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(*P*,*M*)-1,2,3,9,10,11-Hexamethoxy-5,7-dihydrodibenz[*c*,*e*]oxepine and (*P*,*M*)-1,11-dimethyl-5,5,7,7-tetraphenyl-5,7-dihydrodibenz[*c*,*e*]oxepine

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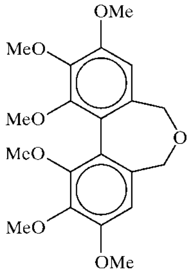
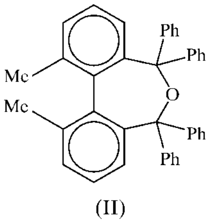
The title compounds, $C_{20}H_{24}O_7$ and $C_{40}H_{32}O$, respectively, are racemic oxepines, the molecules of which contain a chiral axis. Both molecules possess crystallographic C_2 symmetry and the seven-membered ring adopts a twisted-boat conformation.

Comment

Molecules containing a chiral axis are becoming increasingly important in asymmetric synthesis as chiral ligands or auxiliaries (Spring *et al.*, 2002), as well as being potential pharmaceuticals (Bringmann *et al.*, 2002). During our investigation of the synthesis of axially chiral amino alcohols by a simple ring-opening reaction of substituted dibenzo[*c*,*e*]oxepines (Furegati & Rippert, 2002), we obtained crystals of the title compounds (I) and (II). As we are interested in the conformation of dibenzo-annellated seven-membered rings and the angle between the aromatic ring planes in general (Schneider *et al.*, 2000), and, in particular, in the orientation of the phenyl substituents in the molecule of compound (II), we have determined the crystal structures of the title compounds.



(I)



(II)

In both (I) and (II), the bond lengths and angles are within normal ranges. Both molecules possess crystallographic C_2 symmetry, with the twofold axis passing through the middle of the biphenyl bond (which corresponds with the C3—C4 bond in the oxepine nomenclature) and the O atom of the seven-membered ring. In compound (I), the H atoms of the methyl group at atom C9 adopt two disordered nearly equally occupied orientations, which differ by a rotation of the group by approximately 50°.

The oxepine ring in both (I) and (II) adopts a twisted-boat conformation, in which one O—C bond and the opposing C—C bond that is fused to one of the phenyl rings form the floor of the boat [for example, atoms C1, C2, O1 and C7($1-x, y, \frac{1}{2}-z$)]. The choice of O—C bond is irrelevant because of the molecular C_2 symmetry. The angles between the planes defined by this four-atom floor and the three-atom bow plane (atoms C2, C7 and O1) of the boat are 48.22 (12) and 44.03 (14)° for (I) and (II), respectively, while the angles between the floor and the four-atom stern [atoms C1, C1($1-x, y, \frac{1}{2}-z$), C2($1-x, y, \frac{1}{2}-z$) and C7($1-x, y, \frac{1}{2}-z$) for (I), similarly for (II)] of the boat are 52.66 (8) and 54.72 (1)°, respectively. In (I), the angle between the planes of the biphenyl aromatic rings is 52.92 (6), whereas in (II), the angle is almost 9° greater, at 61.47 (8)°. The latter is a rather large angle for a biphenyl with a three-atom bridge and its possible cause is discussed below.

The Cambridge Structural Database (CSD, January 2004 release; Allen, 2002) contains the details of seven structures of 5,7-dihydrodibenz[*c*,*e*]oxepines (no dinaphth[*c*,*e*]oxepines were found). Two of these structures are transition-metal complexes and so were discarded. Out of the remaining five structures, only two had *peri* substituents at the biphenyl moiety (Schmid *et al.*, 1988; Roszak *et al.*, 1996). Both structures show a twisted-boat conformation; the angle between the four-atom floor and the three-atom bow plane is in the range 44.0–50.1°, while the angle between the floor and the four-atom stern of the boat is in the range 54.1–55.5°. The angle between the planes of the biphenyl aromatic rings in

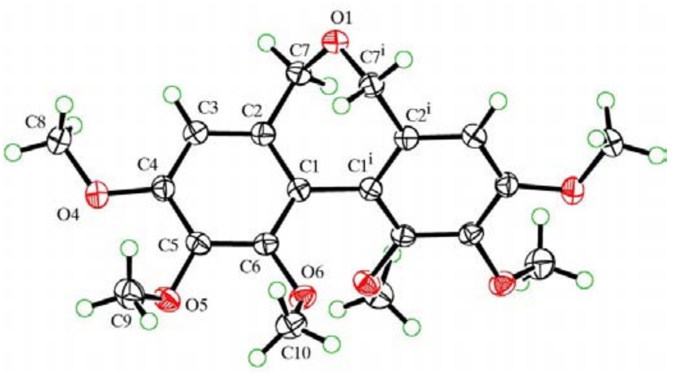


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. Only one of the disordered orientations of the C9 methyl H atoms is shown. [Symmetry code: (i) $1-x, y, \frac{1}{2}-z$.]

