11 202 measured reflections
5500 independent reflections
3 standard reflections
frequency: 120 min
intensity decay: 4.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.120$
$S = 1.055$
5500 reflections
290 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0727P)^2 + 0.5393P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.377$ e Å^{-3}
$\Delta\rho_{\min} = -0.332$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0023 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected torsion angles (°)*

N1—C4—C5—C11	178.99 (11)	C11—C5—C6—C7	2.64 (17)
C3—C4—C5—C11	−1.86 (18)	C1^{i}—C10—C16—C17	60.51 (16)

Symmetry code: (i) $-x, 1-y, -z$.

The title structure was solved by direct methods followed by Fourier synthesis and refined by anisotropic full-matrix least-squares methods for all non-H atoms; the H atoms were placed at calculated positions and refined as riding using *SHELXL*97 (Sheldrick, 1997) defaults [N—H 0.87, C—H 0.94 and C—H(methyl) 0.97 Å]. The two central H atoms (N—H) were located from a ΔF map and found to be disordered over the four N atoms; they were placed in four calculated positions, each with 50% occupancy.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1995). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*-4 (Harms & Wolcaldo, 1996). Program(s) used to solve structure: *SHELXS*90 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97. Molecular graphics: *CAMERON* (Watkin *et al.*, 1993). Software used to prepare material for publication: *SHELXL*97 and *PARST*95 (Nardelli, 1995).

This work was performed at the Chemical Crystallography Laboratory, University of Oxford, and supported by the Engineering and Physical Sciences Research Council (UK), the Finnish Academy and the Emil Aaltonen Foundation. We are very grateful to Dr D. J. Watkin for valuable assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1176). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 664–666

Δ^4-7,7-Ethylenedioxy-10-methyloctal-1-one†

Marcelo Cardoso Branco,[a] Ana Maria Goncalves D. Rodrigues,[a] Maria Teresa do P. Gambardella,[a] Rosana M. Muzzi[b] and Helena M. C. Ferraz[b]

[a]*Instituto de Química de São Carlos, Universidade de São Paulo, Caixa Postal 780, 13560.970 São Carlos, SP, Brazil, and* [b]*Instituto de Química, Universidade de São Paulo, Caixa Postal 26077, 05599.970 São Paulo, SP, Brazil. E-mail: branco@iqsc.sc.usp.br*

(*Received 3 March 1997; accepted 11 December 1997*)

Abstract

The structure of an important decaline intermediate, $C_{13}H_{18}O_3$, in the total synthesis of corymbolone has been determined. The structure is stabilized by van der Waals interactions only.

Comment

Corymbolone is a natural sesquiterpene extracted from an Amazon forest plant called Piri-piri. The unrefined extract from this plant is used by Brazilian Indians to induce abortion. During recent work (Souza *et al.*, 1993; Muzzi & Ferraz, unpublished results) which culminated in the total synthesis of corymbolone, (I) (Garbarino *et al.*, 1985), and corymbolol (Nyasse *et al.*, 1988), the title compound, (II), was obtained as an advanced intermediate in five steps starting from the Wieland–Miescher ketone. The title compound was also observed as an intermediate in other syntheses (Guile *et al.*, 1992).

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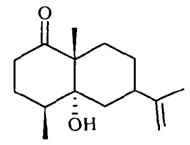
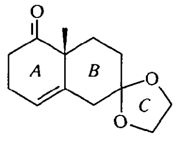
† Alternative name: 4a′-methyl-1′,2′,3′,4′,6′,7′-hexahydrospiro[1,3-dioxolane-2,2′-naphthalen]-5′(4a′H)-one.


(I)



(II)

According to puckering analysis (Cremer & Pople, 1975), the *A* [q_2 = 0.358 (6), q_3 = −0.259 (3), Q = 0.441 (6) Å; θ = 125.9 (7), φ = 272.9 (8)°] and *B* [q_2 = 0.029 (5), q_3 = −0.547 (5), Q = 0.548 (5) Å; θ = 177.0 (5) φ = 48 (9)°] rings have a half-chair and a chair conformation, respectively. The dioxolane ring has a pure envelope conformation [q_2 = 0.343 (3) Å, φ = 110.5 (4)°]. The best plane through the atoms of the dioxolane ring forms an angle of 81.72 (11)° with the best plane through ring *B*.

The decaline system has normal values for bond distances and angles. The largest discrepancy is observed for the two C atoms of the acetal ring. The crystalline packing is stabilized by van der Waals interactions only.

