

enantiomers was 0.76:0.24 in an asymmetric unit of space group $P\bar{1}$, and in the structure of 3-(*o*-chlorophenylimino)camphor (Foulon, Baert & Fouret, 1979), where the ratio of the enantiomer site-occupancy factors was 0.72:0.28 in an asymmetric unit of space group $P2_1/a$. Very similar enantiomeric disorder was found for the spiro compounds showing a 'spiro-coplanar' conformation (Stadnicka & Lebioda, 1979; Stadnicka, Lebioda & Grochowski, 1979) with site-occupancy factors of 0.5.

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The Structure of 7,8,8a,9,10,16c-Hexahydrophenanthro[3,4-*c*]phenanthrene

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Abstract. $C_{26}H_{22}$, orthorhombic, $Pbca$, $a = 18.338$ (2), $b = 23.460$ (2), $c = 8.330$ (1) Å, $Z = 8$, $D_c = 1.24$, $D_m = 1.18$ Mg m⁻³. The structure was refined to $R = 0.057$ for 2352 reflections. The molecule can be regarded as a composite in which two 1,2-substituted naphthalene units are linked to hydrogenated rings. The central hydrogenated rings have the half-boat half-chair conformation. The dihedral angle between two naphthalene rings is 68.1°. No intermolecular distance shorter than a van der Waals contact was observed.

Introduction. It has been widely accepted that highly resolved electronic spectra in *n*-alkane matrices (Shpolskii spectra) can be found only in the case of

planar organic molecules (Nurmukhametov, 1969). So far, only a few exceptions to this rule have been reported. One of the authors has observed highly resolved emission spectra of 7,8,8a,9,10,16c-hexahydrophenanthro[3,4-*c*]phenanthrene* (hexahydrohexahelicene, HHHH) (Palewska & Ruziewicz, 1979). We believe that this was one of a very few examples of the Shpolskii effect found in a molecule consisting of planar 'active' fragments linked to non-planar 'inactive' ones. In connection with these spectroscopic studies, it was necessary to determine the molecular structure.

* Systematic numbering. The crystallographic numbering used throughout the paper is shown in Fig. 1.

HHHH, synthesized according to Newman & Lednicer (1956), was twice recrystallized from benzene-ethanol and chromatographically purified in a column filled with Al_2O_3 .

The space group was determined from Weissenberg photographs. The precise cell constants and intensity

data were obtained with a Rigaku four-circle automatic diffractometer, using graphite-monochromatized Mo $K\alpha$ radiation. 2352 reflections with significant intensities [$|F_o| \geq 3\sigma(F_o)$] were obtained by measuring all reflections in the range $2\theta \leq 55^\circ$. No absorption correction was made ($\mu = 0.072 \text{ mm}^{-1}$).

The structure was solved by direct methods, using *MULTAN* (Germain, Main & Woolfson, 1971). The positions of 23 atoms among the 26 independent C atoms were revealed on the *E* map. A Fourier map revealed another three atoms. After the refinement by block-diagonal least squares with isotropic temperature factors, all the H atoms were found in the *E* map. The refinement was completed with the *UNICS* (1967) full-matrix least-squares program, with anisotropic temperature factors for C atoms and isotropic ones for H. The final *R* was 0.057 for all reflections. The weighting scheme was $w = 1/[\sigma^2(F_o) + (0.05F_o)^2]^{1/2}$. The atomic scattering factors for C were taken from *International Tables for X-ray Crystallography* (1962), and that of H from Stewart, Davidson & Simpson (1965). The atomic coordinates, and the bond lengths

Table 1. Fractional positional parameters ($C \times 10^4$, $H \times 10^3$) with *e.s.d.*'s in parentheses, and equivalent isotropic thermal parameters for carbon atoms and isotropic thermal parameters for hydrogen atoms ($\times 10$)

