

9-Phenyl-3,4,4a,9a-tetrahydrotriptycene and 9-phenyl-1,2,3,4,4a,9a-hexahydrotriptycene

Shaoming Duan, Ronald J. Baker and John Masnovi*

Department of Chemistry, Cleveland State University, Cleveland, OH 44115, USA
Correspondence e-mail: j.masnovi@popmail.csuohio.edu

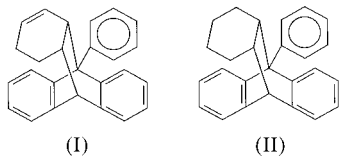
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The structure of 9-phenyl-3,4,4a,9a-tetrahydrotriptycene, $C_{26}H_{22}$, (I), exhibits regiochemistry consistent with a stepwise mechanism for its formation from photocycloaddition of 1,3-cyclohexadiene and 9-phenylanthracene. Bond distances involving the bridgehead C atoms are similar in (I) and the hydrogenated derivative, 9-phenyl-1,2,3,4,4a,9a-hexahydrotriptycene, $C_{26}H_{24}$, (II), with bonds to the quaternary-C atoms exhibiting significant elongation [1.581 (2) Å in (I) and 1.585 (2) Å in (II)]. The molecular geometry precludes significant σ - π overlap between the phenyl groups and the interannular bonds in both compounds, indicating that the origin of the bond lengthening is steric in nature.

Comment

The C12–C13 double bond of (I) is proximal to the phenyl substituent. This regiochemistry is consistent with a stepwise mechanism for formation of (I) which involves the more stable biradical intermediate (Kaupp & Teufel, 1980; Wang *et al.*, 1982). The cyclohexylene ring in (II) adopts a boat conformation. Two H atoms (determined by NMR decoupling experiments to be attached to C12 and C15) are found to be highly shielded in the NMR spectrum of (II).



The H12A and H15A *endo*-H atoms are assigned to these resonances at 0.22 and 0.78 p.p.m., respectively. A single hydrogen (H15A) of (I) appears at a similarly high field (0.84 p.p.m.). The large shieldings of H15A and H12A are ascribed to their positions within the anisotropic shielding regions of two (for H15A) or three (for H12A) neighboring benzene rings.

Bond distances about the C9 and C10 atoms are similar in (I) and (II), and indicate the presence of significant steric effects involving the phenyl group attached to C9 (see Figs. 1

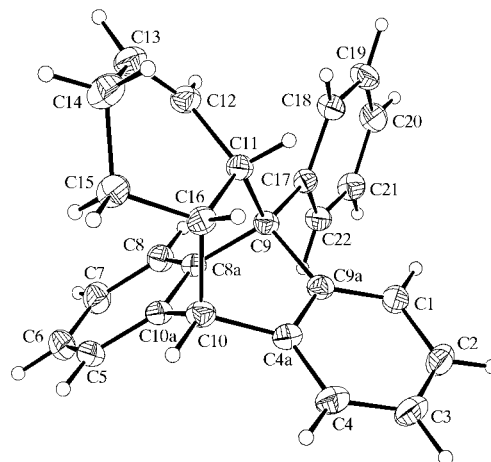


Figure 1
ORTEP (Johnson, 1976) representation of (I) with displacement ellipsoids at 30% probability showing the atom-numbering scheme.

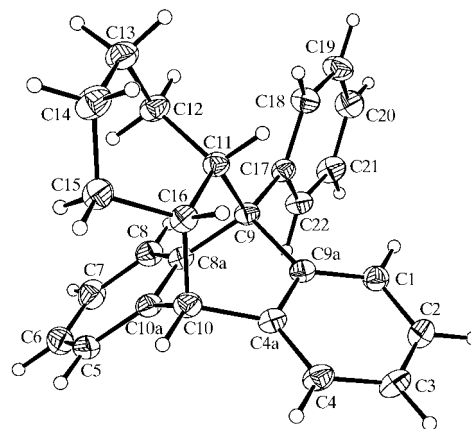


Figure 2
ORTEP (Johnson, 1976) of (II) with displacement ellipsoids at 30% probability showing the atom-numbering scheme.

