Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

2,3,3a,4,9,9a-Hexahydro-9-phenylbenzo[*f*]indene derivatives

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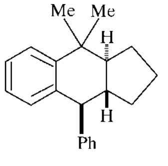
Received 31 January 2000
Accepted 13 March 2000

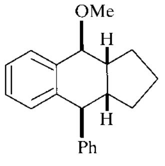
The title compounds, 3a,9a-*trans*-9,9a-*trans*-4,4-dimethyl-9-phenyl-2,3,3a,4,9,9a-hexahydrobenzo[*f*]indene, $C_{21}H_{24}$, (I), and 3a,4-*trans*-3a,9a-*cis*-9,9a-*trans*-4-methoxy-9-phenyl-2,3,-3a,4,9,9a-hexahydrobenzo[*f*]indene, $C_{20}H_{22}O$, (II), are products of the photoinduced electron-transfer reaction of 1,1-diphenyl-1,*n*-alkadienes. The molecular structures are in good agreement with those proposed from the reaction mechanisms. The central rings of the fused systems of both compounds take chair and boat conformations in (I) and (II), respectively. There are no remarkable short contacts shorter than the sum of the van der Waals radii in the crystals, but some weak C—H$\cdots\pi$ interactions are found.

Comment

Photoinduced electron-transfer reactions are recognized as versatile methods for generating radical cation species from electron-rich olefins and aromatic compounds (Neunteufel & Arnold, 1973; Majima *et al.*, 1981; Mattes & Farid, 1986; Hoffmann *et al.*, 1993; Heinemann & Demuth, 1997). Recently, it was found that 1,1-diphenyl-1,*n*-alkadienes (*n* = 6 or 7) were converted into 5/6/6 or 6/6/6 fused-ring systems with high stereoselectivity by photoirradiation in the presence of phenanthrene and 1,4-dicyanobenzene (Ishii *et al.*, 1998). In order to elucidate the molecular geometries of the photoreaction products, X-ray structure analyses of the title compounds, (I) and (II), were carried out. Moreover, these two compounds are considered to be good candidates for examining weak intermolecular interactions, since they have no remarkable pairs of hydrogen-bonding donors or acceptors.



(I)



(II)

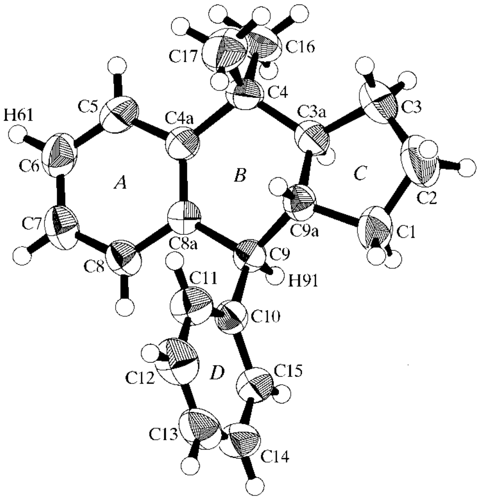


Figure 1
*ORTEP*II (Johnson, 1976) drawing of (I). Displacement ellipsoids are drawn at 50% probability for non-H atoms and H atoms are shown as small spheres of arbitrary radii.

The molecular structure of (I) is shown in Fig. 1, along with the numbering of the atoms and the abbreviations of the rings. There are no anomalous bond lengths and angles. Ring *B* takes a chair conformation. Ring *D* is bonded to ring *B* at the equatorial position and is arranged almost perpendicular to the fused-ring moiety. The two H atoms on the bridge heads between rings *B* and *C* are axial and are *trans* to each other. Ring *C* takes an envelope conformation, with C9a as the apical atom. The stereochemistry of (I) is in good agreement with that proposed from the reaction mechanism (Ishii *et al.*, 1998).

The crystal structure of (I) is shown in Fig. 2. There are no remarkable short contacts shorter than the sum of the van der Waals radii. This indicates that weak interactions play an important role in the formation of the crystal. Such weak interactions contribute over long distances exceeding the sum

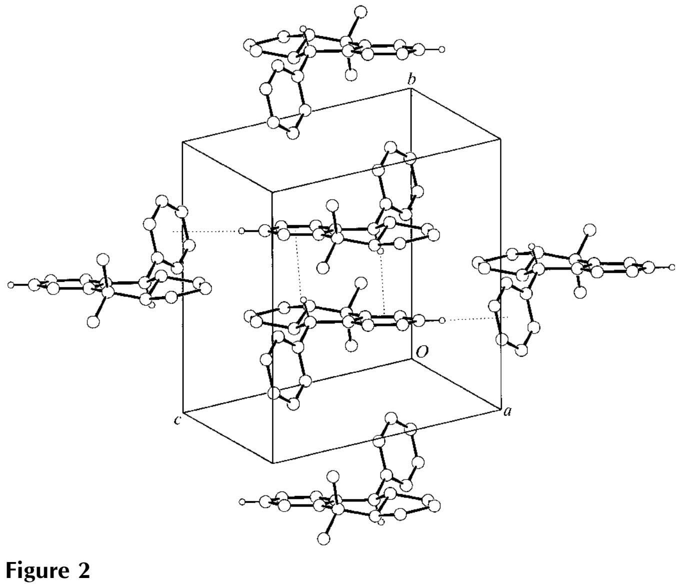


Figure 2
The crystal structure of (I). Broken lines indicate the C—H$\cdots\pi$ interactions.

