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Structural Investigation of Biphenyl Derivatives

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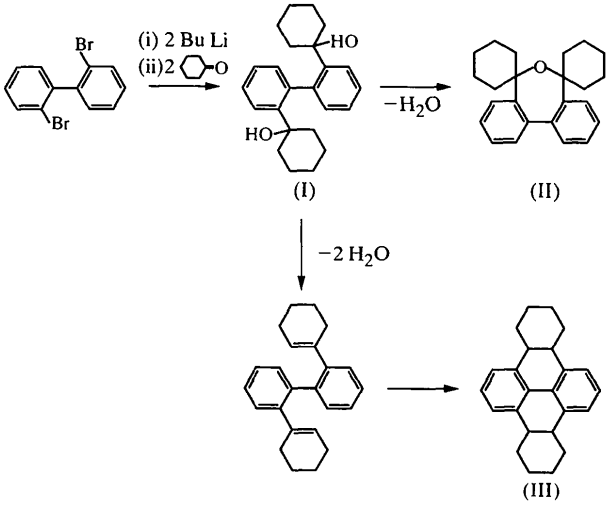
Abstract

The crystal structures of three sterically fixed biphenyls, 2,2′-biphenylbis(1-cyclohexanol), $C_{24}H_{30}O_2$, (I), 2,2;-7,7-bis(pentamethylene)dibenzo[*c*,*e*]dihydrooxepin {alternative name: 2′,7′-dihydrodispiro[cyclohexane-1,2′-dibenzo[*c*,*e*]oxepine-7′,1″-cyclohexane]}, $C_{24}H_{28}O$, (II), and 3b,4,5,6,7,7a,10b,11,12,13,14,14a-dodecahydrodibenzo[*e*,*l*]pyrene, $C_{24}H_{26}$, (III), are described. Results are compared with those from a conformational analysis performed using the molecular modelling program *MOMO*.

Comment

Biphenyls are of interest because of their importance in photophysics. They show strong absorption in the UV range but weak fluorescence. Steric fixing of biphenyls results in a bathochromic shift (Jussofie, 1984). High photostability and good laser quality require maximum delocalization of π electrons, which is achieved by a coplanar arrangement of the biphenyl unit.



The angle between the two phenyl rings of (I) is 88.5 (1)°. There is only one intramolecular hydrogen bond, from O21′ to O21 [O21′···O21 2.893 (2) Å and O21′–H21′···O21 164 (2)°]. The H21 atom does not form any hydrogen bonds at all. Both cyclohexane rings adopt a chair conformation with the hydroxyl groups in axial and the phenyl groups in equatorial positions.

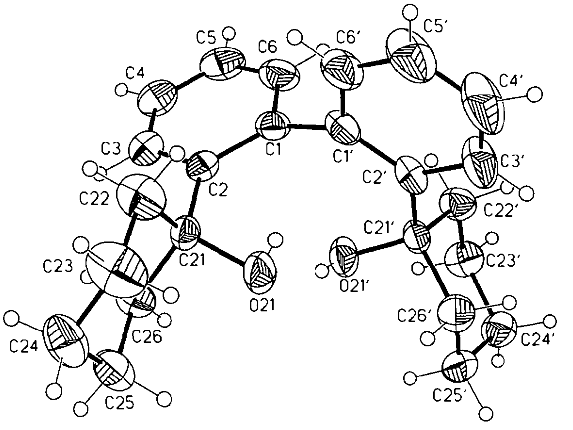
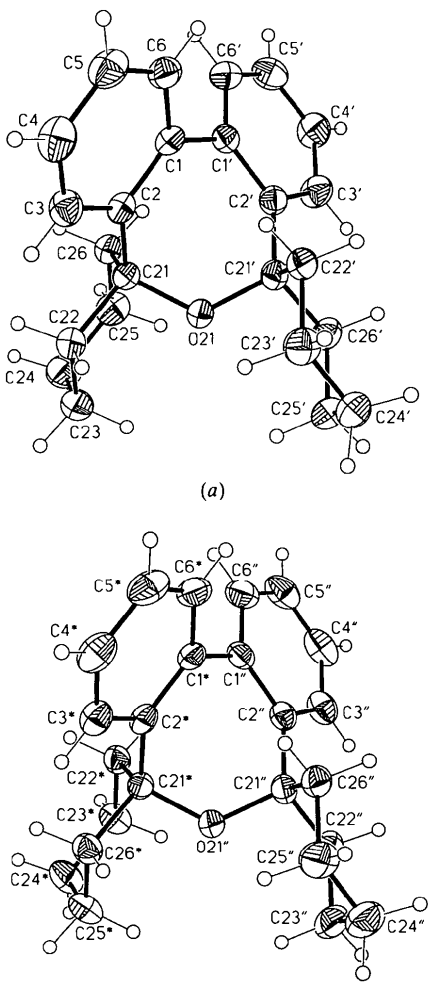


Fig. 1. Perspective view of (I) with the atom numbering; displacement ellipsoids are drawn at the 40% probability level.

