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Structure of (9S,P)-(+)-7,9-Di-*tert*-butyl-9H-naphtho[1',2':3,4]cyclopenta[1,2-c]phenanthrene

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Abstract. $C_{33}H_{32}$, orthorhombic, $P2_12_12_1$, $a = 11\cdot148$ (1), $b = 22\cdot163$ (2), $c = 9\cdot998$ (1) Å, $Z = 4$, $D_x = 1\cdot152$ Mg m^{-3}. The structure was solved by *MULTAN* 78 and refined by the block-diagonal least-squares method to $R = 0\cdot056$ for 2161 observed reflexions. The molecule has a spiral structure, *i.e.* a *rel*-(9S,P) configuration. Distortion from planarity is significant for all the benzene rings. The cyclopentadiene ring is deformed into an envelope form. The consecutive ring planes are considerably bent. The molecule is more stable in the (9S,P) than in the (9S,M) configuration.

Introduction. Recently, the photolysis of (1S)-(−)-3,3'-di-*tert*-butyl-1,1'-spirobi[benz[g]indene] (1) at 238 K has been reported to yield the (9S,M)-(−) configuration (2) of the title compound stereospecifically as the initial product which can be completely converted at room temperature into the title compound (9S,P)-(+)-7,9-di-*tert*-butyl-9H-naphtho-[1',2':3,4]cyclopenta[1,2-c]phenanthrene (3) by epimerization at the helix structure (from left- to right-handed) (Imajo, Shingu, Kuritani & Kato, 1981).

(1)   (2)   (3)
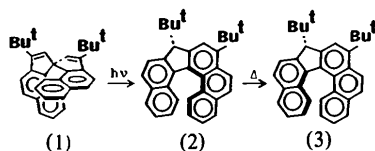
In order to establish the mechanism of this reaction, crystal-structure analysis of (3) was undertaken. The relative configuration of the two chiral centers in (2) was deduced from that of (3). Furthermore, the differences between (2) and (3) in the conformation and strain energy were estimated using the program *MMPI* (Allinger & Yuh, 1977) to seek the factor affecting the stability of (2) and (3).

Yellow needle-like crystals of (3) were obtained from a methyl acetate–ethanol solution. Three-dimensional intensity data were collected on a Rigaku diffractometer with graphite-monochromatized Cu Kα radiation using a crystal of dimensions $0\cdot1 \times 0\cdot2 \times 0\cdot3$ mm. Integrated intensities were measured in the range $\theta \le 70°$ with an $\omega–2\theta$ scan. The intensities of 2601 independent reflexions were corrected for Lorentz and polarization factors, but not for absorption effects.

The structure was solved using the program *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declerq & Woolfson, 1978). In a difference electron-density map calculated after block-diagonal least-squares refinement, all the H atoms were located. Successive refinement of the positional and anisotropic thermal parameters of the non-H atoms gave an R value $(\sum |\Delta F|/\sum |F_o|)$ of 0·056 for 2161 reflexions. The atomic scattering factors were calculated using the analytical expression

$$f = \sum [a_i \exp(-b_i \lambda^{-2} \sin^2 \theta)] + c \quad (i = 1\text{–}4)$$

Table 1. *Atomic coordinates* $(\times 10^4, \times 10^3$ *for* H) *and isotropic temperature factors* $(\text{Å}^2 \times 10)$ *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3} \sum_i \sum_j \beta_{ij}\, \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq}/B
C(1)	4437 (3)	1510 (1)	5915 (4)	36 (1)
C(2)	3912 (4)	1745 (2)	4782 (4)	43 (1)
C(3)	4225 (4)	2323 (2)	4338 (4)	50 (1)
C(4)	5029 (3)	2655 (2)	5047 (4)	42 (1)
C(5)	6285 (3)	2803 (1)	7052 (4)	36 (1)
C(6)	6608 (3)	2624 (1)	8297 (4)	35 (1)
C(7)	6489 (3)	1871 (1)	10194 (4)	33 (1)
C(8)	6040 (3)	1323 (1)	10625 (4)	33 (1)
C(9)	5073 (3)	280 (1)	9993 (3)	35 (1)
C(10)	4961 (4)	−603 (2)	8278 (4)	43 (1)
C(11)	5161 (4)	−792 (2)	6987 (4)	43 (1)
C(12)	5938 (4)	−603 (2)	4729 (4)	46 (1)
C(13)	6512 (4)	−235 (2)	3843 (4)	50 (1)
C(14)	6798 (4)	368 (2)	4207 (4)	46 (1)
C(15)	6445 (3)	591 (2)	5418 (4)	38 (1)
C(16)	5824 (3)	227 (1)	6358 (3)	32 (1)
C(17)	5614 (3)	−390 (2)	6019 (4)	38 (1)
C(18)	5473 (3)	422 (1)	7670 (3)	30 (1)
C(19)	5133 (3)	4 (2)	8614 (4)	35 (1)
C(20)	5627 (3)	1011 (1)	8353 (3)	29 (1)
C(21)	5593 (3)	903 (1)	9718 (3)	32 (1)
C(22)	5790 (3)	1611 (1)	7902 (3)	27 (1)
C(23)	6312 (3)	2035 (1)	8827 (3)	30 (1)
C(24)	5297 (3)	1837 (1)	6652 (3)	30 (1)
C(25)	5552 (3)	2431 (2)	6219 (3)	33 (1)
C(26)	7104 (3)	2297 (1)	11220 (4)	36 (1)
C(27)	8393 (3)	2451 (2)	10744 (4)	48 (1)
C(28)	6343 (4)	2876 (2)	11448 (4)	46 (1)
C(29)	7235 (4)	1992 (2)	12604 (4)	49 (1)
C(30)	3771 (3)	314 (2)	10628 (4)	42 (1)
C(31)	2917 (4)	648 (2)	9671 (5)	61 (1)
C(32)	3789 (4)	647 (2)	11949 (4)	60 (1)
C(33)	3284 (5)	−319 (2)	10875 (5)	74 (2)
H(1)	420 (4)	111 (2)	622 (4)	52
H(2)	330 (4)	152 (2)	422 (4)	60
H(3)	388 (4)	251 (2)	358 (4)	67
H(4)	527 (4)	307 (2)	471 (4)	57
H(5)	644 (4)	321 (2)	678 (4)	50
H(6)	703 (4)	292 (2)	890 (4)	52
H(8)	604 (4)	123 (2)	1158 (4)	50
H(9)	564 (4)	7 (2)	1062 (4)	52
H(10)	472 (4)	−91 (2)	906 (5)	55
H(11)	504 (4)	−125 (2)	668 (4)	60
H(12)	579 (4)	−105 (2)	447 (5)	68
H(13)	672 (5)	−37 (2)	298 (4)	64
H(14)	726 (4)	63 (2)	349 (5)	66
H(15)	663 (4)	102 (2)	566 (4)	53
H(27)	878 (4)	270 (2)	1139 (4)	60
H'(27)	889 (4)	207 (2)	1060 (4)	60
H''(27)	848 (4)	270 (2)	988 (5)	60
H(28)	629 (4)	315 (2)	1055 (4)	59
H'(28)	560 (4)	274 (2)	1192 (4)	59
H''(28)	680 (4)	314 (2)	1209 (4)	59
H(29)	768 (4)	229 (2)	1321 (4)	60
H'(29)	636 (4)	191 (2)	1306 (4)	60
H''(29)	776 (4)	161 (2)	1250 (4)	60
H(31)	283 (5)	41 (2)	883 (5)	73
H'(31)	333 (5)	113 (2)	953 (5)	73
H''(31)	202 (4)	65 (2)	1017 (5)	73
H(32)	398 (5)	111 (2)	1178 (4)	70
H'(32)	296 (5)	59 (2)	1241 (5)	70

