a different φ angle for the crystal and each exposure of 10 s covered 0.3° in ω. The crystal-to-detector distance was 5.01 cm. Coverage of the unique set was over 91% complete to at least 28° in θ. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analysing the duplicate reflections, and was found to be negligible. H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; for H atoms, U(H) = 1.2U_{eq}(C or O) or 1.5U_{eq}(C) for methyl groups.

Data collection: *SMART* (Siemens, 1994*a*). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL/PC* (Siemens, 1994*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury Laboratory (Fletcher *et al.*, 1996) for access to the Cambridge Structural Database (Allen & Kennard, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1247). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.
Kumar, N., Mukherjee, S., Parmar, V. S. & Errington, W. (1996). *Acta Cryst.* C**52**, 2294–2296.
Naruto, S., Mizuta, H., Sawayama, T., Yoshida, T., Uno, H., Kawashima, K., Sohji, Y., Kadokawa, T. & Nishimura, H. (1982). *J. Med. Chem.* **25**, 1240–1245.
Naruto, S., Mizuta, H., Yoshida, T., Uno, H., Kawashima, K., Kadokawa, T. & Nishimura, H. (1983). *Chem. Pharm. Bull.* **31**, 2023–2032.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1994*a*). *SMART Software Reference Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994*b*). *SHELXTL/PC Reference Manual*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1995). *SAINT Software Reference Manual*. Version 4. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1998). C**54**, 1125–1127

9,10-Dihydro-1,4-dimethoxy-5,8-dimethyl-*cis*-9,10-diphenyl-9,10-anthracenediol, a Crowded Planar 9,10-Dihydroanthracene

CLAUS KRIEGER, ALEXANDER R. WARTINI AND FRANZ A. NEUGEBAUER

Arbeitsgruppe Organische Chemie, Max-Planck-Institut für Medizinische Forschung, Jahnstraße 29, D-69120 Heidelberg, Germany. E-mail: krieger@mixi.mpimf-heidelberg.mpg.de

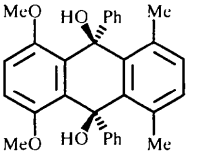
(Received 8 December 1997; accepted 23 February 1998)

Abstract

The crystal structure determination of the title compound, $C_{30}H_{28}O_4$, a key intermediate in the preparation of highly functionalized anthracenes, establishes the geometry at the central 9,10-positions to be *cis*. Owing to the buttressing effect of the methoxy and methyl groups in the *peri*-1,4,5,8-positions on the central 9,10-substituents, the 9,10-dihydroanthracene framework adopts a planar arrangement and the *cis*-9,10-phenyl groups assume a perpendicular conformation with regard to this plane.

Comment

The title compound, (1), and the corresponding *trans* isomer, which exhibit different reactivities, are key intermediates in the preparation of specifically functionalized anthracenes (Wartini, 1997). Therefore, an unambiguous elucidation of their geometry was required.



(1)

The crystal structure determination establishes a *cis* geometry for (1), and reveals that the tricyclic skeleton is essentially planar (Fig. 1). This is substantiated by the interplanar angle of 172.7 (5)° between the C1–C4, C4a, C9a and C5–C8, C8a, C10a arene planes, and by the relevant C10—C4a—C9a—C9 and C9a—C4a—C10—C10a torsion angles of 0.7 (2) and −1.9 (2)°, respectively. In the constrained almost-planar 'twisted pseudo-boat'-shaped 1,4-cyclohexadiene ring, the bridging C9 and C10 atoms deviate from the C4a, C10a, C8a, C9a plane by only 0.025 (1) and 0.016 (1) Å, respectively. The angles at the central ring C9 and C10 atoms are distorted from a tetrahedral arrangement, *e.g.* at C9, C8a—

