The Structure of 9b-Methyl-3aβ,3bα,5aα,9aα,9bβ,11aβ-perhydrophenanthro-[2,1-*b*]furan-7-one

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Abstract. $C_{17}H_{26}O_2$, $M_r = 262$, triclinic, $P\bar{1}$, $a = 8.513$ (2), $b = 8.970$ (2), $c = 11.741$ (3) Å, $\alpha = 120.51$ (5), $\beta = 93.30$ (4), $\gamma = 68.43$ (4)°, $V = 708.9$ Å^3, $Z = 2$, $D_o = 1.213$, $D_c = 1.227$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0.7107$ Å) $= 0.084$ mm^{-1}, $F(000) = 288$. The structure, solved by direct methods, has been refined to an R value of 5.9% using 1361 intensity measurements. The ring junctions, in sequence from either end of the polycycle, are *cis*, *trans* and *cis*.

Introduction. The title compound (I) having six asymmetric centres with desired stereochemical configurations is related to epoxynorcafestanone, an important degradation product of cafestol (Maji, Mukherjee, Mukherjee & Dutta, 1981). One of the salient aspects of the above synthetic compound is the *B/C cis* junction of the perhydrophenanthrene nucleus. This arrangement is less stable thermodynamically than the corresponding all-*trans* configuration which occurs widely in natural compounds. The chemical evidence in favour of the *cis* junction was based on analogy and hence X-ray studies were undertaken to establish the structure proposed and the conformational features of the molecule.

(I)
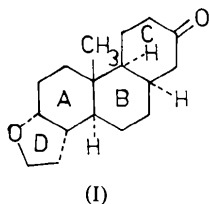
A sample of the title compound, kindly supplied by Professor P. C. Dutta, was crystallized from its concentrated solution in ether to which a few drops of petroleum ether had been added. Preliminary Weissenberg photographs indicated the triclinic space groups $P1$ or $P\bar{1}$. Intensity data were collected with a crystal $0.5 \times 0.4 \times 0.2$ mm on a CAD-4 diffractometer using monochromated Mo $K\alpha$ radiation by the $\omega/2\theta$ scan

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Table 1. *Atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters*

E.s.d.'s are given in parentheses. $B_{eq} = (B_1 B_2 B_3)^{1/3}$.

	x	y	z	B_{eq} (Å^2)
C(1)	6733 (4)	6413 (5)	6304 (3)	3.20
C(2)	5459 (4)	8442 (5)	7005 (4)	3.81
C(3)	3885 (4)	8806 (5)	7816 (3)	3.39
C(4)	4168 (4)	7769 (5)	8552 (3)	2.82
C(5)	5475 (4)	5762 (4)	7762 (3)	2.41
C(6)	5764 (4)	4762 (5)	8531 (3)	3.16
C(7)	6915 (4)	2701 (6)	7677 (4)	3.71
C(8)	8624 (4)	2406 (5)	7074 (3)	3.35
C(9)	8385 (4)	3516 (4)	6391 (3)	2.68
C(10)	7178 (5)	5620 (6)	7232 (3)	2.39
C(11)	10135 (4)	3161 (5)	5769 (3)	3.57
C(12)	11696 (5)	2165 (7)	6224 (4)	4.44
C(13)	11360 (4)	2898 (5)	7679 (3)	3.36
C(14)	9835 (4)	2770 (5)	8129 (3)	3.58
C(15)	7970 (4)	6787 (5)	8380 (4)	3.26
C(16)	1696 (5)	7731 (6)	7474 (4)	4.16
C(17)	2355 (4)	7899 (6)	8757 (4)	3.85
O(3)	2727 (3)	8204 (4)	6917 (2)	3.98
O(13)	12283 (3)	3517 (5)	8445 (3)	5.44
H1(1)	630 (5)	557 (5)	565 (4)	
H2(1)	778 (5)	634 (5)	581 (4)	
H1(2)	521 (5)	897 (6)	638 (4)	
H2(2)	600 (4)	944 (5)	769 (4)	
H(3)	329 (4)	1028 (5)	853 (3)	
H(4)	441 (4)	833 (5)	932 (4)	
H(5)	510 (4)	504 (5)	704 (4)	
H1(6)	622 (4)	555 (5)	933 (4)	
H2(6)	469 (6)	500 (6)	886 (4)	
H1(7)	714 (5)	184 (6)	801 (4)	
H2(7)	643 (5)	209 (6)	705 (4)	
H(8)	918 (5)	84 (6)	632 (4)	
H(9)	789 (4)	306 (5)	574 (4)	
H1(11)	1034 (4)	230 (5)	477 (4)	
H2(11)	1017 (4)	436 (6)	593 (3)	
H1(12)	1180 (5)	93 (7)	577 (5)	
H2(12)	1285 (7)	255 (8)	615 (5)	
H1(14)	1021 (5)	166 (6)	824 (4)	
H2(14)	938 (7)	425 (9)	905 (6)	
H1(15)	901 (7)	650 (7)	798 (5)	
H2(15)	808 (6)	651 (7)	899 (5)	
H3(15)	735 (5)	814 (6)	871 (4)	
H1(16)	56 (4)	861 (5)	766 (3)	
H2(16)	184 (5)	622 (6)	681 (4)	
H1(17)	172 (5)	915 (7)	949 (4)	
H2(17)	224 (5)	689 (6)	882 (4)	