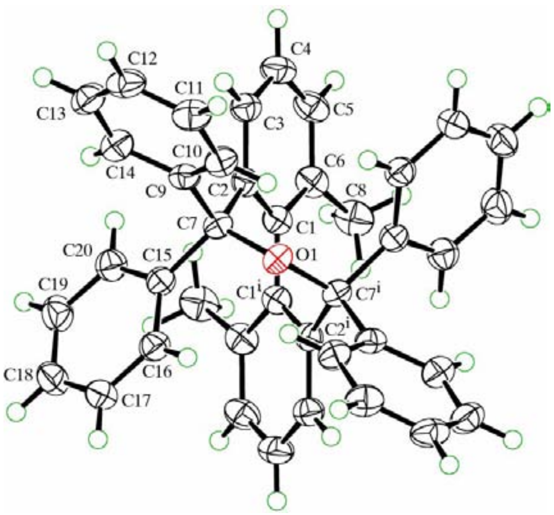


Figure 2
A view of the molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. [Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.]

these compounds is in the range 49.2–56.6°. All of these values are very similar to those in compounds (I) and (II). In the three structures having no substituents at the *peri* positions of the biphenyl moiety (Nieger *et al.*, 1998; Carey *et al.*, 2002), the outlined angles are again in similar ranges; floor/bow: 39.5–46.2°, floor/stern: 48.1–52.5° and biphenyl ring plane angle: 46.2–50.4°. Although two of these structures have a similar 5,5,7,7-tetraphenyl substitution pattern to compound (II), the angles between the planes of the biphenyl aromatic rings are no larger than usual, unlike that in (II). Therefore, the tetraphenyl substitution pattern alone does not introduce sufficient steric constraints to cause an increase in the biphenyl plane angle, but in combination with the addition of substituents at the *peri* position of the biphenyl moiety, as in compound (II), there is apparently sufficient steric strain to cause a significant increase in this angle.

A previous analysis of related dibenz- and dinaphthazepine derivatives (Schneider *et al.*, 2000), which have an N atom in the seven-membered ring in place of the O atom, revealed quite similar conformational properties for both the conformation of the seven-membered ring and the angle between the planes of the biphenyl (or binaphthyl) aromatic rings.

Experimental

The title compounds can be synthesized almost quantitatively by boiling the corresponding biphenyldiol in toluene for 12 h in the presence of catalytic amounts of toluenesulfonic acid with the reaction vessel connected to a water extractor (Wittig & Zimmermann, 1955). Compound (I) (m.p. 422 K) was crystallized from methyl *tert*-butyl ether–toluene (95:5) and compound (II) (m.p. 576 K) was crystallized from neat toluene.

Compound (I)

Crystal data

$C_{20}H_{24}O_7$
$M_r = 376.40$
Monoclinic, $C2/c$
$a = 15.3979$ (3) Å
$b = 10.3781$ (2) Å
$c = 11.8825$ (3) Å
$\beta = 109.9789$ (8)°
$V = 1784.56$ (7) Å^3
$Z = 4$
$D_x = 1.401$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2731 reflections
$\theta = 2.0$–30.0°
$\mu = 0.11$ mm^{-1}
$T = 160$ (1) K
Prism, colourless
$0.25 \times 0.20 \times 0.10$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans with κ offsets
25 172 measured reflections
2607 independent reflections
1974 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\rm max} = 30.0$°
$h = -21 \rightarrow 21$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.130$
$S = 1.06$
2605 reflections
127 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 0.8193P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.25$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}

Compound (II)

Crystal data

$C_{40}H_{32}O$
$M_r = 528.66$
Orthorhombic, $Pbcn$
$a = 16.6918$ (4) Å
$b = 9.6863$ (3) Å
$c = 17.5921$ (5) Å
$V = 2844.32$ (14) Å^3
$Z = 4$
$D_x = 1.235$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2853 reflections
$\theta = 2.0$–25.0°
$\mu = 0.07$ mm^{-1}
$T = 160$ (1) K
Prism, colourless
$0.22 \times 0.15 \times 0.12$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans with κ offset
25 719 measured reflections
2507 independent reflections
1920 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.063$
$\theta_{\rm max} = 25.0$°
$h = -19 \rightarrow 19$
$k = -11 \rightarrow 11$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.129$
$S = 1.04$
2502 reflections
188 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0767P)^2 + 0.6145P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.25$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.011 (2)

For each structure, the methyl H atoms were constrained to an ideal geometry (C—H = 0.98 Å), with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$, but were allowed to rotate freely about the parent C—O or C—C bond. All remaining H atoms were placed in geometrically idealized positions (C—H = 0.95–0.99 Å) and constrained to ride on their parent atoms, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. For (I), a difference Fourier map showed

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that the H atoms of the methyl group at atom C9 adopted two disordered orientations which differ by a rotation of the group by approximately 50°. Therefore, two idealized orientations were defined for these H atoms and constrained refinement of the site-occupation factors led to a value of 0.55 (2) for the major conformation. For (I) and (II), two and five low-angle reflections, respectively, had unexpectedly low intensities as a result of being partially obscured by the beam stop and were omitted.

For both title compounds, data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2004).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1701). Services for accessing these data are described at the back of the journal.

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