C9—C9a 114.9 (2), O9′—C9—C91 111.1 (2), C8a—C9—C91 109.8 (2) and C8a—C9—O9′ 104.3 (2)°. This non-symmetric distortion is obviously influenced by the different steric requirements of the methyl and methoxy *peri* substituents. The significant repulsion of the *peri* substituents also forces the 9,10-phenyl substituents to assume an almost perpendicular arrangement with regard to the tricyclic framework, as indicated by the interplanar angle of 93.9° (95.3°) between the C4a, C8a, C9a, C10a and C91–C96 (C11–C16) planes. This steric interaction leads to a significant deviation of the 5,8-methyl groups from the C5···C8 axis [C6—C5—C5′ 116.9 (2) and C7—C8—C8′ 115.8 (2)°], as well as a bending of the phenyl groups in the direction of the methoxy O1′ and O4′ atoms. The hydroxyl H9′ and H10′ atoms form hydrogen bonds with the O1′ and O4′ atoms, respectively [O9′···O1′ 2.709 (2) and O10′···O4′ 2.699 (2) Å].

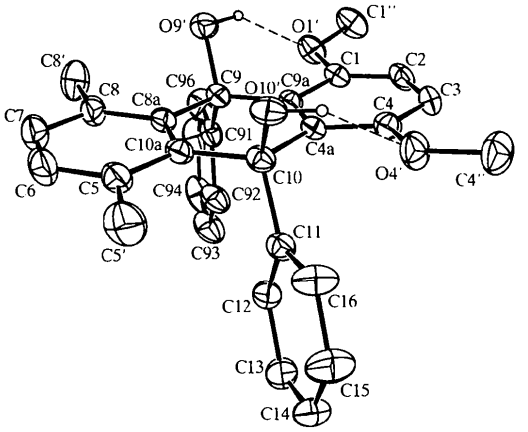


Fig. 1. View of the title molecule showing the atomic numbering scheme. H atoms have been omitted for clarity, except for those of the hydroxyl functions. Displacement ellipsoids are drawn at the 30% probability level.

A range of 9,10-dihydroanthracenes has already been examined in relation to their different conformations. The crystal structure of the parent 9,10-dihydroanthracene adopts a butterfly conformation with an angle of 145° between the planes of the benzene rings (Ferrier & Iball, 1954; Herbstein *et al.*, 1986). 9,10-Dihydro-9,9,10,10-tetrachloroanthracene, on the other hand, has been shown to have a planar ring skeleton (Yannoni & Silverman, 1966). This, however, does not hold for all 9,9,10,10-tetrasubstituted derivatives. Whereas the tricyclic framework of the 9,10-dihydro-*trans*-9,10-diphenylanthracenediol is also essentially planar, the crystal structure of the corresponding *cis* compound shows a butterfly conformation with an angle of 150° between the benzene-ring planes (Ahmad *et al.*, 1985). These variations in conformational preferences of the 1,9-dihydroanthracene framework have been rationalized in terms of two steric effects, namely, the 1,4-transannular effect of bulky substituents across the 1,4-cyclohexadiene ring, which favours ring flattening, and the *peri* interaction of large substituents with adjacent aryl ring H atoms, which apparently promotes greater puckering (Dhar *et al.*, 1992). The results for the title compound, (1), suggest that the buttressing effect of the *peri* substituents strengthens the transannular steric interaction of bulky substituents across the 1,4-cyclohexadiene ring, thus additionally favouring the planarization of the 9,10-dihydroanthracene framework.

Experimental

The title compound, *cis*-(1), and the corresponding *trans* isomer were prepared by addition of phenyllithium to 1,4-dimethoxy-5,8-dimethyl-9,10-anthraquinone and subsequent separation of the isomers by flash chromatography (Wartini, 1997). Repeated recrystallization of the *cis* isomer from acetone provided suitable crystals.

