

Two strained hexahelicenophanes

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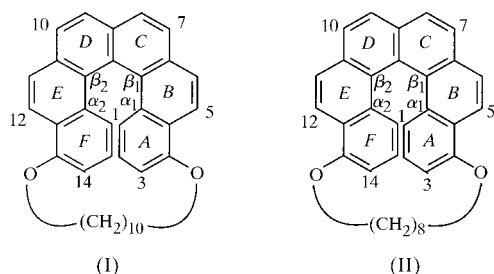
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The crystal structures of the [6]helicenes 4,13-(1,10-decamethylenedioxy)hexahelicene, $C_{36}H_{34}O_2$, (I), and 4,13-(1,8-octamethylenedioxy)hexahelicene, $C_{34}H_{30}O_2$, (II), show strong steric interactions between the terminal benzene rings and the polymethylenedioxy chains. The shortest ring *A* and *F* distances amount to 2.941 (3) and 2.902 (3) Å, respectively. The increased steric energy of the ground state is responsible for a significantly lower racemization barrier of (I) and (II) in comparison to the unsubstituted [6]helicene.

Comment

Recently, we succeeded in the preparation of hexahelicenophanes (Meier *et al.*, 1998) that have polymethylenedioxy chains between positions 4 and 13 in the terminal benzene rings *A* and *F*. It turned out that the racemization barriers ΔG^\ddagger of (I) and (II) at 473 K in 1,2,4-trichlorobenzene are 8.6 and 19.0 kJ mol⁻¹, respectively, lower than in the parent compound [6]helicene. This surprising result must be due to the special geometrical effects of the bridges.



The crystal structure analyses of (I) and (II) revealed different space groups, namely *Pbca* for (I) and *Pna2*₁ for (II). The benzene rings deviate significantly from planarity for both compounds. The helical structures become apparent from the twist angles along the averaged ring planes. Table 1 summarizes these data, whilst Table 2 gives the torsional angles α and β of the inner bonds. The corresponding values for the parent compound were obtained by de Rango *et al.* (1973) and van den Hark & Noordik (1973).

All three molecules display no crystallographic symmetry in the solid state, whereas NMR measurements in solution indicate a C_2 axis. The bond lengths of (I) and (II) resemble those measured for other helicenes; the inner bonds are always longer and the outer bonds shorter than 1.39 Å, the value in benzene (Laarhoven & Prinsen, 1984).

The crucial difference between [6]helicene and (I) and (II) is due to the steric interactions between the terminal rings *A* and *F* and the polymethylenedioxy chain. Table 3 gives a survey of the distances of C3 and C14 to the chain C atoms C17, C18, C19 and to C22/C24, C23/C25, C24/C26, respectively. The conformation of the bridges can be taken from the torsion angles in Table 4 (see also Figs. 1 and 2). The shorter bridge in (II) leads to the shorter distances and hence to the higher steric energy (Schwertel, 1997). Force-field calculations (Serena, 1992) yield a steric energy of 80.43 for (I) and 82.93 kJ mol⁻¹ for (II). The calculated ΔH_f^\ddagger values amount to -4.68 for (I) and +8.71 kJ mol⁻¹ for (II). Concerning the steric energies, the van der Waals interactions between the H atoms on C3, C14 and the methylene-H atoms on C17, 18, 19 and C22, C23, C24 (C24, C25, C26) are most important [shortest contacts: H3...H17A 2.03, H14...H26A 1.99 in (I) and H3...H172 2.09 Å in (II)]. The steric energy, particularly that of (II), raises the energy of the ground states. In the transition states of the racemization of (I) and (II), the bridges are rotated, the C_2 symmetry of the molecules in solution being transformed to a C_s symmetry (Meier *et al.*, 1998), and the steric interactions between the hexahelicene moiety and the bridge are lowered. Thus, we conclude that the decreasing racemization barrier in going from [6]helicene to (I) to (II) is due to the increase of the steric energy in the ground states in