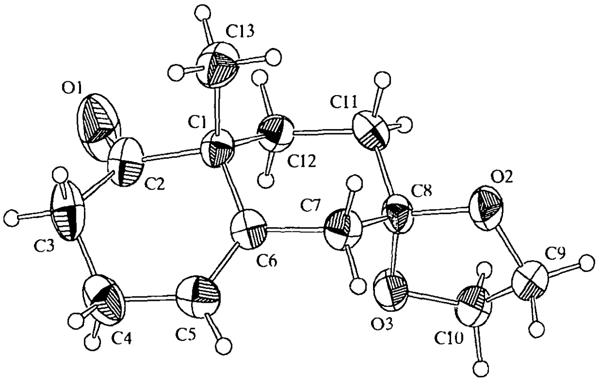


Fig. 1. *ZORTEP* (Zsolnai, 1994) drawing of the title compound showing the atomic labeling. Displacement ellipsoids are plotted at the 40% probability level.

Experimental

Good quality single crystals suitable for X-ray analysis were obtained by slow evaporation of a dichloromethane solution.

Crystal data

$C_{13}H_{18}O_3$
M_r = 222.27
Monoclinic
$P2_1/n$
a = 13.3409 (10) Å
b = 5.8353 (5) Å
c = 15.0408 (10) Å
β = 100.142 (8)°
V = 1152.6 (2) Å^3
Z = 4
D_x = 1.281 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9.6–18.2°
μ = 0.090 mm^{-1}
T = 293 (2) K
Thin plate
0.50 × 0.35 × 0.03 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2435 measured reflections
2330 independent reflections
1303 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.028
$\theta_{\rm max}$ = 26.29°
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 7$
$l = -18 \rightarrow 18$
3 standard reflections
frequency: 120 min
intensity decay: 3.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.174$
S = 1.023
2330 reflections
145 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0886P)^2 + 0.2067P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.338 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.277 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C2	1.206 (3)	C2—C3	1.509 (4)
O2—C9	1.416 (3)	C3—C4	1.506 (5)
O2—C8	1.429 (3)	C4—C5	1.486 (4)
O3—C10	1.417 (3)	C5—C6	1.327 (4)
O3—C8	1.424 (3)	C6—C7	1.507 (3)
C1—C6	1.517 (3)	C7—C8	1.519 (3)
C1—C2	1.525 (4)	C8—C11	1.511 (3)
C1—C12	1.540 (3)	C9—C10	1.499 (4)
C1—C13	1.542 (4)	C11—C12	1.522 (3)
C9—O2—C8	108.1 (2)	C5—C6—C7	121.8 (2)
C10—O3—C8	106.9 (2)	C5—C6—C1	123.2 (2)
C6—C1—C2	110.2 (2)	C7—C6—C1	115.0 (2)
C6—C1—C12	109.0 (2)	C6—C7—C8	111.8 (2)
C2—C1—C12	108.9 (2)	O3—C8—O2	106.1 (2)
C6—C1—C13	111.2 (2)	O3—C8—C11	111.1 (2)
C2—C1—C13	107.5 (2)	O2—C8—C11	109.4 (2)
C12—C1—C13	110.0 (2)	O3—C8—C7	108.6 (2)
O1—C2—C3	122.0 (3)	O2—C8—C7	110.4 (2)
O1—C2—C1	121.9 (3)	C11—C8—C7	111.2 (2)
C3—C2—C1	115.5 (2)	O2—C9—C10	103.6 (2)
C4—C3—C2	111.1 (2)	O3—C10—C9	101.8 (2)
C5—C4—C3	112.5 (3)	C8—C11—C12	110.8 (2)
C6—C5—C4	125.0 (3)	C11—C12—C1	113.7 (2)

All H atoms were positioned according to geometric criteria using *SHELXL*93 (Sheldrick, 1993).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ZORTEP* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL*93.