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}/B_{iso} (\AA^2)
C(1)	1709 (2)	2873 (1)	1955 (4)	36 (1)
C(2)	994 (2)	2971 (1)	1705 (4)	37 (1)
C(2a)	597 (1)	3317 (1)	2761 (3)	32 (1)
C(3)	-223 (2)	3371 (2)	2607 (4)	41 (1)
C(4)	-547 (2)	3257 (1)	4253 (5)	45 (1)
C(4a)	-278 (1)	3686 (1)	5509 (4)	37 (1)
C(5)	-131 (2)	3425 (1)	7132 (4)	46 (1)
C(6)	4 (2)	3884 (2)	8367 (5)	50 (1)
C(6a)	513 (2)	4346 (1)	7785 (4)	37 (1)
C(7)	785 (2)	4731 (2)	8942 (4)	49 (1)
C(8)	1252 (2)	5157 (2)	8523 (5)	50 (1)
C(8a)	1477 (2)	5228 (1)	6917 (4)	40 (1)
C(9)	1990 (2)	5651 (1)	6455 (6)	50 (1)
C(10)	2221 (2)	5697 (1)	4916 (6)	53 (1)
C(11)	1951 (2)	5331 (1)	3745 (5)	45 (1)
C(12)	1454 (2)	4917 (1)	4155 (4)	36 (1)
C(12a)	1205 (1)	4845 (1)	5743 (3)	32 (1)
C(12b)	715 (1)	4397 (1)	6213 (3)	31 (1)
C(12c)	418 (1)	4003 (1)	4930 (3)	29 (1)
C(12d)	924 (1)	3583 (1)	4062 (3)	26 (1)
C(12e)	1674 (1)	3449 (1)	4417 (3)	25 (1)
C(13)	2052 (1)	3629 (1)	5808 (4)	30 (1)
C(14)	2760 (2)	3474 (1)	6087 (4)	34 (1)
C(15)	3139 (2)	3132 (1)	4985 (4)	35 (1)
C(16)	2800 (2)	2946 (1)	3642 (4)	35 (1)
C(16a)	2060 (1)	3092 (1)	3317 (3)	27 (1)
H(1)	197 (1)	266 (1)	119 (3)	43 (6)
H(2)	75 (1)	283 (1)	77 (4)	45 (6)
H(3A)	-36 (2)	377 (1)	217 (4)	45 (7)
H(3B)	-41 (2)	309 (1)	181 (4)	51 (8)
H(4A)	-111 (2)	323 (1)	420 (4)	55 (8)
H(4B)	-39 (2)	285 (1)	466 (4)	51 (8)
H(4a)	-64 (1)	398 (1)	567 (3)	38 (6)
H(5A)	-53 (2)	316 (2)	747 (4)	55 (9)
H(5B)	32 (2)	319 (1)	701 (4)	52 (8)
H(6A)	19 (2)	374 (2)	938 (5)	55 (9)
H(6B)	-46 (2)	405 (2)	868 (4)	57 (9)
H(7)	66 (2)	467 (1)	1006 (4)	55 (8)
H(8)	146 (2)	540 (1)	931 (4)	50 (8)
H(9)	216 (2)	586 (2)	737 (4)	57 (9)
H(10)	258 (2)	602 (2)	468 (4)	60 (9)
H(11)	212 (2)	537 (1)	255 (4)	46 (7)
H(12)	129 (1)	466 (1)	333 (3)	37 (6)
H(12c)	24 (1)	428 (1)	397 (3)	33 (5)
H(13)	181 (1)	384 (1)	666 (3)	33 (5)
H(14)	300 (1)	360 (1)	708 (3)	39 (6)
H(15)	364 (2)	301 (1)	520 (4)	46 (7)
H(16)	304 (1)	272 (1)	283 (3)	44 (7)