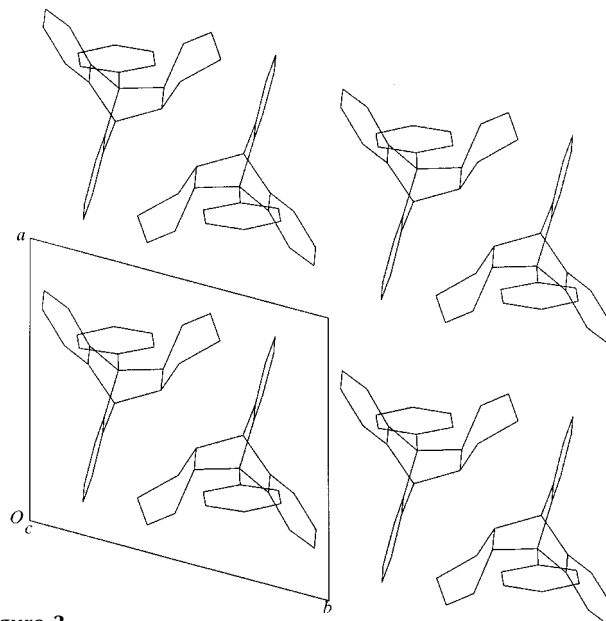


Figure 3
Packing diagram of (I), projection along the *c* axis.

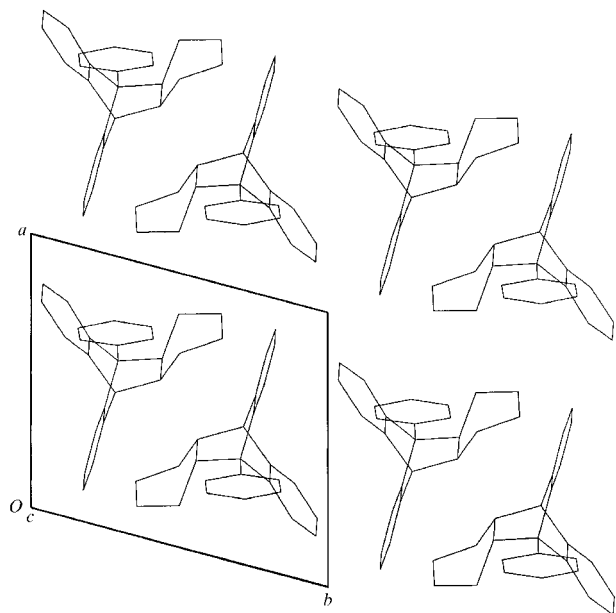


Figure 4
Packing diagram of (II), projection along the *c* axis.

and 2). Thus, the bond distances involving the bicyclic framework about C9 are observed to be 0.022–0.050 Å longer than the corresponding distances about C10. For example, the interannular C9–C11 bond is 1.581 (2) Å in (I) and 1.585 (2) Å in (II), whereas the related C10–C16 bond distances are 1.559 (2) Å in (I) and 1.550 (2) Å in (II). The phenyl substituents are rotated slightly from the plane defined by the bridgehead C atoms (C9, C10, C11 and C16). The dihedral angle between this plane and the plane of the phenyl groups is 12.08 (7)° in (I) and 13.39 (8)° in (II). This orientation precludes significant hyperconjugation between the phenyl substituent and the C9–C11 σ bond, and discounts σ – π through-bond coupling (Osawa *et al.*, 1983) as contributing to elongation of the bonds in these molecules (Baldrige *et al.*, 1997). One C atom (C12) of the double bond of (I) exhibits a close contact [3.022 (2) Å] with a C atom (C8a) of the adjacent phenyl ring. However, the resulting π – π interactions (Dougherty *et al.*, 1986), if any, do not contribute to lengthening of the C9–C11 bond, which is 0.004 Å longer in (II) (in which this bond is saturated) than in (I).

The cell constants of (I) and (II) are similar. Except for atoms near the double bond of (I), the structures of (I) and (II) are nearly superimposable. The resemblance of the polycyclic frameworks of (I) and (II) apparently allows for similar packing in the crystals (Figs. 3 and 4).

Experimental

A Pyrex irradiation vessel equipped with argon inlet and Teflon-coated magnetic stir-bar was charged with benzene (56 ml), 9-phenylanthracene (151 mg, 0.59 mmol), and 1,3-cyclohexadiene