technique to a limit of $\theta = 25°$ using a scan speed of $1°$ min^{-1}. Two reflections were checked after every 50 reflections and they showed only statistical fluctuations. 2332 reflections were measured, of which 1361 were significant $[|F_o| > 2\sigma(|F_o|)]$. Corrections were then made for Lorentz and polarization factors but not for absorption.

The distribution of normalized structure factors was clearly centrosymmetric and the space group $P\bar{1}$ was chosen. The structure was solved using the direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971) with six multisolution symbols; all the nonhydrogen atoms, except C(12), could be recovered from the E map. The position of the missing atom was fixed on stereochemical considerations. The refinement was performed by the least-squares method, using a block-diagonal matrix for initial cycles and full matrix for final cycles. All the H atoms were located in a difference map and were refined isotropically. Using Cruickshank's weighting scheme with $a = 10.0$, $b = 1.0$ and $c = 0.06$, R converged to a final value of 5.9%.

The coordinates of all the atoms (including H) are listed in Table 1. Tables 2 and 3 give the torsional angles and the bond lengths and angles involving the nonhydrogen atoms.*

Discussion. The ring junctions A/B, B/C and A/D are *trans*, *cis* and *cis* respectively as was suggested on chemical grounds (Maji *et al.*, 1981). As can be seen from the torsional angles, rings A and B are in distorted chair forms, whereas ring C is a distorted boat (Bucourt, 1974). Each of the rings A and B is *cis*-fused to another ring and as a result the torsional angles deviate significantly from that found in an ideal chair form, the deviation being more in ring A, where there is marked flattening near the A/D junction. The distortion in ring B, which is *cis* fused to a six-membered ring, is less. The conformation of ring D corresponds more to the envelope form with $\Delta = 21.3°$, $\varphi_m = -40.2°$ (Altona, Geise & Romers, 1968) and atom C(4) deviating by 0.607 Å from the least-squares plane through the remaining four atoms of the ring.

The molecular packing is illustrated in Fig. 1. There are no unusually short intermolecular contacts, so that packing forces are unlikely to influence the geometry of the molecule to any appreciable extent. The overall shape of the molecule is like a 'chair' (Fig. 2). There is an intramolecular contact of 3.337 (6) Å between C(15) and C(13).

The C(13)=O(13) bond length of 1.210 (5) Å is the same as that obtained by electron diffraction studies on some carbonyl compounds [1.211 (4) Å] (Kato, Konaka, Iijima & Kimura, 1969); carbonyl groups not

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35894 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Torsional angles (°) in the rings*