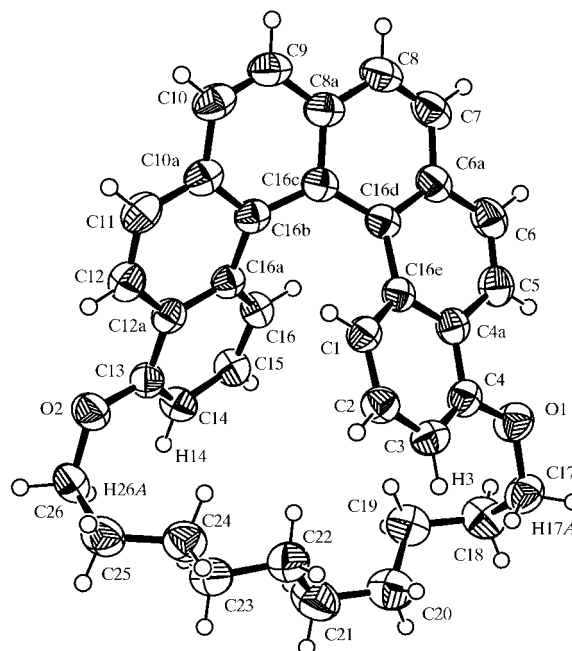


Figure 1
ORTEP (Johnson, 1976) view of (I). Displacement ellipsoids are shown at the 50% probability level and H atoms as spheres of arbitrary radii.

this series whereas the transition states are less affected. Because of the strain in the compounds (I) and (II), the structures in the crystalline state should be reasonably good models for the structures in solution.

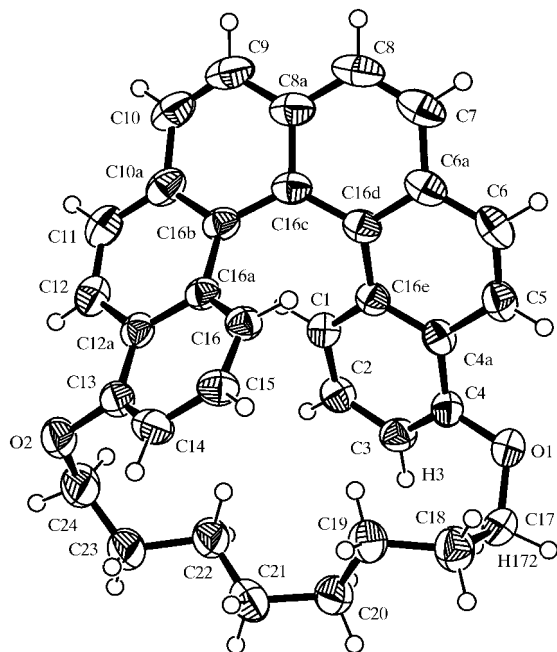


Figure 2
ORTEPII (Johnson, 1976) view of (II). Displacement ellipsoids are shown at the 50% probability level and H atoms as spheres of arbitrary radii.

Experimental

Compounds (I) and (II) were prepared according to the literature (Meier *et al.*, 1998) and recrystallized from chloroform.

Compound (I)

Crystal data

$C_{36}H_{34}O_2$
 $M_r = 498.63$
Orthorhombic, $Pbca$
 $a = 16.8803$ (5) Å
 $b = 16.1855$ (4) Å
 $c = 19.3262$ (6) Å
 $V = 5280.2$ (3) Å³
 $Z = 8$
 $D_x = 1.254$ Mg m⁻³

Cu $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 65\text{--}74^\circ$
 $\mu = 0.586$ mm⁻¹
 $T = 298$ (2) K
Rectangular block, yellow
 $0.56 \times 0.53 \times 0.35$ mm

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
5436 measured reflections
5436 independent reflections
4367 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 75.06^\circ$

$h = -21 \rightarrow 0$
 $k = 0 \rightarrow 20$
 $l = 0 \rightarrow 24$
3 standard reflections
frequency: 60 min
intensity decay: 5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.156$
 $S = 1.047$
5436 reflections
368 parameters
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0843P)^2 + 1.8869P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.46$ e Å⁻³
 $\Delta\rho_{\min} = -0.28$ e Å⁻³
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.00122 (13)

Table 1

Angles ($^\circ$) between the averaged planes (least squares) of the benzene rings A–F of the hexaheliceneophanes (I) and (II).

