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Small Helical Aromatic Molecules. 2.* 5α-(α-Hydroxybenzyl)phenanthrene-4-carbolactone

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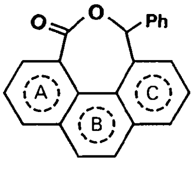
Abstract. $C_{22}H_{14}O_2$, $M_r = 310{\cdot}36$, monoclinic, $P2_1/c$, $a = 11{\cdot}436$ (2), $b = 13{\cdot}685$ (2), $c = 10{\cdot}167$ (2) Å, $\beta = 103{\cdot}22$ (2)°, $V = 1549{\cdot}0$ Å^3, $Z = 4$, $D_x = 1{\cdot}33$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}5$ cm^{-1}, $F(000) = 648$, $T = 293$ K. $R = 0{\cdot}049$ for 2574 unique $[> 4\sigma(F)]$ observed reflections. The phenanthrene skeleton is helical, and the atom C(27) is chiral; this would give rise to diastereoisomerism. The present structure contains only the *R, M* and *S, P* isomers. The major distortion of the aromatic framework is associated with the seven-membered fused ring, with a torsion angle C(4)C(4a)C(4b)C(5) of 20°. The seven-membered ring itself adopts an envelope conformation.

Introduction. Small helical aromatic molecules offer an opportunity to study the action of non-bonded steric repulsion. Close through-space contacts of substituent groups, such as those encountered in 4,5-disubstituted phenanthrenes, are expected to distort the generally planar carbon skeleton of phenanthrene and thus induce a helical structure. In a previous communication (Schrumpf & Jones, 1988), we studied the combined effect of a 4-carboxyl and a 5-propyl substituent on the geometry of the phenanthrene and the 9,10-dihydrophenanthrene skeletons. In the crystalline state, both molecules (PPC and DPPC respectively) are distinctly distorted and display a helical carbon skeleton. In the present study, we investigate the effect of an annellated seven-membered ring on the geometry of the aromatic system. Whereas in PPC and DPPC the steric repulsion originated from the interference between a carboxyl group and an sp^3-hybridized CH_2 group, in the present compound (PPL) these centres are connected by a covalent bond.



Experimental. The synthesis, separation and characterization of the title molecule will be published elsewhere (Schrumpf, 1987). Colourless crystals were obtained by liquid–liquid diffusion from acetic acid–water. The crystals slowly become pale yellow on standing.

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* Part 1: Schrumpf & Jones (1988).

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A hexagonal tablet-shaped crystal 0·75 × 0·45 × 0·3 mm was used to collect 3840 profile-fitted intensities (Clegg, 1981) on a Stoe–Siemens four-circle diffractometer (monochromated Mo $K\alpha$ radiation, $2\theta_{max}$55°). Of 3547 unique reflections (R_{int} 0·018), 2574 with $F > 4\sigma(F)$ were used for all calculations (programs *SHELXS*86 and *SHELX*76, Sheldrick, 1986, 1976). Cell constants were refined from 2θ values of 58 reflections in the range 20–23°. Three check reflections showed no significant intensity change. No correction for absorption.

The structure was solved by routine direct methods and refined to R 0·049, wR 0·050 [full-matrix refinement on F, non-H atoms anisotropic, H atoms included using a riding model with C—H 0·96 Å, but H(27) refined freely]. The weighting scheme was $w^{-1} = \sigma^2(F)+0·0002F^2$. Max. shift/e.s.d. 0·02; max. features in final difference map +0·15, −0·2 e Å^{-3}; 221 parameters; $S = 1·93$. Atomic scattering factors from *SHELX*76.

Discussion. Final atomic coordinates and derived structural parameters are given in Tables 1 and 2.* The molecule is depicted in Fig. 1, the packing diagram in Fig. 2.

