484 (2)	−0.0451 (2)	0.0481 (5)
C15	−0.28260 (12)	0.1152 (2)	−0.2597 (2)	0.0534 (6)
C16	−0.39920 (14)	0.1859 (4)	−0.2920 (3)	0.0724 (8)

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

O1—C13	1.178 (3)	C1—C6	1.558 (3)
O2—C14	1.374 (3)	C2—C14	1.505 (3)
O2—C13	1.376 (3)	C2—C3	1.555 (3)
O3—C14	1.181 (3)	C3—C4	1.492 (3)
O4—C15	1.191 (3)	C3—C15	1.509 (3)
O5—C15	1.319 (3)	C4—C5	1.313 (3)
O5—C16	1.436 (3)	C5—C6	1.514 (3)
C1—C13	1.507 (3)	C6—C7	1.508 (3)
C1—C2	1.515 (3)		
C14—O2—C13	110.7 (2)	C7—C6—C5	117.3 (2)
C15—O5—C16	117.6 (2)	C7—C6—C1	113.6 (2)
C13—C1—C2	104.0 (2)	C5—C6—C1	108.4 (2)
C13—C1—C6	111.8 (2)	O1—C13—O2	119.6 (2)
C2—C1—C6	113.6 (2)	O1—C13—C1	130.1 (2)
C14—C2—C1	104.6 (2)	O2—C13—C1	110.3 (2)
C1—C2—C3	113.7 (2)	O3—C14—O2	120.3 (2)
C4—C3—C15	115.4 (2)	O3—C14—C2	129.6 (2)
C4—C3—C2	108.5 (2)	O2—C14—C2	110.1 (2)
C15—C3—C2	112.0 (2)	O4—C15—O5	123.7 (2)
C5—C4—C3	119.1 (2)	O4—C15—C3	125.2 (2)
C4—C5—C6	118.6 (2)	O5—C15—C3	111.1 (2)

Data collection, cell refinement and data reduction: AFC-5 software. Programs used for structure solution and refinement: *MULTAN*88 (Debaerdemaeker *et al.*, 1988); *SHELXL*93 (Sheldrick, 1993). Software used for geometric calculations: *PARST* (Nardelli, 1983). Software used to prepare material for publication: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). All calculations were performed using a VAX3400 computer at the Computer Center, Indian Association for the Cultivation of Science.

The authors thank Dr Subhagata Chattophadhaya for providing suitable crystals used in the X-ray analysis.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1094). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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α,α-Bis(1-methyl-4-trifluoromethyl-5-pyrazolyl)benzyl Benzoate and α-(1-Methyl-4-trifluoromethyl-3-pyrazolyl)-α-(1-methyl-4-trifluoromethyl-5-pyrazolyl)benzyl Benzoate: an Investigation into the Direction of Diazomethane Addition to α,α-Bis(3,3,3-trifluoropropynyl)benzyl Benzoate

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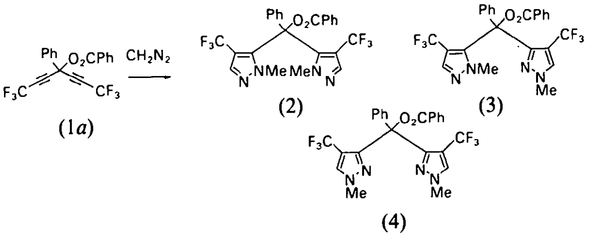
(*Received* 25 *January* 1994; *accepted* 7 *March* 1994)

Abstract

The structures of the title compounds, two isomers of $C_{24}H_{18}F_6N_4O_2$, may be compared by considering the geometry about the tetrahedral benzyl C atoms. In each compound the planar phenyl and benzoate systems are aligned approximately parallel to the ester C—O bond with the latter substituent projecting between the phenyl and 1-methyl-4-trifluoromethylpyrazolyl rings. However, while both CF_3 substituents in the first molecule project away from the ester C—O bond [O—C—C—C(CF_3) −138.5 (5), −122.2 (6)°], removal of a methyl group to an outer N atom has reversed the situation in the second compound [O—C—C—C(CF_3) −63 (1), −41 (1) and 65 (1), 34 (1)° for the two molecules in the asymmetric unit, respectively].

Comment

The structure determinations reported herein form part of a general investigation of the reaction of 1,4-diynyl esters of type $(CF_3C{\equiv}C)_2CRO_2CR$ (1) with dienes and 1,3-dipolar reagents (Tajammal 1991; Barlow, Tajammal & Tipping 1992). The structures of the two crystalline bis(methylpyrazoles) (2) and (3) were required to determine the direction of addition of diazomethane to the 1,4-diynyl ester [(1*a*), *R* = Ph] and to establish the identity of the third isolated bis(methylpyrazole) (4).



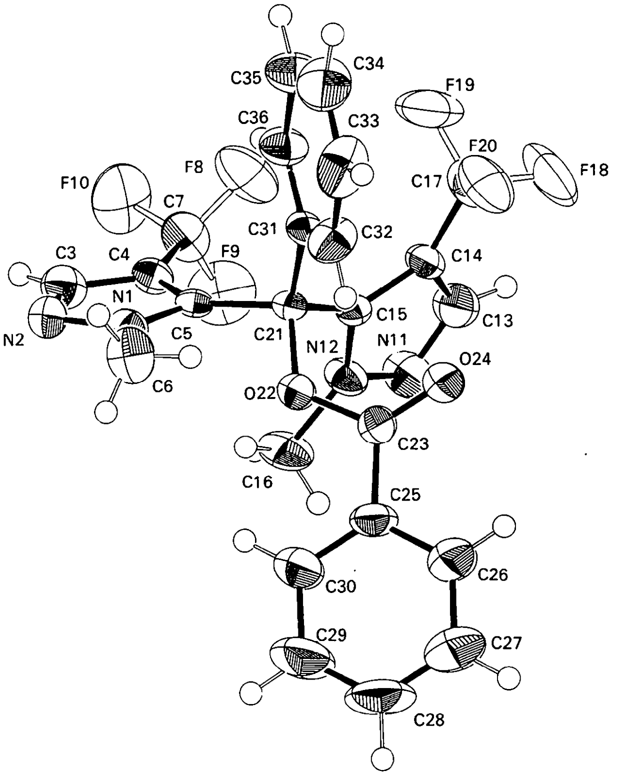


Fig. 1. α,α-Bis(1-methyl-4-trifluoromethylpyrazol-5-yl)benzyl benzoate, including atomic numbering scheme, drawn using *ORTEP*II (Johnson, 1976). Displacement ellipsoids are plotted at the 50% probability level.

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