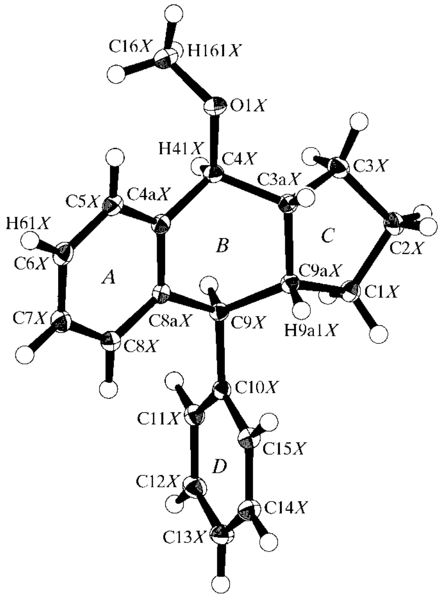


Figure 3
*ORTEP*II (Johnson, 1976) drawing of (II). Displacement ellipsoids are drawn at 50% probability for non-H atoms and H atoms are shown as small spheres of arbitrary radii.

of the van der Waals radii (Dunitz, 1996). The fused-ring moieties are arranged almost parallel to the (010) plane and those in molecules which are related by the inversion centre are face-to-face with each other, forming a dimer. The C9—H91 bond is directed towards ring *A* and C6—H61 is directed towards ring *D* of adjacent molecules; the detailed geometries (Table 1) are indicative of C—H···π interactions between them (Desiraju & Gavezzotti, 1989).

The molecular structure of (II) is shown in Fig. 3. Only the structure of one molecule, labelled *X* in Fig. 4, of the two crystallographically independent molecules is shown in Fig. 3. The structures of the independent molecules are almost the same, except for the conformations of the methoxy groups. There are no anomalous bond lengths and angles. Ring *B* adopts a boat conformation. The phenyl and methoxy groups are bonded to ring *B* at the equatorial positions to avoid steric repulsion between them and are *cis* with each other. The two H atoms on the bridge heads are bonded on the axial positions and are also *cis* with each other. This leads to an envelope conformation of ring *C* and the apical atom C2*X* is *exo* to ring *A*. The stereochemistry of (II) is in good agreement with that proposed from the reaction mechanism (Ishii, 1999).

The crystal structure of (II) is shown in Fig. 4. As in the case of (I), there are no remarkable short contacts shorter than the sum of the van der Waals radii. Each independent molecule is arranged alternately along the *b* axis and the fused-ring systems of molecules *X* and *Y*, as shown in Fig. 4, are almost parallel to the (100) and (01$\bar{1}$) planes, respectively. Three of the possible independent C—H···π interactions are shown in Fig. 4, with full details of the geometry in Table 2.

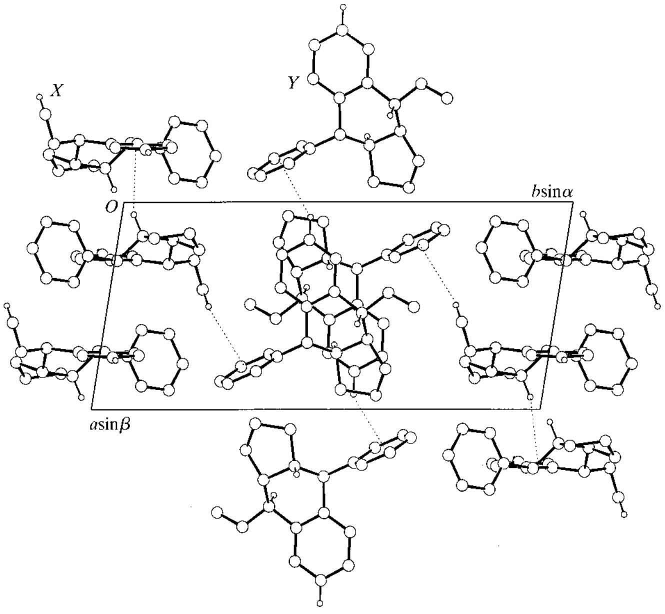


Figure 4
The crystal structure of (II) viewed along the *c* axis. Broken lines indicate the C—H···π interactions.

Experimental

The syntheses of the title compounds have been reported previously by Ishii *et al.* (1998). Crystals of (I) and (II) were obtained from solutions in methanol.

