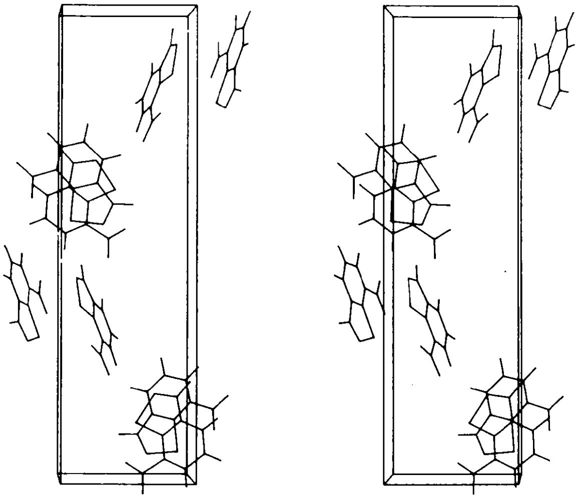

Fig. 2. Vue stéréoscopique selon [010] de la structure.

précédemment, notamment dans la structure du diséléniure de bis(*p*-nitrophényl) (Morris & Einstein, 1986). Ceux-ci concluent que ces distorsions ne paraissent pas résulter d'encombrement stérique mais plutôt de forces très faibles. Il en est de même, mais dans une moindre mesure, pour les deux autres substitutions sur le benzène: C(7)—C(6) et N(1)—C(2). C(7) est hors du plan *P*2 avec les écarts suivants: 0,035 (8) (*A*) et 0,035 (9) Å (*B*), tandis que N(1) dévie de 0,037 (7) (*A*) et −0,018 (8) Å (*B*). On peut considérer l'ensemble de la molécule comme plane. Aucun angle de torsion n'a une valeur moyenne calculée sur *A* et *B* dépassant 5 (1)°, en valeur absolue. L'ensemble des interactions intermoléculaires correspond à des liaisons du type van der Waals. Les distances intermoléculaires les plus courtes sont O(11)···O(13) $(-1+x, y, z)$ et N(1)···O(3) $(y, -x, 0{,}25+z)$, qui valent toutes deux 3,07 (2) Å. La Fig. 2 montre une vue (010) de la structure.

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Small Helical Aromatic Molecules. 1. 5-Propylphenanthrene-4-carboxylic Acid (PPC) and 5-Propyl-9,10-dihydrophenanthrene-4-carboxylic Acid (DPPC)

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Abstract. PPC, $C_{18}H_{16}O_2$, $M_r = 264{\cdot}3$, monoclinic, $P2_1/c$, $a = 9{\cdot}966$ (2), $b = 12{\cdot}666$ (3), $c = 10{\cdot}689$ (2) Å, $\beta = 92{\cdot}02$ (2)°, $V = 1348{\cdot}4$ Å^3, $Z = 4$, $D_x = 1{\cdot}30$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}5$ cm^{-1}, $F(000) = 560$, $T = 293$ K. $R = 0{\cdot}054$ for 1668 unique [$>4\sigma(F)$] observed reflections. DPPC, $C_{18}H_{18}O_2$, $M_r = 266{\cdot}4$, monoclinic, $P2_1/c$, $a = 9{\cdot}736$ (3), $b = 12{\cdot}795$ (5), $c = 11{\cdot}073$ (2) Å, $\beta = 94{\cdot}52$ (2)°, $V = 1375{\cdot}4$ Å^3, $Z = 4$, $D_x = 1{\cdot}29$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}7$ cm^{-1}, $F(000) = 568$, $T = 293$ K. $R = 0{\cdot}055$ for 1749 unique observed reflections. The compounds are to a good approximation isostructural, although the helicity of DPPC is greater than that of PPC. The helicity is induced by the bulky substituents at C(4) and C(5); the steric strain is relaxed primarily by conformational rotation of the substituent groups,

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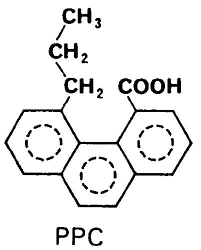
but also by deformations of bond lengths, bond angles and torsion angles. Both molecules form the usual carboxylic acid dimers by hydrogen bonding.

