organic compounds

3,4-(4-Methoxybenzo):8,9-benzo-bicyclo[4.4.1]undeca-3,8-dien-11-one ethylene acetal

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The title compound, 5-methoxyspiro[tetracyclo[8.8.1.0^{3,8}.-0^{12,17}]nonadeca-3,5,7,12,14,16-hexene-19,2′-[1,3]dioxolane], $C_{22}H_{24}O_3$, exhibits a twin-chair conformation with the aromatic rings overlying each other. Comparison of the dihedral angle between these two rings with those from previously reported [3.3]orthocyclophanes of this type suggests the presence of a weak attractive charge-transfer interaction between the two, different, stacked arenes.

Comment

We have recently reported the synthesis of a series of hydroxy[3.3]orthocyclophanes based on the diannelated bicyclo[4.4.1]undeca-3,9-dien-11-one skeleton (Liu et al., 2002), which were intended to model the phenoxyl radical co-factor of the enzyme galactose oxidase (GOase; Halcrow et al., 2000).

(I)
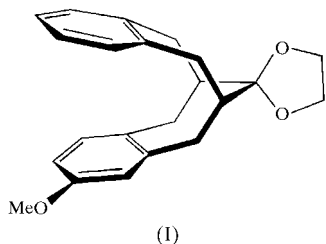
The conformational properties of this class of compounds make them ideal for this purpose. The parent 3,4:8,9-dibenzo-bicyclo[4.4.1]undeca-3,9-dien-11-ones adopt a boat–chair conformation, in which the two benzo groups are well separated. However, acetalation of the ketone group causes a switch to a twin-chair conformation, in which the two anne-lated rings overlie each other (Mataka et al., 2000). This should be an effective model for the phenoxyl moiety in the GOase-active site, which is sterically protected by a π–π interaction with a neighbouring tryptophan side chain. In our original study, we obtained crystal structures of two 3,4-(4-hydroxy-benzo):8,9-benzobicyclo[4.4.1]undeca-3,9-dien-11-one deriva-tives, but were unable to crystallize any of their acetals (Liu et

al., 2002). We were interested in obtaining such an analysis in order to determine whether substitution of one benzo ring results in any steric repulsions with the other benzo group in these compounds. With this in mind, we have synthesized and crystallized the title compound, 3,4-(4-methoxybenzo):8,9-benzobicyclo[4.4.1]undeca-3,8-dien-11-one ethylene acetal, (I).

The asymmetric unit of (I) contains one molecule which lies on a general position. As with other 3,4:8,9-dibenzobi-cyclo[4.4.1]undeca-3,9-dien-11-one acetals, (I) adopts a twin-chair conformation in the solid, in which the two benzo groups overlie each other (Fig. 1). All the bond lengths and angles in the molecule are within the expected ranges. However, the relative positions of the two benzo moieties in the molecule are of interest. This has been defined by the three parameters shown in Fig. 2 (Mataka et al., 2000). The closest approach of the two rings in (I) (labelled 'a' in Fig. 2), as defined by the closest C(bridgehead)···C(bridgehead) distance, is C6···C18 of 3.020 (3) Å. This lies within the range shown by the seven other structurally characterized 3,4:8,9-dibenzobicyclo[4.4.1]-undeca-3,9-dien-11-one acetal derivatives, which all show 'a' values in the range 3.00–3.10 Å (Mataka et al., 2000); this distance is well within the sum of the van der Waals radii for two benzene rings of 3.4 Å (Pauling, 1960). The pitch of the two benzo rings is defined by the closest $C_\beta \cdots C_\beta$ distance ('b' in Fig. 2), which is C4···C16 of 3.828 (3) Å in (I), and by the dihedral angle between the least-squares planes of the two rings ('θ' in Fig. 2), which is 19.77 (10)°. Comparison with the literature structures shows that these parameters are similar to those shown by compounds containing two different anne-lated rings, for which b = 3.80–4.02 Å and θ = 19.7–23.2° (Mataka et al., 1997; Taniguchi et al., 1999). In contrast, 3,4:8,9-dibenzobicyclo[4.4.1]undeca-3,9-dien-11-one acetals contain-ing two identical annelated rings show increased values of b = 4.09–4.32 Å and θ = 25.0–29.0° (Mataka et al., 1987, 2000; Taniguchi et al., 1998; Thiemann et al., 1999). This is unlikely to be an electrostatic effect, because the electron-donating methoxy group in (I) would be expected to make the substituted benzo ring more electron-rich, and thus increase the electrostatic repulsion between the two benzo groups. Rather, these differences presumably reflect a weak charge-
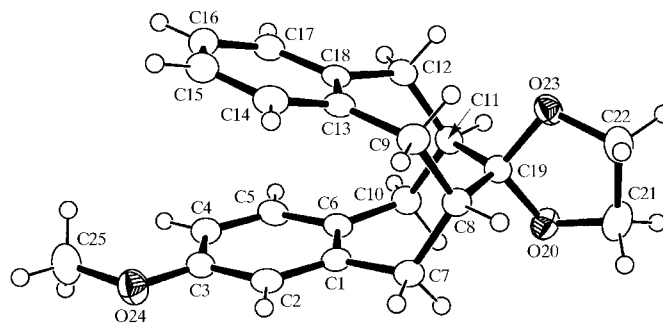