Table 2. Bond lengths (\AA) and angles ($^\circ$) and their *e.s.d.*'s

C(1)-C(2)	1.347 (5)	C(8a)-C(12a)	1.419 (4)
C(1)-C(16a)	1.402 (4)	C(9)-C(10)	1.354 (7)
C(2)-C(2a)	1.401 (4)	C(10)-C(11)	1.391 (5)
C(2a)-C(3)	1.514 (4)	C(11)-C(12)	1.375 (4)
C(2a)-C(12d)	1.387 (3)	C(12)-C(12a)	1.410 (4)
C(3)-C(4)	1.518 (5)	C(12a)-C(12b)	1.437 (3)
C(4)-C(4a)	1.533 (4)	C(12b)-C(12c)	1.514 (3)
C(4a)-C(5)	1.508 (4)	C(12c)-C(12d)	1.534 (3)
C(4a)-C(12c)	1.554 (3)	C(12d)-C(12e)	1.441 (3)
C(5)-C(6)	1.510 (5)	C(12e)-C(13)	1.415 (4)
C(6)-C(6a)	1.510 (5)	C(12e)-C(16a)	1.429 (3)
C(6a)-C(7)	1.412 (5)	C(13)-C(14)	1.368 (4)
C(6a)-C(12b)	1.366 (4)	C(14)-C(15)	1.403 (4)
C(7)-C(8)	1.362 (6)	C(15)-C(16)	1.352 (5)
C(8)-C(8a)	1.410 (5)	C(16)-C(16a)	1.426 (4)
C(8a)-C(9)	1.421 (4)		
C(2)-C(1)-C(16a)	120.6 (3)	C(11)-C(12)-C(12a)	122.2 (3)
C(1)-C(2)-C(2a)	120.5 (3)	C(12)-C(12a)-C(12b)	123.1 (2)
C(2)-C(2a)-C(3)	120.7 (2)	C(12)-C(12a)-C(8a)	117.2 (2)
C(2)-C(2a)-C(12d)	121.8 (2)	C(8a)-C(12a)-C(12b)	119.7 (2)
C(3)-C(2a)-C(12d)	117.2 (2)	C(12a)-C(12b)-C(12c)	118.6 (2)
C(2a)-C(3)-C(4)	107.3 (3)	C(12a)-C(12b)-C(6a)	119.7 (2)
C(3)-C(4)-C(4a)	112.0 (3)	C(6a)-C(12b)-C(12c)	121.7 (2)
C(4)-C(4a)-C(5)	113.7 (2)	C(12b)-C(12c)-C(12d)	120.5 (2)
C(4)-C(4a)-C(12c)	111.5 (2)	C(12b)-C(12c)-C(4a)	111.6 (2)
C(5)-C(4a)-C(12c)	109.0 (2)	C(4a)-C(12c)-C(12d)	109.6 (2)
C(4a)-C(5)-C(6)	110.5 (3)	C(12c)-C(12d)-C(12e)	128.3 (2)
C(5)-C(6)-C(6a)	113.2 (3)	C(12d)-C(12e)-C(2a)	113.3 (2)
C(6)-C(6a)-C(7)	117.3 (3)	C(2a)-C(12d)-C(12e)	118.3 (2)
C(6)-C(6a)-C(12b)	122.6 (3)	C(12d)-C(12e)-C(13)	124.8 (2)
C(7)-C(6a)-C(12b)	120.2 (3)	C(12d)-C(12e)-C(16a)	118.0 (2)
C(6a)-C(7)-C(8)	121.1 (3)	C(16a)-C(12e)-C(13)	117.2 (2)
C(7)-C(8)-C(8a)	120.9 (4)	C(12e)-C(13)-C(14)	121.7 (3)
C(8)-C(8a)-C(9)	122.2 (3)	C(13)-C(14)-C(15)	120.7 (3)
C(8)-C(8a)-C(12a)	118.5 (3)	C(14)-C(15)-C(16)	119.9 (3)
C(9)-C(8a)-C(12a)	119.2 (3)	C(15)-C(16)-C(16a)	121.1 (3)
C(8a)-C(9)-C(10)	121.3 (4)	C(16)-C(16a)-C(12e)	119.4 (2)
C(9)-C(10)-C(11)	120.2 (3)	C(16)-C(16a)-C(1)	120.2 (3)
C(10)-C(11)-C(12)	119.9 (4)	C(12e)-C(16a)-C(1)	120.4 (2)