Ring A		Ring B	
C(5)–C(10)–C(1)–C(2)	59.9 (4)	C(9)–C(10)–C(5)–C(6)	54.8 (4)
C(10)–C(1)–C(2)–C(3)	−49.4 (5)	C(10)–C(5)–C(6)–C(7)	−58.8 (4)
C(1)–C(2)–C(3)–C(4)	37.8 (5)	C(5)–C(6)–C(7)–C(8)	55.2 (5)
C(2)–C(3)–C(4)–C(5)	−39.1 (5)	C(6)–C(7)–C(8)–C(9)	−49.9 (5)
C(3)–C(4)–C(5)–C(10)	51.5 (4)	C(7)–C(8)–C(9)–C(10)	49.8 (4)
C(4)–C(5)–C(10)–C(1)	−60.7 (4)	C(8)–C(9)–C(10)–C(5)	−51.5 (4)

Ring C		Ring D	
C(14)–C(8)–C(9)–C(11)	54.5 (4)	C(17)–C(4)–C(3)–O(3)	−39.5 (4)
C(8)–C(9)–C(11)–C(12)	−12.8 (5)	C(4)–C(3)–O(3)–C(16)	28.5 (4)
C(9)–C(11)–C(12)–C(13)	−40.7 (5)	C(3)–O(3)–C(16)–C(17)	−4.8 (4)
C(11)–C(12)–C(13)–C(14)	56.7 (5)	O(3)–C(16)–C(17)–C(4)	−20.4 (4)
C(12)–C(13)–C(14)–C(8)	−15.7 (5)	C(16)–C(17)–C(4)–C(3)	35.7 (4)
C(13)–C(14)–C(8)–C(9)	−40.7 (4)		

Table 3. *Bond distances (Å) and angles (°)*

C(1)–C(2)	1.515 (6)	C(8)–C(9)	1.523 (6)
C(1)–C(10)	1.541 (6)	C(8)–C(14)	1.547 (5)
C(2)–C(3)	1.522 (5)	C(9)–C(10)	1.546 (6)
C(3)–C(4)	1.516 (6)	C(10)–C(15)	1.532 (5)
C(3)–O(3)	1.439 (4)	C(9)–C(11)	1.547 (5)
C(4)–C(5)	1.513 (5)	C(11)–C(12)	1.542 (7)
C(4)–C(17)	1.528 (5)	C(12)–C(13)	1.487 (5)
C(5)–C(6)	1.522 (6)	C(13)–C(14)	1.492 (5)
C(5)–C(10)	1.547 (5)	C(13)–O(13)	1.210 (5)
C(6)–C(7)	1.511 (6)	C(16)–C(17)	1.530 (6)
C(7)–C(8)	1.528 (5)	C(16)–O(3)	1.413 (5)

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C(2)–C(1)–C(10)	113.5 (3)	C(8)–C(9)–C(11)	110.7 (3)
C(1)–C(2)–C(3)	113.2 (3)	C(10)–C(9)–C(11)	113.9 (3)
C(2)–C(3)–C(4)	116.9 (3)	C(1)–C(10)–C(5)	106.2 (3)
C(2)–C(3)–O(3)	108.6 (3)	C(1)–C(10)–C(9)	108.8 (3)
C(4)–C(3)–O(3)	104.7 (3)	C(1)–C(10)–C(15)	109.4 (4)
C(3)–C(4)–C(5)	113.4 (3)	C(5)–C(10)–C(9)	108.3 (3)
C(3)–C(4)–C(17)	100.0 (3)	C(5)–C(10)–C(15)	111.3 (3)
C(5)–C(4)–C(17)	113.0 (3)	C(9)–C(10)–C(15)	112.6 (3)
C(4)–C(5)–C(6)	112.5 (3)	C(9)–C(11)–C(12)	114.7 (3)
C(4)–C(5)–C(10)	112.5 (3)	C(11)–C(12)–C(13)	111.4 (4)
C(6)–C(5)–C(10)	111.8 (3)	C(12)–C(13)–C(14)	115.5 (4)
C(5)–C(6)–C(7)	111.9 (3)	C(12)–C(13)–O(13)	122.4 (4)
C(6)–C(7)–C(8)	112.0 (4)	C(14)–C(13)–O(13)	122.1 (4)
C(7)–C(8)–C(9)	112.0 (3)	C(13)–C(14)–C(8)	112.3 (3)
C(7)–C(8)–C(14)	110.7 (3)	C(3)–O(3)–C(16)	109.2 (3)
C(9)–C(8)–C(14)	113.9 (3)	O(3)–C(16)–C(17)	106.7 (4)
C(8)–C(9)–C(10)	115.5 (3)	C(16)–C(17)–C(4)	103.1 (4)
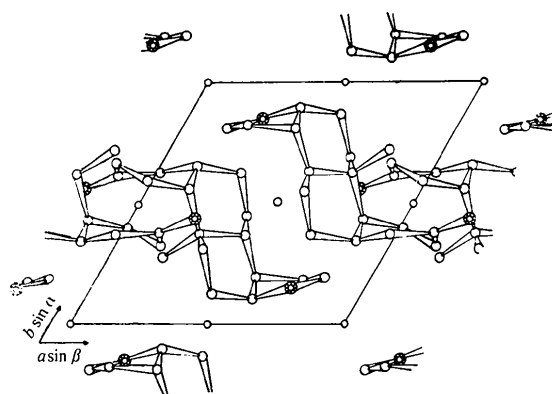
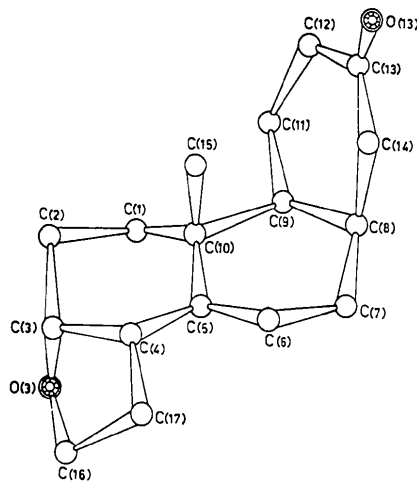Fig. 1. Packing of the molecules viewed down the *c* axis.