Figure 1
The molecular structure of the title compound with 50% probability displacement ellipsoids, showing the atom-numbering scheme employed.
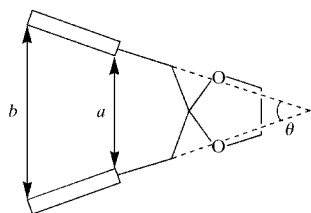
Figure 2
The parameters defining the relative positions of the annelated rings in [3.3]orthocyclophanes (Mataka *et al.*, 2000).

transfer interaction between the annelated rings in those compounds where these are different.

The methoxy substituent is not quite coplanar with its benzo ring, being slightly twisted towards the other benzo group; the relevant torsion angles are C2—C3—O24—C25 of 173.19 (19)° and C4—C3—O24—O25 of −6.2 (3)°. This probably reflects a close contact of 3.369 (2) Å between C25 and O20^i [symmetry code: (i) $1 - x$, $1 - y$, $\frac{1}{2} + z$], which is essentially equal to the sum of the van der Waals radii of a methyl group (2.0 Å) and an O atom (1.4 Å; Pauling, 1960). There are no other noteworthy intermolecular contacts in the structure.

Experimental

A mixture of 3,4-(4-methoxybenzo):8,9-benzobicyclo[4.4.1]undeca-3,9-dien-11-one (0.50 g, 1.7 mmol; Liu *et al.*, 2002), 1,2-dihydroxy-ethane (0.53 g, 8.0 mmol) and toluenesulfonic acid monohydrate (20 mg) in toluene (10 ml) was refluxed under N_2 for 24 h, using a condenser fitted with activated molecular sieves. The solvent was removed to give a white residue, which was recrystallized from MeOH (yield: 0.39 g, 68%). Found: C 53.4, H 4.5%; calculated for $C_{22}H_{24}O_3$: C 53.4, H 4.8%.

Crystal data

$C_{22}H_{24}O_3$	Mo $K\alpha$ radiation
$M_r = 336.41$	Cell parameters from 24 364
Orthorhombic, $Pca2_1$	reflections
$a = 13.3194 (3)$ Å	$\theta = 3.1–27.4°$
$b = 7.7311 (1)$ Å	$\mu = 0.09$ mm^{-1}
$c = 16.5545 (3)$ Å	$T = 150 (2)$ K
$V = 1704.68 (5)$ Å^3	Rectangular prism, colourless
$Z = 4$	$0.34 \times 0.23 \times 0.13$ mm
$D_x = 1.311$ Mg m^{-3}	

Data collection

Nonius KappaCCD area-detector diffractometer	1989 independent reflections
	1841 reflections with $I > 2\sigma(I)$
Area-detector scans	$R_{int} = 0.069$
Absorption correction: multi-scan (Blessing, 1995)	$\theta_{max} = 27.4°$
	$h = -17 \rightarrow 17$
$T_{min} = 0.971$, $T_{max} = 0.989$	$k = -9 \rightarrow 9$
24 364 measured reflections	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.049P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.034$	$+ 0.241P]$
$wR(F^2) = 0.084$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
1989 reflections	$\Delta\rho_{max} = 0.20$ e Å^{-3}
227 parameters	$\Delta\rho_{min} = -0.19$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.014 (3)

All H atoms were placed in calculated positions and refined using a riding model. The fixed C—H distances were aryl C—H = 0.95 Å, methyl C—H = 0.98 Å, secondary C—H = 0.99 Å and tertiary C—H = 1.00 Å. A Flack (1983) parameter of 0.8 (9) was refined from 1840 Friedel pairs, making it impossible to determine the absolute structure of the compound unambiguously. The Friedel opposites in the data were merged for the final cycles of least-squares refinement.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: local program.

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