The main result of the present study is that the aromatic skeleton of the title molecule is helical. In the two previously studied compounds PPC and DPPC (Schrumpf & Jones, 1988), the steric strain between the substituents was distributed over several C atoms of the aromatic systems, mainly in the centre of the molecule. In the present case, the rings A and C (see formula) are less distorted than those in PPC and DPPC (Fig. 3). The best planes through the six-membered rings have the following r.m.s. deviations: ring A: 0·029 (PPL), 0·037 (PPC); ring B: 0·036 (PPL), 0·080 (PPC); ring C: 0·029 (PPL), 0·036 Å (PPC). The major torsion-angle distortion is associated with the seven-membered ring, with torsion angles about C(4a)C(4b) of 20° [C(4)C(4a)C(4b)C(5)] and 12° [C(8a)C(4b)-C(4a)C(10a)]. On the opposite side of the molecule, the distortion is small; C(8a)C(9)C(10)C(10a) is only 5°. (Torsion-angle e.s.d.'s ≤ 0·5°.)

In PPL, because of the smaller dihedral angle between the rings A and C of 16°, the central bond C(4a)C(4b) (1·453 Å) is shorter than in PPC and DPPC by about 0·02 to 0·03 Å; it has the value observed in phenanthrene (1·457 Å; Kay, Okaya & Cox, 1971).

The seven-membered lactone ring assumes an envelope conformation with C(27) out of the somewhat boat-shaped lactone-ring plane (Fig. 4). The envelope form with the sp^3 oxygen out-of-plane, related to the observed structure by a pseudorotation, is not adopted in the solid. The COOC(27) ester grouping is approxi-

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic displacement parameters* (Å^2× 10^3)

	x	y	z	U_{eq}*
C(1)	1670 (2)	2573 (1)	−868 (2)	67 (1)
C(2)	2810 (2)	2828 (1)	−922 (2)	69 (1)
C(3)	3320 (2)	3658 (1)	−247 (2)	53 (1)
C(4)	2725 (1)	4203 (1)	546 (2)	40 (1)
C(4a)	1577 (1)	3897 (1)	729 (2)	40 (1)
C(4b)	908 (1)	4364 (1)	1611 (2)	39 (1)
C(5)	1447 (1)	4982 (1)	2698 (2)	40 (1)
C(6)	751 (1)	5437 (1)	3453 (2)	51 (1)
C(7)	−487 (2)	5280 (2)	3192 (2)	62 (1)
C(8)	−1006 (2)	4621 (2)	2239 (2)	59 (1)
C(8a)	−328 (1)	4137 (1)	1449 (2)	47 (1)
C(9)	−857 (2)	3381 (2)	534 (2)	59 (1)
C(10)	−205 (2)	2863 (1)	−150 (2)	62 (1)
C(10a)	1030 (2)	3098 (1)	−81 (2)	51 (1)
O(1)	3205 (1)	5626 (1)	2067 (1)	43 (1)
O(2)	3777 (1)	5616 (1)	167 (1)	51 (1)
C(21)	3313 (1)	5518 (1)	4432 (2)	40 (1)
C(22)	3510 (2)	6511 (1)	4581 (2)	53 (1)
C(23)	3937 (2)	6912 (2)	5855 (2)	63 (1)
C(24)	4167 (2)	6320 (2)	6974 (2)	62 (1)
C(25)	3984 (2)	5333 (2)	6838 (2)	58 (1)
C(26)	3562 (2)	4927 (1)	5569 (2)	49 (1)
C(27)	2797 (1)	5058 (1)	3078 (2)	38 (1)
C(28)	3271 (1)	5181 (1)	914 (2)	39 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and angles* (°)