Crystal data

$C_{30}H_{28}O_4$
M_r = 452.55
Triclinic
$P\bar{1}$
a = 8.229 (3) Å
b = 11.522 (3) Å
c = 14.430 (4) Å
α = 66.33 (2)°
β = 79.23 (2)°
γ = 70.08 (2)°
V = 1176.0 (7) Å^3
Z = 2
D_x = 1.279 Mg m^{-3}
D_m = 1.300 Mg m^{-3}
D_m measured by flotation in heptane/tetrachloromethane
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 30 reflections
θ = 12–16°
μ = 0.078 mm^{-1}
T = 298 K
Prism
0.3 × 0.2 × 0.2 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4782 measured reflections
4611 independent reflections
3366 reflections with $I > 0.5\sigma(I)$
R_{int} = 0.017
θ_{max} = 25.03°
h = 0 → 10
k = −12 → 14
l = −17 → 17
3 standard reflections
frequency: 60 min
intensity decay: 2.9%

Refinement

Refinement on F
R = 0.068
wR = 0.056
S = 1.022
3366 reflections
335 parameters
H atoms riding
$w = 1/[\sigma^2(F_o) + 0.0021F_o^2]$
$(\Delta/\sigma)_{max}$ = 0.0235
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Extinction correction: none
Scattering factors from Waasmaier & Kirfel (1995)

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

C1—C9a	1.413 (2)	C8—C8′	1.513 (3)
C1—O1′	1.380 (2)	C8a—C9	1.531 (2)
C4—C4a	1.411 (2)	C8a—C10a	1.405 (3)
C4—O4′	1.383 (2)	C9—C91	1.551 (2)
C4a—C9a	1.392 (2)	C9—C9a	1.522 (2)
C4a—C10	1.526 (2)	C9—O9′	1.448 (2)
C5—C10a	1.417 (3)	C10—C11	1.544 (2)
C5—C5′	1.518 (3)	C10—C10a	1.534 (2)
C8—C8a	1.415 (2)	C10—O10′	1.449 (2)
C10—C4a—C9a	122.9 (2)	C10—C10a—C8a	122.7 (2)
C9—C8a—C10a	122.1 (2)	C9—C9a—C4a	122.9 (2)
C8a—C9—C9a	114.9 (2)	C10a—C10—C4a	114.4 (2)
C8a—C9—O9′	104.3 (2)	C4a—C10—O10′	107.1 (2)
C8a—C9—C91	109.8 (2)	C11—C10—C4a	109.4 (2)
C9a—C9—O9′	107.2 (2)	C10a—C10—O10′	104.4 (2)
C91—C9—C9a	109.3 (2)	C11—C10—C10a	110.4 (2)
C91—C9—O9′	111.1 (2)	C11—C10—O10′	111.0 (2)
C6—C5—C5′	116.9 (2)	C7—C8—C8′	115.8 (2)
C10a—C5—C5′	124.8 (2)	C8′—C8—C8a	125.9 (2)
C4—C4a—C9a—C1	0.5 (2)	C8—C8a—C10a—C5	1.5 (2)
C10—C4a—C9a—C9	0.7 (2)	C9—C8a—C10a—C10	1.7 (2)
C9a—C4a—C10—C10a	−1.9 (2)	C10a—C8a—C9—C9a	−2.7 (2)
C4—C4a—C10—C10a	174.1 (2)	C8—C8a—C9—C9a	175.1 (2)
C4a—C10—C10a—C5	−177.0 (2)	C8a—C9—C9a—C1	−174.0 (2)
C4a—C10—C10a—C8a	0.7 (2)	C8a—C9—C9a—C4a	1.6 (2)
C4—C4a—C10—O10′	58.7 (2)	C8—C8a—C9—O9′	58.0 (2)
C4—C4a—C10—C11	−61.7 (2)	C8—C8a—C9—C91	−61.1 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O9′—H9′···O1′	0.950 (2)	1.892 (2)	2.709 (2)	142.5 (2)
O10′ H10′···O4′	0.924 (2)	1.946 (2)	2.699 (2)	137.3 (2)

The title structure was solved by direct methods (*SIR*; Burla *et al.*, 1989) assuming the non-centrosymmetric space group $P1$; an *E* map revealed all non-H-atom positions, and aromatic H atoms were placed at geometrically calculated positions. The remaining hydroxyl and methyl H atoms emerged in a subsequent difference Fourier map after transformation to the centrosymmetric space group $P\bar{1}$. H atoms were included using a riding model.