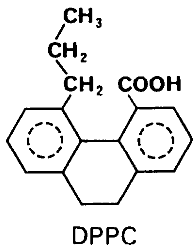
Introduction. Although hexahelicene is considered the lowest member of the helicenes (compounds with *ortho*-annellated aromatic rings) (Newman & Lednicer, 1956), molecules having fewer than six such rings may well have helical structures if suitably substituted. Phenanthrene is nearly planar in the solid state, *i.e.* the repulsion between the H atoms in the 4- and 5-positions is too small to cause an appreciable deviation of the aromatic system from planarity. Recently, a preliminary report of the crystal structure of 4,5-dimethylphenanthrene has appeared (Takegoshi, Imashiro, Terao & Saika, 1984). The molecule is distinctly non-planar. It is thus interesting to study the effect of bulkier substituents at C(4) and C(5) on the extent of helical deviation from planarity. We would also like to use these deformations as a gauge for the steric requirements of various substituents.

Since only a few 4,5-disubstituted phenanthrenes are known and the chemistry at these positions is not well developed, a project was initiated to synthesize appropriate model compounds. These can be used to investigate the transition of the phenanthrene ring system into a helical structure on substitution by various functional groups at the 4- and 5-positions. Comparison between the phenanthrene and the corresponding 9,10-dihydrophenanthrene derivatives should furnish information about the steric pressure between the substituents, which is expected to be somewhat relaxed in the bridged biphenyl system of the 9,10-dihydrophenanthrenes.

In the present communication, we report X-ray studies of 5-propylphenanthrene-4-carboxylic acid (PPC) and 5-propyl-9,10-dihydrophenanthrene-4-carboxylic acid (DPPC).



PPC



DPPC

Experimental. The synthesis and characterization of the two title compounds will be published elsewhere (Schrumpf, 1987). Colourless prisms of PCC and DPPC were obtained by liquid–liquid diffusion with acetic acid–water.

PPC: A colourless prism 0·55 × 0·4 × 0·25 mm was used to collect 2591 profile-fitted intensities (Clegg, 1981) on a Stoe–Siemens four-circle diffractometer (monochromated Mo $K\alpha$ radiation, $2\theta_{\max}$ 50°). Of 2368 unique reflections ($R_{\rm int}$ 0·028), 1668 with $F > 4\sigma(F)$ were used for all calculations (programs *SHELXS*86 and *SHELX*76, Sheldrick, 1986, 1976). Three check reflections showed no intensity change. No correction for absorption. The cell constants were refined from 2θ values of 40 reflections in the range 20–23°.

The structure was solved by routine direct methods and refined on F to R 0·054, wR 0·053 (non-H atoms anisotropic, H atoms included using a riding model with C—H 0·96 Å, H—C—H 109·5°). The weighting scheme was $w^{-1} = \sigma^2(F) + 0{\cdot}00025F^2$. Max. shift/e.s.d. 0·001; max. features in final difference map ±0·2 e Å^{-3}; 187 parameters; $S = 1{\cdot}86$. Atomic scattering factors from *SHELX*76.

DPCC: as for PPC, but with the following differences: crystal 0·8 × 0·5 × 0·3 mm, 3614 reflections, 2418 unique ($R_{\rm int}$ 0·055), 1749 observed, program system *SHELXTL* (Sheldrick, 1978), R 0·055, wR 0·055, weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}0002F^2$, max. shift/e.s.d. 0·003, max. features in final difference map +0·2, −0·25 e Å^{-3}, 187 parameters, $S = 1{\cdot}59$.

Discussion. Final atomic coordinates and derived bond lengths and angles are presented in Tables 1 and 2.* The molecules are illustrated in Figs. 1 and 2. The compounds are essentially isostructural.

The main result is that both title molecules are helical. The propyl and the carboxyl group point towards opposite faces of the aromatic skeleton. In the following, we shall first discuss the main features of the two molecules separately.

5-*Propylphenanthrene*-4-*carboxylic acid* (*PPC*)

In non-symmetrical molecules, there are different ways of quantitatively defining the extent of helicity. The linear deviation of C(4) and C(5) from a 'best' plane might be considered. We calculated these deviations from differently defined planes. Plane (I) was calculated including all aromatic C atoms. Plane (II) included all aromatic C atoms except C(4), C(5), C(8a), C(9), C(10) and C(10a), for which the largest out-of-plane deviations could be expected. Plane (III) was chosen to include the long axis of the molecule through C(2), C(4a), C(4b) and C(7) and the midpoint of the bond C(9)C(10). The deviations of the heavy atoms from these planes are listed in Table 3.