C(1)—C(2)	1·363 (3)	C(1)—C(10a)	1·400 (2)
C(2)—C(3)	1·385 (2)	C(3)—C(4)	1·385 (2)
C(4)—C(4a)	1·430 (2)	C(4)—C(28)	1·489 (2)
C(4a)—C(4b)	1·453 (2)	C(4a)—C(10a)	1·424 (2)
C(4b)—C(5)	1·416 (2)	C(4b)—C(8a)	1·419 (2)
C(5)—C(6)	1·375 (2)	C(5)—C(27)	1·508 (2)
C(6)—C(7)	1·397 (2)	C(7)—C(8)	1·357 (3)
C(8)—C(8a)	1·403 (2)	C(8a)—C(9)	1·429 (2)
C(9)—C(10)	1·334 (3)	C(10)—C(10a)	1·434 (2)
O(1)—C(27)	1·448 (2)	O(1)—C(28)	1·339 (2)
O(2)—C(28)	1·210 (2)	C(21)—C(22)	1·379 (2)
C(21)—C(26)	1·386 (2)	C(21)—C(27)	1·506 (2)
C(22)—C(23)	1·388 (2)	C(23)—C(24)	1·373 (3)
C(24)—C(25)	1·368 (3)	C(25)—C(26)	1·386 (2)

C(10a)—C(1)—C(2)	121·5 (2)	C(3)—C(2)—C(1)	119·2 (2)
C(4)—C(3)—C(2)	121·5 (2)	C(4a)—C(4)—C(3)	120·4 (1)
C(28)—C(4)—C(3)	113·3 (1)	C(28)—C(4)—C(4a)	125·1 (1)
C(4b)—C(4a)—C(4)	125·5 (1)	C(10a)—C(4a)—C(4)	116·4 (1)
C(10a)—C(4a)—C(4b)	118·1 (1)	C(5)—C(4b)—C(4a)	123·2 (1)
C(8a)—C(4b)—C(4a)	118·9 (1)	C(8a)—C(4b)—C(5)	117·8 (1)
C(6)—C(5)—C(4b)	120·2 (1)	C(27)—C(5)—C(4b)	118·6 (1)
C(27)—C(5)—C(6)	121·0 (1)	C(7)—C(6)—C(5)	121·0 (2)
C(8)—C(7)—C(6)	119·8 (2)	C(8a)—C(8)—C(7)	121·0 (2)
C(8)—C(8a)—C(4b)	119·7 (2)	C(9)—C(8a)—C(4b)	119·7 (2)
C(9)—C(8a)—C(8)	120·5 (2)	C(10)—C(9)—C(8a)	121·4 (2)
C(10a)—C(10)—C(9)	121·1 (2)	C(4a)—C(10a)—C(1)	120·4 (2)
C(10)—C(10a)—C(1)	119·6 (2)	C(10)—C(10a)—C(4a)	119·9 (2)
C(28)—O(1)—C(27)	118·0 (1)	C(26)—C(21)—C(22)	119·1 (2)
C(27)—C(21)—C(22)	122·1 (1)	C(27)—C(21)—C(26)	118·8 (1)
C(23)—C(22)—C(21)	120·4 (2)	C(24)—C(23)—C(22)	119·9 (2)
C(25)—C(24)—C(23)	120·2 (2)	C(26)—C(25)—C(24)	120·1 (2)
C(25)—C(26)—C(21)	120·2 (2)	O(1)—C(27)—C(5)	109·4 (1)
C(21)—C(27)—C(5)	115·3 (1)	C(21)—C(27)—O(1)	107·6 (1)
O(1)—C(28)—C(4)	121·6 (1)	O(2)—C(28)—C(4)	121·2 (1)
O(2)—C(28)—O(1)	117·2 (1)		

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44432 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

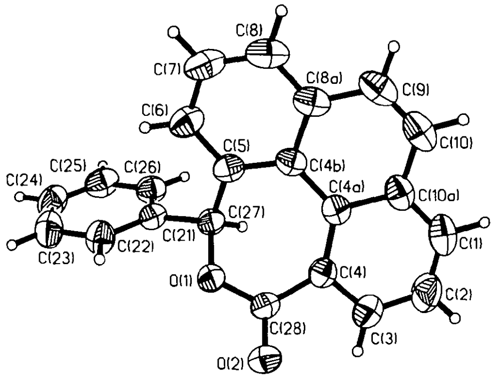

Fig. 1. Thermal-ellipsoid plot (50% level) of the title molecule (PPL), showing the atom-numbering scheme. H-atom radii are arbitrary.