Compound (I)

Crystal data

$C_{21}H_{24}$
M_r = 276.40
Triclinic, $P\bar{1}$
a = 9.483 (2) Å
b = 11.042 (2) Å
c = 9.394 (2) Å
α = 104.14 (2)°
β = 101.45 (2)°
γ = 114.03 (2)°
V = 820.4 (3) Å^3
Z = 2
D_x = 1.119 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
θ = 14–15°
μ = 0.063 mm^{-1}
T = 298 K
Block, colourless
0.3 × 0.3 × 0.2 mm

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.920, $T_{\max}$ = 0.987
4073 measured reflections
3769 independent reflections
2621 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.019
$\theta_{\max}$ = 27.5°
$h = 0 \rightarrow 12$
$k = -14 \rightarrow 13$
$l = -12 \rightarrow 11$
3 standard reflections every 100 reflections intensity decay: 0.39%

Table 1
Hydrogen-bonding and short contact geometry (Å, °) for (I).

Cg indicates an aromatic ring centroid, *e.g.* *CgA* represents the centroid of ring *A*.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H91···C8$^{\rm i}$	0.98	3.01	3.848 (2)	144
C9—H91···*CgA*$^{\rm i}$	0.98	2.90	3.86	166
C6—H61···C14$^{\rm ii}$	0.93	3.00	3.687 (3)	131
C6—H61···*CgD*$^{\rm ii}$	0.93	3.04	3.91	157

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x, y, z-1$.

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.149$
$S = 1.025$
3769 reflections
207 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0726P)^2 + 0.1178P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Compound (II)

Crystal data

$C_{20}H_{22}O$
$M_r = 278.38$
Triclinic, $P\overline{1}$
$a = 9.0001$ (8) Å
$b = 19.287$ (2) Å
$c = 8.9918$ (8) Å
$\alpha = 96.654$ (8)°
$\beta = 101.494$ (7)°
$\gamma = 97.908$ (8)°
$V = 1498.4$ (2) Å^3

$Z = 4$
$D_x = 1.234$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 14$–15°
$\mu = 0.074$ mm^{-1}
$T = 100$ K
Block, colourless
0.30 × 0.19 × 0.12 mm

Data collection

Rigaku *AFC*-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ-scan North *et al.*, 1968
$T_{\min} = 0.965$, $T_{\max} = 0.991$
12 299 measured reflections
8747 independent reflections
6799 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.016$
$\theta_{\max} = 30°$
$h = -8 \rightarrow 12$
$k = -27 \rightarrow 26$
$l = -12 \rightarrow 12$
3 standard reflections every 100 reflections intensity decay: 0.73%

Table 2

Hydrogen-bonding and short contact geometry (Å, °) for (II).

Cg indicates an aromatic ring centroid, *e.g.* *CgA* represents the centroid of ring *A*.

D—H···A	D—H	H···A	D···A	D—H···A
C9aX—H9a1X···C5$X^{\rm i}$	0.990 (15)	3.067 (15)	3.9559 (15)	150.0 (11)
C9aX—H9a1X···$CgAX^{\rm i}$	0.990 (15)	2.87	3.74	148
C6X—H61X···C11$X^{\rm ii}$	0.980 (14)	2.861 (14)	3.6807 (15)	141.7 (11)
C6X—H61X···$CgDX^{\rm ii}$	0.980 (14)	2.76	3.63	148
C9aY—H9a1Y···C5$Y^{\rm iii}$	0.995 (14)	3.066 (14)	3.9790 (16)	153.2 (10)
C9aY—H9a1Y···$CgAY^{\rm iii}$	0.995 (14)	2.80	3.71	152
C4Y—H41Y···C4a$Y^{\rm iv}$	1.029 (14)	2.840 (14)	3.7503 (15)	147.6 (10)
C4Y—H41Y···$CgAY^{\rm iv}$	1.029 (14)	2.94	3.93	162
C6Y—H61Y···C10$Y^{\rm v}$	0.966 (16)	2.983 (17)	3.9331 (16)	167.9 (12)
C6Y—H61Y···$CgDY^{\rm v}$	0.966 (16)	2.67	3.53	150
C16X—H161X···C14$Y^{\rm iii}$	1.014 (17)	3.050 (16)	3.6331 (18)	117.6 (11)
C16X—H161X···$CgDY^{\rm iii}$	1.014 (17)	3.14	3.99	142

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $x, y, z-1$; (iii) $1-x, 1-y, 1-z$; (iv) $1-x, 1-y, -z$; (v) $1+x, y, z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.121$
$S = 1.040$
8747 reflections
555 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 0.3481P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

For both compounds, data collection: *MSC*/*AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC*/*AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1993); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990) for compound (I), *SIR*97 (Altomare *et al.*, 1999) for compound (II); for both compounds, program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SV* (Nemoto & Ohashi, 1993); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1579). Services for accessing these data are described at the back of the journal.

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