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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 44431 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic displacement parameters* (Å² × 10³)

	PPC				DPPC			
	x	*y*	*z*	U_{eq}*	*x*	*y*	*z*	U_{eq}*
C(1)	5848 (3)	4676 (3)	6663 (2)	57 (1)	6049 (2)	4319 (2)	6554 (2)	52 (1)
C(2)	5086 (3)	5519 (3)	7003 (2)	57 (1)	5360 (2)	5204 (2)	6846 (2)	52 (1)
C(3)	3694 (3)	5465 (2)	6814 (2)	48 (1)	3958 (2)	5235 (1)	6635 (2)	44 (1)
C(4)	3087 (2)	4550 (2)	6355 (2)	37 (1)	3215 (2)	4363 (1)	6198 (2)	35 (1)
C(4a)	3851 (2)	3626 (2)	6150 (2)	37 (1)	3902 (2)	3410 (1)	6028 (2)	35 (1)
C(4b)	3288 (2)	2582 (2)	5834 (2)	36 (1)	3225 (2)	2379 (1)	5743 (2)	34 (1)
C(5)	2050 (2)	2186 (2)	6242 (2)	38 (1)	2057 (2)	2007 (1)	6293 (2)	37 (1)
C(6)	1610 (3)	1208 (2)	5803 (2)	51 (1)	1561 (2)	1017 (1)	5955 (2)	47 (1)
C(7)	2360 (3)	602 (2)	4990 (3)	58 (1)	2175 (2)	403 (2)	5134 (2)	55 (1)
C(8)	3603 (3)	926 (2)	4697 (2)	56 (1)	3354 (2)	745 (1)	4660 (2)	49 (1)
C(8a)	4119 (3)	1888 (2)	5146 (2)	46 (1)	3909 (2)	1712 (1)	4977 (2)	42 (1)
C(9)	5519 (3)	2121 (3)	5050 (3)	63 (1)	5289 (2)	2037 (2)	4596 (2)	53 (1)
C(10)	6082 (3)	2926 (3)	5683 (3)	64 (1)	6114 (2)	2498 (2)	5682 (3)	56 (1)
C(10a)	5267 (2)	3740 (2)	6207 (2)	48 (1)	5358 (2)	3428 (2)	6138 (2)	43 (1)
C(41)	1700 (2)	4680 (2)	5834 (2)	37 (1)	1767 (2)	4554 (1)	5748 (2)	37 (1)
O(1)	942 (2)	5339 (1)	6427 (2)	55 (1)	1123 (1)	5267 (1)	6305 (2)	63 (1)
O(2)	1323 (2)	4247 (1)	4844 (1)	46 (1)	1241 (1)	4108 (1)	4831 (1)	49 (1)
C(51)	1259 (2)	2677 (2)	7289 (2)	41 (1)	1395 (2)	2546 (1)	7311 (2)	39 (1)
C(52)	−250 (2)	2769 (2)	7057 (2)	49 (1)	−162 (2)	2647 (2)	7145 (2)	52 (1)
C(53)	−935 (3)	3210 (3)	8187 (3)	64 (1)	−763 (2)	3093 (2)	8249 (3)	64 (1)

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

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

	PPC	DPPC		PPC	DPPC
C(1)–C(2)	1·367 (4)	1·368 (4)	C(1)–C(10a)	1·400 (4)	1·384 (4)
C(2)–C(3)	1·397 (3)	1·367 (4)	C(3)–C(4)	1·389 (3)	1·396 (4)
C(4)–C(4a)	1·417 (3)	1·411 (4)	C(4)–C(41)	1·481 (3)	1·479 (4)
C(4a)–C(4b)	1·472 (3)	1·497 (4)	C(4a)–C(10a)	1·418 (3)	1·413 (4)
C(4b)–C(5)	1·416 (3)	1·414 (4)	C(4b)–C(8a)	1·429 (3)	1·406 (4)
C(5)–C(6)	1·390 (3)	1·397 (4)	C(5)–C(51)	1·525 (3)	1·510 (4)
C(6)–C(7)	1·396 (3)	1·373 (4)	C(7)--C(8)	1·352 (4)	1·371 (4)
C(8)–C(8a)	1·400 (4)	1·385 (4)	C(8a)–C(9)	1·434 (4)	1·498 (4)
C(9)–C(10)	1·336 (4)	1·512 (4)	C(10)–C(10a)	1·438 (4)	1·507 (4)
C(41)–O(1)	1·305 (3)	1·291 (4)	C(41)–O(2)	1·238 (2)	1·240 (3)
C(51)–C(52)	1·520 (3)	1·518 (4)	C(52)–C(53)	1·515 (3)	1·509 (5)