There are two nearly identical molecules of (II) in the asymmetric unit (a least-squares fit of all non-H atoms in the two molecules gave an r.m.s. deviation of 0.05 Å). The molecules are related by a non-crystallographic centre of symmetry at approximately $(0,0,\frac{1}{4})$. Only the O atoms and the biphenyl fragments fulfill the centrosymmetry conditions. Each molecule shows C_2 symmetry with the twofold axis through the O atom and the centre of the biphenyl bond perpendicular to the *b* axis. The angles between the two planar phenyl rings are 47.7 (1) and 46.7 (1)° in the two independent molecules. The seven-membered oxepine ring adopts a twisted boat conformation, while the cyclohexane rings exhibit chair conformations.

Compound (III) possesses crystallographic C_i symmetry with the inversion centre located in the middle of the biphenyl bond. The cyclohexane rings exhibit chair forms, and the six-membered ring formed by atoms C1, C2, C21, C22, C6^{i} and C1^{i} [symmetry code: (i) $1-x$, $1-y$, $1-z$] exhibit a half-chair conformation, with atoms C2, C1, C1^{i} and C6^{i} in a common plane (r.m.s. deviation 0.013 Å). Atoms C21 and C22 deviate from this plane by 0.308 (2) and −0.321 (2) Å, respectively. The fixed biphenyl fragment is planar (r.m.s. deviation 0.055 Å). The H atoms at the racemic centres C21 and C22 are in axial positions.

For the conformational analysis with the molecular modelling program *MOMO* (Bolte *et al.*, 1991), 1000 starting permutations were generated by assigning random values for the five acyclic torsion angles of (I). The minimized structures were grouped into



(a)

(b)

Fig. 2. Perspective views of (*a*) molecule 1 and (*b*) molecule 2 of (II) with the atom numbering; displacement ellipsoids are drawn at the 40% probability level.

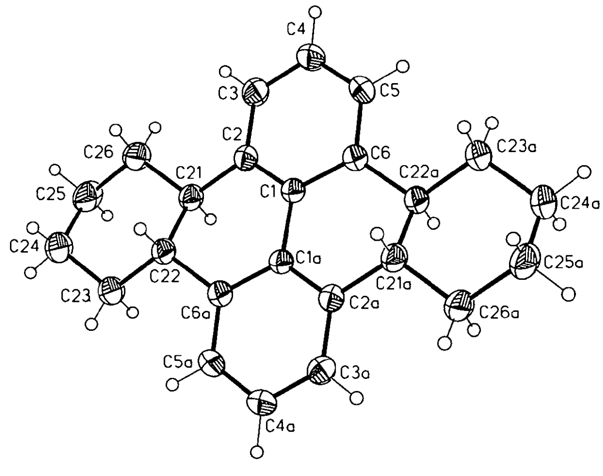


Fig. 3. Perspective view of (III) with the atom numbering; displacement ellipsoids are drawn at the 40% probability level.

133 clusters. The torsion angles vary markedly despite the small energy differences between the clusters, but they show the following preferences: C2—C1—C1'—C2' lies close to 90°, while values of about 60, 180 and −60° are found for C2—C21—O21—H21 and C2'—C21'—O21'—H21'. No preferred range can be assigned to C21—C2—C1—C1' and C1'—C2'—C21'—O21'. The conformations with a hydrogen bond are favoured energetically compared with those without one. The conformation with the lowest energy agrees well with the crystal structure (r.m.s. deviation 0.32 Å, fitting the atoms O21, C21, C2, C1, O21', C21', C2' and C1'), but there is no significant energy gap to the second conformation. The energy hypersurface of that molecule seems to contain many conformationally different minima of a similar energy.

For the conformational analysis of (II), the five non-aromatic torsion angles of the oxepine ring were varied. 2000 starting permutations were generated by opening the bond C21—O21. 58 permutations fulfilled the ring-closure criteria (distance C21—O21 between 1.0 and 2.0 Å, and angles C2—C21—O21 and C21—O21—C21' between 80 and 180°) and were minimized. The cluster analysis led to one cluster with 32 and its inverse with 26 objects. The minimized conformations agree excellently with the crystal structure (r.m.s. deviations of 0.026 and 0.028 Å for the two molecules, fitting the seven atoms of the oxepine ring). As expected, the program calculates nearly the same values for the symmetry-equivalent torsion angles, while the crystal structure is a little distorted from C_2 symmetry.