(5.9 ml, 1.0 M) (Kaupp & Teufel, 1980). The solution was deaerated by purging with argon for 30 min prior to irradiation. Irradiation of the solution was performed with stirring under argon, using a Hanovia 450 W medium pressure mercury lamp housed in a water-cooled quartz immersion well. A cylindrical uranium glass filter was used to cut off light with wavelengths shorter than about 330 nm. The temperature of the solution during irradiation was maintained at 292 (2) K. Progress of the reaction was monitored by means of thin-layer chromatography and NMR spectroscopic analysis. When complete (3 h), the irradiation was stopped and the solvent was evaporated under reduced pressure. The crude product was chromatographed over Woelm (activity I) alumina. Products eluted fractionally with dichloromethane and petroleum ether. Fractions determined to contain adduct (I) were combined and recrystallized from dichloromethane-ethanol to afford colorless prisms, m.p. 459 K, $^1\text{H NMR}$ (chloroform-*d*): 7.56 (*m*), 7.47 (*m*), 7.31 (*m*), 7.11 (*m*), 6.92 (*m*), 6.25 (*d*, 7.7 Hz), 5.78 (*m*), 5.68 (*m*), 4.18 (*d*, 1.9 Hz), 3.07 (*bd*, 10.0 Hz), 2.42 (*m*), 1.88 (*m*), 1.67 (*m*), 1.23 (*m*), 0.84 p.p.m. (*m*). Adduct (I) (100 mg) was dissolved in 50 ml ethyl acetate in a 100 ml round-bottom flask containing a magnetic stir-bar, and 25 mg of 10% Pd/C powder was added. The stirred suspension was deaerated by repeated evacuation and charging with hydrogen gas. Hydrogenation was effected by allowing the mixture to stir for 24 h at room temperature under a slight positive pressure of hydrogen (although the initial uptake of hydrogen was rapid, suggesting that the reaction probably was complete in about 30 min). The product was collected by filtration through Celite, and the solvent was removed at reduced pressure. The crude product was passed through a short column of Woelm alumina (ICN, activity I) eluting with dichloromethane-petroleum ether. Fractions containing product (II) were combined and recrystallized from ethyl acetate to afford 87 mg (86%) of colorless needles, $^1\text{H NMR}$ (chloroform-*d*): 7.55 (*m*), 7.42 (*m*), 7.32 (*m*), 7.05–7.19 (*m*), 6.91 (*m*), 6.20 (*d*, 8.1 Hz), 4.06 (*d*, 8.1), 2.46 (*m*), 2.04 (*m*), 1.64 (*m*), 1.27–1.53 (*m*), 0.78 (*m*), 0.22 p.p.m. (*m*).

Compound (I)

Crystal data

$\text{C}_{26}\text{H}_{22}$	$Z = 2$
$M_r = 334.46$	$D_x = 1.248 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.3991$ (7) Å	Cell parameters from 25 reflections
$b = 9.7733$ (4) Å	$\theta = 7.9$ – 18.3°
$c = 10.5899$ (7) Å	$\mu = 0.07 \text{ mm}^{-1}$
$\alpha = 90.376$ (4)°	$T = 293 \text{ K}$
$\beta = 71.465$ (5)°	Prism, colorless
$\gamma = 104.463$ (5)°	$0.48 \times 0.47 \times 0.47 \text{ mm}$
$V = 890.29$ (10) Å ³	

Data collection

Nonius CAD-4 diffractometer	$h = -11 \rightarrow 10$
ω scans	$k = 0 \rightarrow 11$
3306 measured reflections	$l = -12 \rightarrow 12$
3120 independent reflections	5 standard reflections
2527 reflections with $I_{\text{net}} > 2\sigma(I_{\text{net}})$	frequency: 120 min
$R_{\text{int}} = 0.009$	intensity decay: 1.5%
$\theta_{\text{max}} = 24.93^\circ$	

Refinement

Refinement on F	$w = 1/[\sigma^2(F) + 0.0003F^2]$
$R = 0.042$	$(\Delta\rho)_{\text{max}} < 0.001$
$wR = 0.050$	$\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$
$S = 2.03$	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
2526 reflections	Extinction correction: Larson (1970)
236 parameters	Extinction coefficient: 0.79 (11)
H-atom parameters not refined	

Table 1
Selected geometric parameters (Å) for (I).