	PPC	DPPC
C(10a)–C(1)–C(2)	121·8 (2)	121·8 (3)
C(4)–C(3)–C(2)	120·6 (3)	121·2 (3)
C(41)–C(4)–C(3)	115·4 (2)	116·0 (3)
C(4b)–C(4a)–C(4)	125·1 (2)	125·8 (3)
C(10a)–C(4a)–C(4b)	118·1 (2)	117·1 (3)
C(8a)–C(4b)–C(4a)	116·6 (2)	116·1 (3)
C(6)–C(5)–C(4b)	118·7 (2)	117·6 (3)
C(51)–C(5)–C(6)	116·5 (2)	117·1 (3)
C(8)–C(7)–C(6)	119·5 (3)	119·5 (3)
C(8)–C(8a)–C(4b)	119·9 (2)	120·1 (3)
C(9)–C(8a)–C(8)	120·1 (3)	121·2 (3)
C(10a)–C(10)–C(9)	120·8 (3)	109·4 (3)
C(10)–C(10a)–C(1)	120·7 (3)	121·7 (3)
O(1)–C(41)–C(4)	115·9 (2)	116·2 (3)
O(2)–C(41)–O(1)	122·3 (2)	122·2 (3)
C(53)–C(52)–C(51)	111·6 (2)	112·4 (3)
C(3)–C(2)–C(1)	118·8 (3)	119·1 (3)
C(4a)–C(4)–C(3)	121·0 (2)	120·0 (3)
C(41)–C(4)–C(4a)	122·2 (2)	123·2 (3)
C(10a)–C(4a)–C(4)	116·7 (2)	117·2 (3)
C(5)–C(4b)–C(4a)	125·2 (2)	124·2 (3)
C(8a)–C(4b)–C(5)	117·9 (2)	119·4 (3)
C(51)–C(5)–C(4b)	124·1 (2)	125·0 (3)
C(7)–C(6)–C(5)	122·0 (3)	122·5 (3)
C(8a)–C(8)–C(7)	120·9 (3)	120·7 (3)
C(9)–C(8a)–C(4b)	119·5 (3)	118·6 (3)
C(10)–C(9)–C(8a)	120·9 (3)	108·4 (3)
C(4a)–C(10a)–C(1)	120·0 (3)	120·0 (3)
C(10)–C(10a)–C(4a)	119·0 (3)	118·0 (3)
O(2)–C(41)–C(4)	121·6 (2)	121·3 (3)
C(52)–C(51)–C(5)	116·4 (2)	115·5 (3)

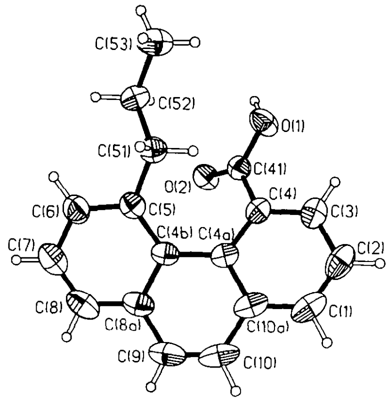

Fig. 1. Thermal-ellipsoid plot (50% level) of PPC, showing the atom-numbering scheme. H-atom radii are arbitrary.

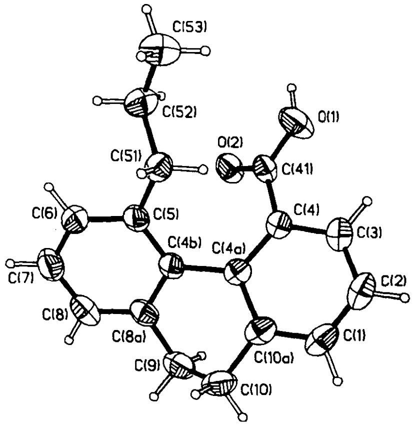

Fig. 2. Thermal-ellipsoid plot (50% level) of DPPC, showing the atom-numbering scheme. H-atom radii are arbitrary.