Since (III) is a rigid molecule with no torsional freedom at all, no conformational analysis was performed for this compound.

Experimental

The sterically-fixed biphenyls (II) and (III) were synthesized *via* (I) starting from 2,2'-dibromobiphenyl (Jussofie, 1984). Crystals of (I) and (II) were obtained by recrystallization from ethanol, and crystals of (III) were obtained from toluene.

Compound (I)

Crystal data

$C_{24}H_{30}O_2$
$M_r = 350.48$
Triclinic
$P\overline{1}$
$a = 10.082\,(2)$ Å
$b = 10.187\,(1)$ Å
$c = 10.304\,(2)$ Å
$\alpha = 88.50\,(2)°$
$\beta = 70.62\,(1)°$
$\gamma = 88.19\,(2)°$
$V = 997.7\,(3)$ Å^3
$Z = 2$
$D_x = 1.167$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 62 reflections
$\theta = 20$–$25°$
$\mu = 0.072$ mm^{-1}
$T = 295\,(2)$ K
Plate
0.90 × 0.40 × 0.20 mm
Colourless

Data collection

Stoe–Siemens AED diffractometer
Profile-fitting (Clegg, 1981) scans
Absorption correction: none
5638 measured reflections
3493 independent reflections
2592 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.021$
$\theta_{\rm max} = 25°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -12 \rightarrow 5$
3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.123$
$S = 1.061$
3493 reflections
241 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2 + 0.1181P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.159$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.220$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C1—C1′	1.510 (2)	C21′—O21′	1.4314 (18)
C21—O21	1.4400 (19)		
C1′—C1—C2—C21	−8.8 (2)	C1—C1′—C2′—C21′	−8.0 (2)
C1—C2—C21—O21	−27.0 (2)	C1′—C2′—C21′—O21′	−17.2 (2)
C2—C1—C1′—C2′	99.7 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O21′—H21′···O21	0.837 (15)	2.080 (16)	2.893 (2)	164 (2)

Compound (II)

Crystal data

$C_{24}H_{28}O$
$M_r = 332.46$
Monoclinic
$P2_1$
$a = 10.062$ (1) Å
$b = 16.307$ (1) Å
$c = 11.398$ (2) Å
$\beta = 97.83$ (1)°
$V = 1852.8$ (4) Å^3
$Z = 4$
$D_x = 1.192$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 58 reflections
$\theta = 20$–$25°$
$\mu = 0.070$ mm^{-1}
$T = 295$ (2) K
Block
0.90 × 0.60 × 0.40 mm
Colourless

Data collection

Stoe–Siemens AED diffractometer
Profile-fitting (Clegg, 1981) scans
Absorption correction: none
4271 measured reflections
3370 independent reflections
2891 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\rm max} = 25°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 19$
$l = -13 \rightarrow 2$
3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.091$
$S = 1.096$
3370 reflections
451 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0460P)^2 + 0.1183P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.151$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.172$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

C1—C2	1.410 (4)	C1″—C2″	1.410 (4)
C1—C1′	1.487 (4)	C1″—C1*	1.483 (4)
C2—C21	1.531 (4)	C2″—C21″	1.526 (4)
O21—C21	1.457 (3)	O21″—C21″	1.454 (3)
O21—C21′	1.458 (3)	O21″—C21*	1.456 (3)
C1′—C2′	1.407 (4)	C1*—C2*	1.405 (4)
C2′—C21′	1.526 (4)	C2*—C21*	1.530 (3)
C2—C1—C1′	121.6 (2)	C2″—C1″—C1*	122.0 (2)
C1—C2—C21	120.9 (2)	C1″—C2″—C21″	120.9 (2)
C21—O21—C21′	125.47 (18)	C21″—O21″—C21*	125.55 (17)
O21—C21—C2	111.3 (2)	O21″—C21″—C2″	112.0 (2)
C2′—C1′—C1	122.0 (2)	C2*—C1*—C1″	122.3 (2)
C1′—C2′—C21′	121.6 (2)	C1*—C2*—C21*	121.7 (2)
O21—C21′—C2′	111.2 (2)	O21″—C21*—C2*	111.3 (2)
C1′—C1—C2—C21	−2.1 (4)		
C21′—O21—C21—C2	−39.0 (3)		
C1—C2—C21—O21	64.8 (3)		
C2—C1—C1′—C2′	−46.0 (4)		
C1—C1′—C2′—C21′	−0.3 (4)		
C21—O21—C21′—C2′	−38.2 (3)		
C1′—C2′—C21′—O21	63.1 (3)		
C1*—C1″—C2″—C21″	−0.2 (4)		
C21*—O21″—C21″—C2″	−40.6 (3)		
C1″—C2″—C21″—O21″	63.5 (3)		
C2″—C1″—C1*—C2*	−45.0 (4)		
C1″—C1*—C2*—C21*	−2.9 (4)		
C21″—O21″—C21*—C2*	−36.0 (3)		
C1*—C2*—C21*—O21″	63.5 (3)		