Table 3. *Least-squares molecular planes*

Plane	Atom Nos.*	R.m.s.†	Deviations (Å)		Equation-of-plane coefficients‡			
			Max.‡		A	B	C	D
I (ring <i>AB</i>)	1, 2, 2a, 12d, 12e, 13, 14, 15, 16, 16a	0.014	C(2a);	0.061 (2)	-0.2867	-0.8091	0.5129	-5.491
II (ring <i>EF</i>)	6a, 7, 8, 8a, 9, 10, 11, 12, 12a, 12b	0.007	C(8a);	-0.036 (3)	0.7635	-0.6217	0.1747	-4.515
III (ring <i>B</i>)	1, 2, 2a, 12d, 12e, 16a	0.011	C(12d);	-0.040 (2)	-0.2560	-0.8001	0.5424	-5.284
IV (ring <i>A</i>)	12e, 13, 14, 15, 16, 16a	0.002	C(16a);	0.008 (2)	-0.3110	-0.8152	0.4887	-5.746
V (ring <i>E</i>)	6a, 7, 8, 8a, 12a, 12b	0.001	C(12a);	-0.002 (2)	0.7777	-0.6069	0.1640	-4.392
VI (ring <i>F</i>)	8a, 9, 10, 11, 12, 12a	0.002	C(12a);	0.009 (2)	0.7494	-0.6351	0.1875	-4.674
VII	2a, 3, 12c, 12d	0.029	C(12d);	0.064 (2)	-0.1805	-0.7449	0.6424	-4.457
			C(4);	1.223 (3)				
			C(4a);	1.056 (3)				
VIII	6, 6a, 12b, 12c	0.004	C(6a);	-0.010 (3)	0.7751	-0.6141	0.1487	-4.558
			C(4a);	-0.465 (2)				
			C(5);	0.321 (3)				

* Includes only those atoms used to determine the best plane.

† Based only on plane-determining atoms.

‡ E.s.d.'s are given in parentheses.

§ The equation has the form $AX + BY + CZ = D$.

and angles involving only C atoms are listed in Tables 1 and 2 respectively.*

Discussion. Fig. 1 shows the arrangement of molecules in the crystal. There is no intermolecular distance shorter than the usual van der Waals contacts.

The equations of several planes are listed in Table 3. Rings *A*, *B*, *E* and *F* are more planar than the corresponding six-membered rings in 2-methylhexahelicene (Frank, Hefelfinger & Lightner, 1973) and the two ten-membered rings (rings *AB* and *EF*) can be considered to be planar. Therefore, because of the

* Lists of structure factors, anisotropic thermal parameters and the bond lengths and angles involving the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36421 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

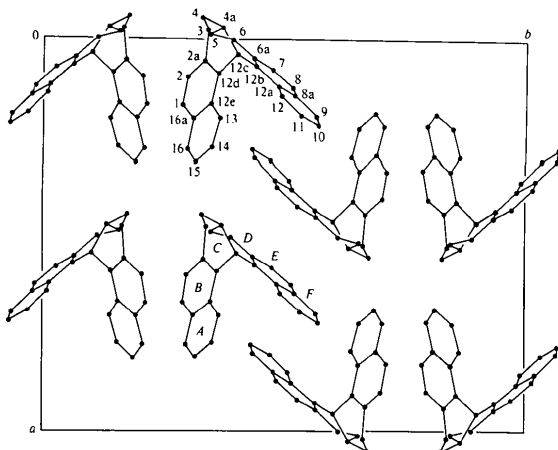


Fig. 1. Projection of the crystal structure along the *c* axis.

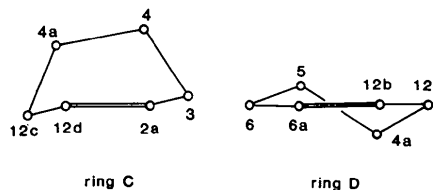


Fig. 2. Conformation of the central hydrogenated rings.

hydrogenation of the central rings (rings *C* and *D*), the strain which exists in the hexahelicene skeleton is absent and the molecule can be regarded as a composite in which two 1,2-substituted naphthalene units are linked to hydrogenated rings. The dihedral angle between the two naphthalene units is 68.1° .