Table 3. *Deviations* (Å × 10^2) *of* C *atoms from different molecular planes of PPC and DPPC*

For definition of planes see text. E.s.d.'s <0·01 Å.

	Plane (I)		Plane (II)		Plane (III)	
C atom	PPC	DPPC	PPC	DPPC	PPC	DPPC
1	30	44	27	38	23	42
2	11	16	8	12	3	11
3	−28	−37	−23	−38	−34	−43
4	−41	−55	−44	−55	−44	−60
4a	−6	−11	−7	−14	−7	−13
4b	1	−5	1	−8	3	−5
5	38	41	38	40	42	39
6	32	44	33	43	39	44
7	−7	6	−4	3	1	9
8	−29	−31	−27	−36	−23	−26
8a	−20	−33	−19	−39	−17	−31
9	−17	−56	−15	−64	−16	−52
10	18	47	18	38	16	49
10a	18	31	17	25	15	30
41	−121	−139	−124	−138	−122	−146
51	104	100	102	102	108	95
R.m.s. (of defining atoms)	21	32	17	24	3	8

A common feature of these calculations is that C(4) and C(5) are farthest off the planes however defined. This would be expected for a helical structure. However, the deviations from plane (III) are the most informative. The signs of the deviations vary around the perimeter in a regular manner; the deviations of C(4) and C(3) are negative, C(1), C(10a), C(10) positive, C(9), C(8a), C(8) again negative and C(6) and C(5) positive. This is to be expected when the main mode of steric relaxation is a torsion about the central bond C(4a)C(4b).

The bond angles (e.s.d.'s ≤0·3°) and the torsion angles (e.s.d.'s ≤0·5°) allow us to trace the origin and the relaxation path of the steric pressure. The torsion angle about the central bond C(4a)C(4b) (corresponding to the inter-ring angle in biphenyl; the angle between the ring planes here is 29°) is 32° [C(4)C(4a)C(4b)-C(5)] and 24° [C(8a)C(4b)C(4a)C(4)], while it is 16·5° about the bond C(9)C(10). These angles indicate that the torsional deformation of the molecular structure decreases on moving away from the origin of the deformation of C(4) and C(5), which might have been expected.

The torsion angles about the peripheral bonds from C(4) to C(10) and from C(5) to C(9) are between 1 and 6°, while those about bonds in the inner part of the molecule involving C(4a) and C(4b) are between 11 and 14°. Clearly, the strain is predominantly relaxed along the bonds in the molecular centre.

This is also evident from the bond angles. C(4a)-C(4)C(41) (122·2°) and C(4b)C(5)C(51) (124·0°) are opened up because of steric repulsion between the propyl and the carboxyl group. Both bonds C(4)C(41) and C(5)C(51) are bent away from each other towards C(3) and C(6), respectively. That the intra-annular angle C(3)C(4)C(4a) (115·4°) is less affected than C(6)C(5)C(4b) (116·6°) might be attributable to the better conformational relaxation of the planar carboxyl group.

Surprisingly, the angles C(4)C(4a)C(4b) (125·3°) and C(5)C(4b)C(4a) (125·2°) are more strongly affected than those discussed above. This means that the two phenyl rings of the 'biphenyl' moiety are bent in the aromatic planes, *i.e.* the axis C(7)···C(4b) is not collinear with the axis C(2)···C(4a) (they make an angle of 6·6°). This is analogous to the situation found in fluorene (Belsky, Zavodnik & Vozzhennikov, 1984; Gerkin, Lundstedt & Reppart, 1984).

The conformational degrees of freedom are those with the softest potential. Thus, the carboxyl group is rotated by 30 to 40° out of the 'plane' of the adjacent aromatic ring. The angle between the best planes through O(1),O(2),C(4),C(41) and C(3),C(4a),C(41), C(4) is 34·3°. The best planes through C(5),C(51), C(52) and C(4b),C(6),C(51),C(5) make an interplanar angle of 48·3°. The C atoms of the propyl chain are in an *anti* position, as usual in saturated straight-chain hydrocarbons. The heavy atoms of the carboxyl groups in both molecules PPC and DPPC are slightly pyramidal, *i.e.* the deviation of C(41) from the best plane (r.m.s. 0·013 Å) is 0·026 Å, C(41) pointing towards the propyl chains in both molecules.