	AB	BC	CD	DE	EF	AF
[6]helicene	9.8	15.2	14.4	15.2	11.5	58.5
(I)	11.5 (1)	11.1 (1)	11.2 (1)	14.5 (1)	12.7 (1)	45.2 (1)
(II)	13.2 (1)	11.0 (1)	15.4 (1)	17.2 (1)	15.3 (1)	57.5 (1)

Table 2

α and β torsion angles ($^\circ$) of the hexaheliceneophanes (I) and (II).

	α_1	β_1	β_2	α_2
[6]helicene	11.2	30.0	30.3	15.2
(I)	-16.3 (3)	-24.0 (3)	-28.2 (3)	-18.2 (3)
(II)	16.0 (2)	25.4 (2)	35.9 (2)	18.4 (2)

Compound (II)

Crystal data

$C_{34}H_{30}O_2$
 $M_r = 470.58$
Orthorhombic, $Pna2_1$
 $a = 18.1447$ (4) Å
 $b = 12.3799$ (3) Å
 $c = 10.8228$ (3) Å
 $V = 2431.12$ (10) Å³
 $Z = 4$
 $D_x = 1.286$ Mg m⁻³

Cu $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 66\text{--}74^\circ$
 $\mu = 0.606$ mm⁻¹
 $T = 298$ (2) K
Rectangular block, yellow
 $0.41 \times 0.41 \times 0.32$ mm

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
4962 measured reflections
4962 independent reflections
4855 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 74.97^\circ$

$h = -22 \rightarrow 22$
 $k = -15 \rightarrow 15$
 $l = -13 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity decay: 5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.111$
 $S = 1.068$
4962 reflections
348 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0742P)^2 + 0.2614P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.34$ e Å⁻³
 $\Delta\rho_{\min} = -0.18$ e Å⁻³
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0050 (3)

Table 3

Non-bonding interactions (Å) between the benzene rings *A* and *F*, and between C14 and the corresponding chain segments.

	(I)	(II)
C3...C17	2.941 (3)	2.902 (3)
C3...C18	3.733 (3)	3.547 (3)
C3...C19	3.509 (3)	3.302 (3)
C1...C16	3.102 (3)	3.347 (2)
C2...C15	4.182 (3)	4.748 (2)
C14...C22		3.318 (3)
C14...C23		3.297 (3)
C14...C24	3.491 (3)	3.231 (3)
C14...C25	3.749 (3)	
C14...C26	2.925 (3)	

Table 4

Torsion angles (°) of the chain segments.

	(I)	(II)
C4—O1—C17—C18	93.8 (2)	-72.9 (2)
O1—C17—C18—C19	-73.3 (3)	78.5 (2)
C17—C18—C19—C20	-77.2 (3)	67.6 (2)
C18—C19—C20—C21	175.0 (2)	169.0 (2)
C19—C20—C21—C22	-80.9 (3)	76.7 (2)
C20—C21—C22—C23	-175.3 (2)	-178.8 (2)
C21—C22—C23—C24	175.0 (2)	164.1 (2)
C22—C23—C24—C25	163.3 (2)	
C23—C24—C25—C26	-73.3 (3)	
C24—C25—C26—O2	-66.1 (3)	
C25—C26—O2—C13	95.8 (2)	
C22—C23—C24—O2		-88.4 (3)
C23—C24—O2—C13		66.0 (3)

H atoms for (I) and (II) were placed at calculated positions and refined isotropically with a riding model.

For both compounds, data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CORINC* (Dräger & Gattow, 1971); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1383). Services for accessing these data are described at the back of the journal.

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