$$C_{17}H_{26}O_2$$

Fig. 2. Perspective view of the molecule (down **a**), showing the numbering of the nonhydrogen atoms.

involved in any hydrogen bonding show a similar bond length (Craven, Cusatis, Gartland & Vizzini, 1973). The $C(sp^3)$—$C(sp^3)$ bond lengths vary from 1·511 (6) to 1·547 (5) Å with an average value of 1·530 Å. In ring D, bonds involving O(3) show different lengths [1·439 (4), 1·413 (5) Å]. Such disproportionation has been found in other five- or six-membered rings containing oxygen (Hanson, 1977; Fujiwara & van der Veen, 1979) and in sugar molecules (Jeffrey, Pople, Binkley & Vishveshwara, 1978; Takagi, Nordenson & Jeffrey, 1979). Further, the angle at oxygen is found to be the largest within the ring (Takusagawa & Jacobson, 1978; Fujiwara & van der Veen, 1979; Takagi,

Nordenson & Jeffrey, 1979), with the angles at the two adjacent C atoms significantly larger than those at the other two C atoms (Singh & Ahmed, 1969; De Graaff, Admiraal, Koen & Romers, 1977).

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Structure of 7,14-Dibutylacenaphtho[1,2-k]fluoranthene

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Abstract. $C_{34}H_{30}$, $M_r = 438$, monoclinic, $P2_1/c$, $a = 4·704$ (2), $b = 12·52$ (1), $c = 20·11$ (1) Å, $\beta = 96·01$ (2)°, $V = 1177·87$ Å^3, $Z = 2$, $D_m = 1·22$ (1), $D_c = 1·235$ Mg m^{-3}, μ(Cu $K\alpha$) = 0·526 mm^{-1}, $F(000) = 468$. The structure was solved by direct methods; final $R = 0·085$ for 1100 photographic data. The fluoranthene molecule is planar and the butyl group is parallel to the a axis forming a zigzag chain. The butyl group has the normal configuration and dimensions, with C—C distances varying from 1·504 (8) to 1·527 (7) Å and is nearly perpendicular to the fluor-

anthene ring. Bond lengths and angles are close to normal values.

Introduction. The crystal structures of many aromatic hydrocarbons have already been investigated by X-ray analysis. The structure of the medium-sized non-alternant hydrocarbon fluoranthene has been determined by Hazell, Jones & Sowden (1977). We have determined the crystal structure of 7,14-dibutyl-acenaphtho[1,2-k]fluoranthene by X-ray diffraction to investigate whether or not the structure is planar and