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD-4 Operations Manual*. Data reduction: *maXus* (Mackay *et al.*, 1998). Program(s) used to refine structure: *maXus*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *maXus*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1274). Services for accessing these data are described at the back of the journal.

References

Ahmad, N., Goddard, R. J., Hatton, I. K., Howard, J. A. K., Lewis, N. J. & MacMillan, J. (1985). *J. Chem. Soc. Perkin Trans.* 1, pp. 1859–1863.

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.

Dhar, R. K., Sygula, A., Fronczek, F. R. & Rabideau, P. W. (1992). *Tetrahedron*, **48**, 9417–9426.

Enraf–Nonius (1977). *CAD-4 Operations Manual*. Enraf–Nonius, Delft, The Netherlands.

Ferrier, W. G. & Iball, J. (1954). *Chem. Ind. (London)*, pp. 1296–1297.

Herbstein, F. H., Kapon, M. & Reisner, G. M. (1986). *Acta Cryst.* B**42**, 181–187.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Mackay, S., Gilmore, C. J., Edwards, C., Tremayne, M., Stuart, N. & Shankland, K. (1998). *maXus. A Computer Program for the Solution and Refinement of Crystal Structures from Diffraction Data*. University of Glasgow, Scotland, Nonius BV, Delft, The Netherlands, and MacScience Co. Ltd, Yokohama, Japan.

Waasmaier, D. & Kirfel, A. (1995). *Acta Cryst.* A**51**, 416–431.

Wartini, A. R. (1997). Dissertation, University of Heidelberg, Germany.

Yannoni, N. F. & Silverman, J. (1966). *Acta Cryst.* **21**, 390–396.

Acta Cryst. (1998). C**54**, 1127–1130

Characterization of Quinoline Derivatives. II. 7-(4-Methyl-1-piperazinyl)-6*H*-[1]benzopyrano[3,4-*c*]quinoline†

GIANLUCA GIORGI,[a] ANDREA CAPPELLI,[b] MAURIZIO ANZINI[b] AND SALVATORE VOMERO[b]

[a]*Centro Interdipartimentale di Analisi e Determinazioni Strutturali, Università di Siena, via Aldo Moro, 53100 Siena, Italy, and* [b]*Dipartimento Farmaco Chimico Tecnologico, Università di Siena, via Banchi di Sotto 55, 53100 Siena, Italy. E-mail: ciads@unisi.it*

(Received 10 December 1996; accepted 9 March 1998)

Abstract

The title compound, $C_{21}H_{21}N_3O$, belongs to a new class of novel, potent and selective serotonin 5-HT_3 receptor antagonists based on the arylpiperazine skeleton. The molecular topology is not flat, but the molecule is bent in a helicene-like manner. The pyran ring has a half-boat conformation. This, together with the fusion to the quinoline nucleus, determines the orientation of the fused benzene ring, the role of which is important for the biological activity of the compound. The piperazine ring has a chair conformation. The crystal packing is stabilized by stacking interactions between the quinoline nuclei.

Comment

In the course of a research program aimed at synthesizing new serotonin (5-hydroxytriptamine, 5-HT) receptor ligands, we found that conformationally restrained arylquinoline derivatives may act as antagonists with enhanced selectivity towards the 5-HT_3 receptor subtype (Anzini *et al.*, 1995). We wish to report here on the crystal and molecular structure of 7-(4-methyl-1-piperazinyl)-6*H*-[1]benzopyrano[3,4-*c*]quinoline, (I), the most biologically active member of this class.

† Part I: Giorgi *et al.* (1997).