Together with the distortion of the aromatic skeleton, these conformations allow interatomic C—H···O and C—H···C distances that are not abnormally short. Thus, H(52*b*) and H(51*b*), the only protons possibly involved in steric interference, display distances to O(1) and O(2) of between 2·82 and 3·16 Å, and to C(41) of 2·97 and 2·48 Å, (e.s.d.'s *ca* 0·01 Å), although the latter is shorter than a van der Waals H···C contact of 2·7 Å. This apparent penetration of H(51*b*)···C(41) cannot be interpreted here, because (1) we are not aware of sound information on the van der Waals radius of carbon and (2) the repulsive potential about a trigonal carbon of a carbonyl group is certainly very anisotropic. A single average van der Waals radius is thus not very meaningful.

Not all of the bond lengths are similar to those of phenanthrene within the error limits given in that study (about 0·006 Å) (Kay, Okaya & Cox, 1971). C(4)-C(4a), C(4b)C(5), and C(4a)C(4b) are about 2σ larger than in phenanthrene. These small, but consistently positive differences are probably bond elongations due to steric strain. The elongation of C(4a)C(4b) might also reflect a lower π-bond order because of the dihedral angle of about 29° between the aromatic planes. The largest deviations (−0·025 and −0·018 Å) occur for C(1)C(10a) and C(8)C(8a), respectively. We interpret this as bond-length compression supporting the bend of the two axes passing through C(2)C(4a) and through C(7)C(4b), respectively, as discussed above.

5-*Propyl*-9,10-*dihydrophenanthrene*-4-*carboxylic acid* (*DPPC*)

The helical deformation of the 9,10-dihydro analogue DPPC is larger than that of PPC. The distribution of the deviations of the heavy atoms from the different planes (see above) again depends on the definition of the planes, but is similar for the two molecules when we consider the deviations from plane (III) (Table 3). Simplified views of PPC and DPPC [plane (III) approximately perpendicular to the paper plane] are shown in Figs. 3 and 4.

The torsion angles about the central 'biphenyl' single bond C(4a)C(4b) are 42° [C(4)C(4a)C(4b)C(5)] and 35° [C(8a)C(4b)C(4a)C(10a)], some 10° larger than in PPC. The corresponding angle between the aromatic-ring planes is 39°. Clearly, this is made feasible by the rotationally flexible single bond C(9)C(10), in contrast to the C(9)C(10) double bond in PPC. In turn, this allows a more efficient relaxation of the strain produced by the substituents in DPPC. Thus, although the opening of the angles C(4a)C(4)C(41) (123·2°) and C(4b)C(5)C(51) (125·0°) is 1° larger than in PPC, the torsional angles about the bonds in the aromatic rings are on the whole smaller than in PPC. Most of the other bond angles are similar in the two molecules, except those in the ring containing the bridging atoms C(9) and C(10).

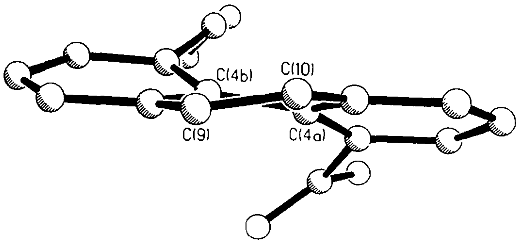

Fig. 3. A view of PPC, approximately in the direction joining the midpoints of C(9)C(10)and C(4a)C(4b), showing the helicity of the ring system.

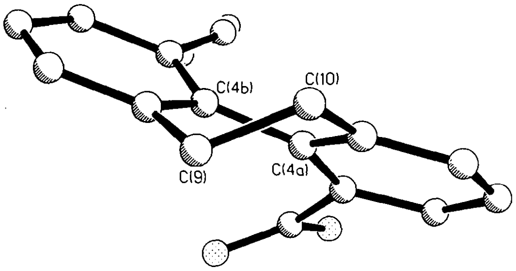

Fig. 4. A view of DPPC analogous to that of PPC in Fig. 3.