C4a—C10	1.497 (2)	C11—C12	1.512 (2)
C8a—C9	1.535 (2)	C11—C16	1.567 (2)
C9—C9a	1.547 (2)	C12—C13	1.319 (2)
C9—C11	1.581 (2)	C13—C14	1.484 (3)
C9—C17	1.528 (2)	C14—C15	1.519 (2)
C10—C10a	1.506 (2)	C15—C16	1.527 (2)
C10—C16	1.559 (2)		

Compound (II)*Crystal data*

$C_{26}H_{24}$	$D_x = 1.243 \text{ Mg m}^{-3}$
$M_r = 336.47$	Mo $K\alpha$ radiation
Triclinic, $P\bar{1}$	$\lambda = 0.70930 \text{ \AA}$
$a = 9.2213 (6) \text{ \AA}$	Cell parameters from 25 reflections
$b = 9.8777 (10) \text{ \AA}$	$\theta = 8.4\text{--}17.6^\circ$
$c = 10.7390 (8) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$\alpha = 90.738 (8)^\circ$	$T = 293 \text{ K}$
$\beta = 107.829 (6)^\circ$	Needle, colorless
$\gamma = 104.052 (7)^\circ$	$0.30 \times 0.30 \times 0.30 \text{ mm}$
$V = 899.28 (13) \text{ \AA}^3$	
$Z = 2$	

Data collection

Nonius CAD-4 diffractometer	$\theta_{\max} = 25.0^\circ$
ω scans	$h = -10 \rightarrow 10$
Absorption correction: none	$k = 0 \rightarrow 11$
3334 measured reflections	$l = -12 \rightarrow 12$
3147 independent reflections	3 standard reflections
2444 reflections with $I_{\text{net}} > 2\sigma(I_{\text{net}})$	frequency: 120 min
$R_{\text{int}} = 0.014$	intensity decay: 1.5%

Refinement

Refinement on F	$w = 1/[\sigma^2(F) + 0.0002F^2]$
$R = 0.041$	$(\Delta/\sigma)_{\max} < 0.001$
$wR = 0.044$	$\Delta\rho_{\max} = 0.15 \text{ e \AA}^{-3}$
$S = 1.94$	$\Delta\rho_{\min} = -0.17 \text{ e \AA}^{-3}$
2442 reflections	Extinction correction: Larson (1970)
236 parameters	Extinction coefficient: 0.57 (7)
H-atom parameters not refined	

H atoms were located but not refined [C—H 0.957–1.019 Å for (I) and 0.96–1.03 Å for (II)]; for (I) the temperature factors of the H atoms were refined in the early stages of refinement, but were fixed in the later stages.

For both compounds, data collection: *CAD-4-PC* (Enraf–Nonius, 1993); cell refinement: *SET4* and *CELDIM* in *CAD-4-PC*; data reduction: *DATRD2* in *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SOLVER* in *NRCVAX*; program(s) used to

Table 2
Selected geometric parameters (Å, °) for (II).

C4a—C10	1.503 (2)	C11—C12	1.528 (2)
C8a—C9	1.534 (2)	C11—C16	1.566 (2)
C9—C9a	1.542 (2)	C12—C13	1.524 (2)
C9—C11	1.585 (2)	C13—C14	1.522 (3)
C9—C17	1.527 (2)	C14—C15	1.514 (3)
C10—C10a	1.500 (2)	C15—C16	1.527 (2)
C10—C16	1.550 (2)		
C4—C4a—C9a	120.84 (15)	C4a—C10—C16	105.55 (13)
C4—C4a—C10	126.02 (15)	C10a—C10—C16	108.35 (13)
C9a—C4a—C10	113.10 (13)	C5—C10a—C8a	120.44 (15)
C8—C8a—C9	127.93 (14)	C5—C10a—C10	125.31 (15)
C8—C8a—C10a	118.66 (15)	C8a—C10a—C10	114.24 (14)
C9—C8a—C10a	113.24 (13)	C9—C11—C12	113.48 (13)
C8a—C9—C9a	106.04 (12)	C9—C11—C16	110.01 (12)
C8a—C9—C11	104.34 (12)	C12—C11—C16	110.19 (13)
C8a—C9—C17	115.20 (12)	C11—C12—C13	111.27 (14)
C9a—C9—C11	106.01 (12)	C12—C13—C14	113.13 (14)
C9a—C9—C17	110.25 (13)	C13—C14—C15	111.48 (14)
C11—C9—C17	114.25 (12)	C14—C15—C16	110.77 (15)
C1—C9a—C4a	118.81 (14)	C10—C16—C11	109.19 (12)
C1—C9a—C9	126.94 (14)	C10—C16—C15	112.30 (14)
C4a—C9a—C9	114.25 (14)	C11—C16—C15	112.45 (13)
C4a—C10—C10a	107.87 (13)		

refine structure: *LSTSQ* in *NRCVAX*; molecular graphics: *NRCVAX*; software used to prepare material for publication: *TABLES* in *NRCVAX* (version of January 94).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1498). Services for accessing these data are described at the back of the journal.

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