The authors wish to thank FINEP, CNPq and FAPESP (Brazilian agencies) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1036). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 666–668

7-Benzoyl-2,3,4a,6-tetraphenyl-4a,5,6,7-tetrahydro-1*H*-[1,3]oxazino[3,2-*a*][1,5]-benzodiazepin-1-one

JIAXI XU,[a] SHENG JIN,[a] ZEYING ZHANG[b] AND THOMAS C. W. MAK[b]

[a]*College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China, and* [b]*Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong. E-mail: jxxu@chemms.chem.pku.edu.cn*

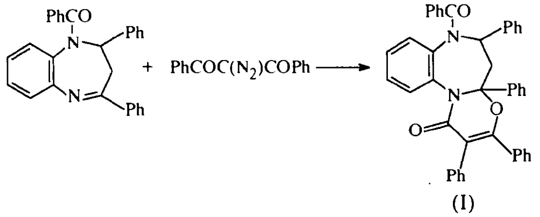
(*Received 28 April 1997; accepted 21 November 1997*)

Abstract

The title compound, $C_{43}H_{32}N_2O_3$, has a *cis*-ring-fusion tricyclic structure which is formed from a benzene ring, a seven-membered diazepine ring and a 1,3-oxazinone ring. The 1,5-diazepine ring has a slightly distorted boat-like conformation, whereas the 1,3-oxazinone ring adopts a half-chair conformation.

Comment

Benzodiazepines are important pharmaceutical agents (Bunin *et al.*, 1994; Bock *et al.*, 1989). 4a,5,6,7-Tetrahydro-1*H*-[1,3]oxazino[3,2-*a*][1,5]benzodiazepin-1-ones (1,5-benzodiazepines fused with 1,3-oxazinone) with potential anxiolytic, anticonvulsant and antihypnotic activities (Sternbach, 1979), have been synthesized by Diels–Alder reactions of 2,4-diaryl-1-benzoyl-2,3-dihydro-1*H*-1,5-benzodiazepines and α-diazo-β-diketones (Capuano & Gartner, 1981; Capuano & Wamprecht, 1986). 2-Diazo-1,3-diphenyl-1,3-propanedione could take part in a thermal Wolff rearrangement to generate benzoyl phenylketene as the diene participating in the Diels–Alder reactions with 2,4-diaryl-1-benzoyl-2,3-dihydro-1*H*-1,5-benzodiazepines to obtain 4a,6-diaryl-1-benzoyl-2,3-diphenyl-4a,5,6,7-tetrahydro-1*H*-[1,3]oxazino[3,2-*a*][1,5]benzodiazepin-1-ones (Xu & Jin, 1994). Crystal structures of such compounds have not been reported. In order to elucidate the structures of the cycloadducts in these Diels–Alder reactions and to study their conformations, one of them, the title compound, (I), was subjected to X-ray diffraction analysis.



(I)

The molecular backbone of (I) is a tricyclic system formed by a benzene ring, a seven-membered diazepine ring and a 1,3-oxazinone ring. The central seven-membered ring is in a slightly distorted boat-like conformation, and is *cis*-fused to the 1,3-oxazinone ring at atoms N2 and C9, while the latter moiety is in a half-chair conformation. The phenyl group on C7 and the benzoyl group on N1 are both equatorial, and the phenyl group on C9 is axial to the central ring (Fig. 1), *i.e.* the cycloaddition reaction is a *cis*-addition reaction.

The interesting feature of the molecule is that the central ring adopts a slightly twisted boat-like conformation which is energetically not so favourable; this conformation is probably stabilized by the presence of the heteroatoms, especially the N atom with a large benzoyl group attached, and by the influence of the exocyclic bulky phenyl substituents attached to atoms C7 and C9.

The molecule contains two chiral C atoms, C7 and C9. The compound has a *rel*-(*R*–*S*) configuration. As a whole, the molecule possesses only C_1 symmetry because of the unsymmetrical nature of the substituents.

The two molecules in the asymmetric unit of the title compound are different because of packing effects, as can be deduced from their geometric parameters and the puckering parameters of their diazepine and oxazinone rings. The heterocyclic diazepines adopt twisted boat-like conformations. Atomic deviations with respect to the plane defined by atoms N1, N2 and C9 in molecule *A* are 0.824 (3), 0.830 (2), 0.389 (3) and 0.921 (3) Å for atoms C1, C6, C7 and C8, respectively. However, atomic deviations with respect to the plane defined by atoms N3, N4 and C52 in molecule *B* are 0.777 (3), 0.785 (2), 0.399 (3) and 0.944 (2) Å for atoms C44, C49, C50 and C51, respectively. The conformations of the oxazinones were determined using the least-squares plane passing through atoms C11, C12 and O3 in molecule *A*, and that passing through atoms C54, C55 and

Acta Crystallographica Section C
ISSN 0108-2701 © 1998