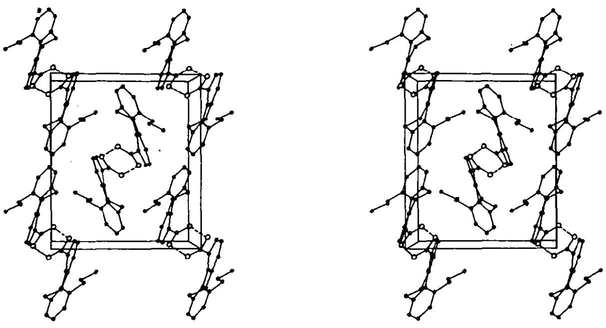

Fig. 5. The molecular packing of DPPC, showing the hydrogen bonds of the carboxylic acid dimers (dashed lines). H atoms are omitted for clarity. The packing in PPC is exactly analogous.

The conformations of the substituent groups relative to the adjacent rings are practically the same in both molecules (angles between best planes: DPPC: 32·1, COOH: 51·0°, propyl group; PPC, see above).

The bond lengths show three interesting points. (1) Whereas C(4)C(41), joining the carboxyl group to the aromatic ring, is about the same in PPC (1·481 Å) and DPPC (1·479 Å), C(5)C(51) between the propyl group and the aromatic ring differs by 0·015 Å (4σ), being smaller in the more relaxed DPPC (1·510 Å). (2) In the more twisted DPPC, the central bond C(4a)C(4b) is longer than in PPC by 0·025 Å. This is due to the reduced conjugation between the two aromatic rings and not to reduced strain, which would be expected to shorten all bonds in the region of C(4), C(4a), C(4b) and C(5). (3) The bond lengths in the periphery of the aromatic system about C(2) and C(7) in DPPC are similar to each other, whereas those in PCC alternate more strongly. This reflects the phenanthrene-like nature of PPC and the biphenyl-like structure of DPPC.

The molecular packing (see Fig. 5) incorporates the formation of carboxylic acid dimers by hydrogen bonding; $O(2)\cdots O(1^i)(-x, 1-y, 1-z)$ is 2·65 (1) Å for PPC, 2·66 (1) Å for DPPC.

In summary, the data of the two structures determined in this study allow the following conclusions. The two molecules are helical, DPPC more so than PPC. The origin of the helicity is the steric strain between the substituents in the 4- and 5-positions.* The steric interference is primarily relaxed by conformational rotation of the substituent groups, but also by in-plane (bond angle) and out-of-plane (torsion angle) deformations, by bond-length elongations in the region of the substitution loci and compressions on the opposite side of the molecules.

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Note added in proof: The crystal structures of 9,10-dihydrophenanthrene and 4,5-dimethylphenanthrene have recently been reported [Cosmo, R.,

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* A referee has commented that 9,10-dihydrophenanthrene would be helical even without the 4,5-substitution, because of the saturation of the C(9)C(10) bond. The crystal structure of 9,10-dihydrophenanthrene is not known (it melts at 308 K). Molecular models suggest a small torsion angle about its central C(4a)C(5a) bond, but such models do not take into account the conjugative interaction between the biphenyl moieties. The extent of helicity in the unsubstituted molecule must therefore be considered unknown.

Hambley, R. W. & Sternhell, S. (1987). *J. Org. Chem.* **52**, 3119–3123]. The torsion angle in the former is 20·7° (av.) and in the latter 33, 22°.

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

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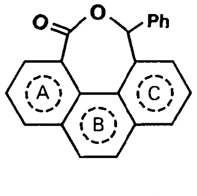
Abstract. $C_{22}H_{14}O_2$, $M_r = 310\cdot36$, monoclinic, $P2_1/c$, $a = 11\cdot436\ (2)$, $b = 13\cdot685\ (2)$, $c = 10\cdot167\ (2)$ Å, $\beta = 103\cdot22\ (2)$°, $V = 1549\cdot0$ Å^3, $Z = 4$, $D_x = 1\cdot33$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0\cdot71069$ Å, $\mu = 0\cdot5$ cm^{-1}, $F(000) = 648$, $T = 293$ K. $R = 0\cdot049$ 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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