The C—C bond lengths in rings *A*, *B*, *E* and *F* average 1.397 \AA . The conformations of rings *C* and *D* are shown in Fig. 2. Ring *C* has a half-boat conformation and ring *D* a half-chair. The average value of the C—C single-bond length is 1.522 \AA .

The computer used was HITAC-200H at the Computer Center, University of Tokyo, with the UNICS (1967) system of programs

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Acta Cryst. (1982). **B38**, 991–993

Structure and Conformation of 2-Methyl-2-(2-naphthyloxy)-4*H*-1,3-benzodioxin-4-one

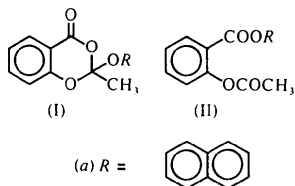
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Abstract. C₁₉H₁₄O₄, monoclinic, $P2_1/c$, $a = 15.32$ (2), $b = 7.59$ (1), $c = 13.16$ (2) Å, $\beta = 80.7$ (8)°, $Z = 4$, $U = 1509$ Å³, $D_c = 1.35$ Mg m⁻³, $\mu = 0.1079$ mm⁻¹, $R = 0.068$ for 1204 reflexions [$I > 3\sigma(I)$] and 236 parameters. The β -naphthyloxy group is axial to the *B* ring which has an envelope conformation.

Introduction. The synthesis of the title compound (Ia) was first reported by Rüchardt & Rochlitz (1974). It has been prepared in this laboratory together with ten other cyclic *ortho* esters of the type 2-substituent-2-methyl-4*H*-1,3-benzodioxin-4-one (I) in a search for acetylsalicylic acid (aspirin) prodrugs (Hansen & Senning, 1981). Analogous compounds with the 1,3-benzodioxin moiety as part of a triglyceride structure have been prepared and tested for anti-inflammatory activity recently (Paris, Garmaise, Cimon, Swett, Carter & Young, 1980).



Compounds of type (I) are cyclic isomers of normal esters of acetylsalicylic acid (II). They are formed *via* an intermediate 2-methyl-4-oxo-4*H*-1,3-benzodioxin-2-ylum ion in a kinetically controlled reaction between acetylsalicyloyl chloride and alcohols/phenols. However, this acid chloride shows ambivalent reactivity and, depending on reaction conditions, varying amounts of the normal esters of type (II) are also

formed. The reaction of acetylsalicyloyl chloride with β -naphthol (in acetonitrile at 253 K) yielded (Ia) as the main product. By repeated recrystallization from petroleum ether (b.p. 313–323 K) and subsequent drying *in vacuo*, transparent, pale-yellow single crystals (m.p. 361.7–362.7 K) were obtained for X-ray analysis.

X-ray structure analysis was carried out to ascertain the cyclic structure of (Ia) and to confirm the interpretation of spectroscopic data for type (I) compounds. Prior to the X-ray investigation reported here, the cyclic structure of type (I) compounds had been deduced solely from spectroscopic data (Rüchardt & Rochlitz, 1974; Hansen & Senning, 1981). Knowledge of the conformation is also of importance for the interpretation of the hydrolysis data of compounds of type (I) (Hansen & Senning, 1981). Furthermore, this is, to our knowledge, the first X-ray structure analysis of this type of cyclic *ortho* ester.

The crystal used for the structure determination was grown from a petroleum ether solution and had approximate dimensions 0.80 × 0.55 × 0.35 mm. The space group $P2_1/c$ was determined from the systematic absences on precession pictures of the (0*kl*) and (*h*0*l*) layers. Weissenberg pictures of zero and first-layer lines showed spots with tails, indicating a large mosaic spread. Cell dimensions were calculated from the setting angles of 14 reflexions measured on a Picker FACS-1 diffractometer using Mo $K\alpha$ radiation.

The data were collected on a Buerger automated X-ray diffractometer from Charles Supper Company, Inc., using Mo $K\alpha$ radiation. The crystal was mounted with the *b* axis as rotation axis. Reflexions with $k = 0$ and $k = 1$ were measured out to $\sin \theta = 0.50$. Other reflexions were measured out to $\sin \theta = 0.45$. 3155 independent reflexions were measured, and back-

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