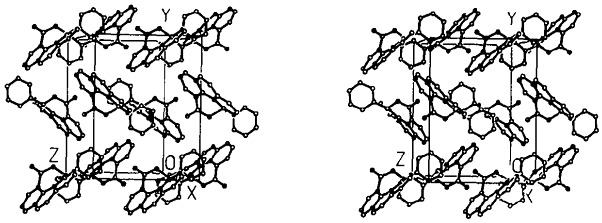

Fig. 2. Stereographic packing diagram of the title compound. H atoms are omitted for clarity.

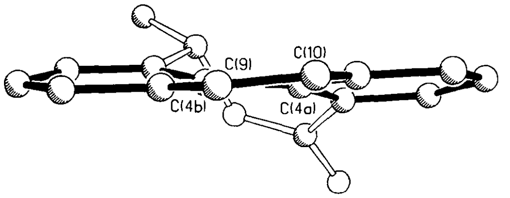

Fig. 3. A view of the phenanthrene skeleton of PPL, approximately in the direction joining the midpoints of C(9)C(10) and C(4a)C(4b), showing the helicity of the ring system.

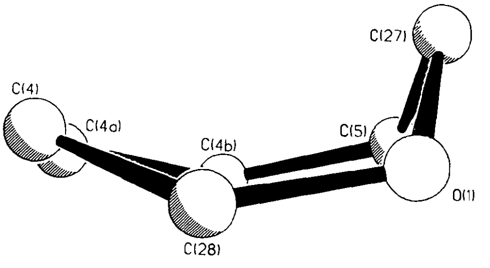

Fig. 4. A view of the lactone ring of PPL, approximately in the direction joining C(28) and C(4b), showing the conformation of the seven-membered ring. All other atoms are omitted for clarity.

mately coplanar (torsion angle of 169°) as in saturated seven-membered lactones, where the lactone also forms the flat portion of the molecule (Overberger & Kaye, 1967). In PPL, this is achieved at the expense of conjugative energy between the aromatic and ester groups, because the dihedral angle between these is 39°.

The chiral carbon C(27) gives rise to two possible diastereomers, depending on *P* or *M* helicity of the phenanthrene skeleton. The two diastereomers are interconvertible *via* a conformational change (without bond-breaking), *i.e.* by a transition from a *P* to an *M* helix. For the unsubstituted lactone, this is a low-energy process ($G^{\neq} < 21\ \text{kJ mol}^{-1}$; Schrumpf, unpublished results). The present structure contains only one independent molecule, which means that only one racemate (*R*, *M* and *S*, *P*) is present in the crystal (see Fig. 2). From molecular models, it is evident that the lactone ring of the other diastereomer would adopt another conformation. In the isomer observed here [the envelope form with C(27) up], the phenyl group is equatorial, but it will probably be axial in the other diastereomer, where it would assume an equatorial position only in the envelope form with O(1) up. It thus seems that the conformational energy in the lactone ring determines the diastereomeric preference.

The conformation of the phenyl ring relative to the substituents at C(27) is perpendicular, *i.e.* the bond C(5)C(27) is perpendicular to the phenyl-ring plane [C(26)C(21)C(27)C(5) is 88°]. Thus, the two aromatic systems in the molecule are also approximately orthogonal. The observed conformation about the C(21)C(27) bond is not unusual in phenyl-substituted compounds (see, *e.g.*, Kessler, 1968), although in simple benzyl derivatives this conformational problem is not yet settled.

As can be seen from the packing diagram (Fig. 2), the crystal structure is characterized by dipole–dipole attraction of the carbonyl groups of two molecules across an inversion centre and by phenyl-group stacking. The phenanthrene moieties are not involved in face-to-face contacts.

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