Compound (III)

Crystal data

$C_{24}H_{26}$
$M_r = 314.45$
Triclinic
$P\bar{1}$
$a = 5.308$ (1) Å
$b = 7.781$ (1) Å
$c = 10.453$ (1) Å
$\alpha = 99.38$ (1)°
$\beta = 95.87$ (1)°
$\gamma = 99.93$ (1)°
$V = 415.8$ (1) Å^3
$Z = 1$
$D_x = 1.256$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 52 reflections
$\theta = 20$–$25°$
$\mu = 0.070$ mm^{-1}
$T = 295$ (2) K
Block
0.70 × 0.40 × 0.30 mm
Colourless

Data collection

Stoe–Siemens AED diffractometer
Profile-fitting (Clegg, 1981) scans
Absorption correction: none
$R_{\rm int} = 0.009$
$\theta_{\rm max} = 25°$
$h = -6 \rightarrow 0$
$k = -9 \rightarrow 9$
$l = -12 \rightarrow 12$

1474 measured reflections
1466 independent reflections
1168 reflections with $I > 2\sigma(I)$

3 standard reflections every 200 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.125$
$S = 1.066$
1466 reflections
110 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0610P)^2 + 0.0766P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.193$ e Å^{-3}
$\Delta\rho_{\min} = -0.143$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.066 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 4. *Selected geometric parameters (Å, °) for (III)*

C1—C1^{i}	1.480 (3)	C2—C21	1.5208 (19)

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

In all cases, rather large crystals were used because the specimens turned out to be very brittle and cracked into tiny pieces when we tried to cut them. All H atoms were located by difference syntheses and refined with fixed individual displacement parameters using a riding model [C—H(aromatic) = 0.93, C—H(secondary) = 0.97 and C—H(tertiary) = 0.98 Å], except for the hydroxyl H atoms in (I), whose coordinates were refined. As compound (II) contains only C, H and O atoms, and Mo $K\alpha$ radiation was used, its absolute structure could not be determined.

For all compounds, data collection: *DIF*4 (Stoe & Cie, 1984*a*); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1984*b*); program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1161). Services for accessing these data are described at the back of the journal.

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6-Amino-9-(carboxymethyl)-2-methoxypurine Methyl Ester†

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Abstract

The hydrogenolysis of 6-azido-9-(carboxymethyl)-2-methoxypurine methyl ester, (3), formed in a single step from 2,6-dichloro-9-(carboxymethyl)purine ethyl ester, (2), gave the title compound, $C_9H_{11}N_5O_3$, (1). The side chain attached at N9 avoids steric hindrance with the heterocycle by emerging almost orthogonally [C8—N9—C10—C11 −104.5 (2)°] and the amino group at N6 donates intermolecular hydrogen bonds to the ring N1 and ester carbonyl O11 atoms.

Comment

2,6-Dichloro-9-(carboxymethyl)purine ethyl ester, (2) (Chan *et al.*, 1995), with its displaceable Cl atoms, has provided a useful building block for the synthesis of base-modified intermediates (Sood *et al.*, 1997*a*,*b*) for incorporation into peptidic nucleic acids (Hyrup & Nielsen, 1996). At elevated temperatures, prolonged treatment of (2) in the presence of excess sodium azide, acetone and methanol yields predominantly 2,6-diazido-9-(carboxymethyl)purine ethyl ester through displacement of both chloro groups by azide. Two minor by-products arise from transesterification *in situ*, *i.e.* the methyl ester homologue (Sood *et al.*, 1997*a*) and a second methyl ester bearing one azido group and one methoxyl group attached at the heterocyclic ring. Hydrogenolysis of the methoxyl-containing intermediate converted the azido group to an amino group giving compound (1). We undertook the crystal structure determination of (1) to unambiguously establish the substitution pattern at the heterocyclic ring. This revealed that the amino and methoxyl groups were attached at C6 and C2, respectively, in (1) and that the azido group was attached at C6 in the precursor (3).

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† Alternative name: methyl 6-amino-2-methoxypurine-9-acetate.