Table 1 (*cont.*)

	x	y	z	B
H''(32)	439 (4)	52 (2)	1259 (5)	70
H(33)	321 (5)	−52 (2)	1005 (5)	85
H'(33)	256 (5)	−32 (2)	1140 (5)	85
H''(33)	372 (5)	−53 (2)	1146 (5)	85

(*International Tables for X-ray Crystallography*, 1974). The weighting scheme was $w = 1/\sigma^2(F_o)$ for $|F_c| \geq \sigma(F_o)$ and $w = 0$ for $|F_c| < \sigma(F_o)$ or $|\Delta F| \geq 3\sigma(F_o)$. $\sigma(F_o)$ was estimated as $\sigma(F_o) = [\sigma_1^2(F_o) + 0.00101|F_o|^2]^{1/2}$, where $\sigma_1(F_o)$ is the standard deviation due to counting errors (Grant, Killean & Lawrence, 1969).*

Discussion. Atomic coordinates and isotropic thermal parameters are in Table 1. A perspective view of the molecule with atom-numbering and ring-labelling systems is shown in Fig. 1 and a stereoscopic view in Fig. 2. The molecule has the *rel*-(9*S*,*P*) configuration, *i.e.* a helical form with *P* helicity with respect to the *S* configuration at the C(9) atom. Thus, (2), the precursor of (3), must have the *rel*-(9*S*,*M*) configuration, in accordance with the previously assumed stereo-

* Lists of structure factors, anisotropic thermal parameters of the non-H atoms, bond lengths and angles involving only non-H atoms, and equations of the least-squares planes and deviations of the atoms from the planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36942 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
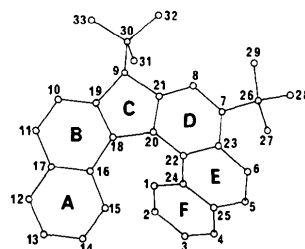

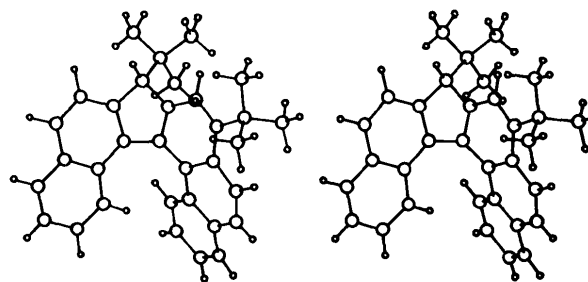Fig. 1. Perspective view of the molecule with atom-numbering and ring-labelling systems.

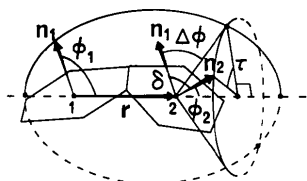Fig. 2. Stereoscopic view of the molecule.

Fig. 3. Definition of the angles δ, τ, φ_1, φ_2, and $\Delta\varphi$. n_1 and n_2 represent the vectors normal to the ring planes of 1 and 2, respectively. r is the vector connecting the centers of the rings 1 and 2.

chemistry of the photolysis reaction (suprafacial 1,5-migration of the vinyl group followed by a suprafacial 1,5-hydrogen shift).

The best planes of the rings $A-F$ were calculated: r.m.s. deviations of the atoms from the planes are respectively 0·020, 0·036, 0·064, 0·074, 0·061, and 0·015 Å for the rings $A-F$. Distortion from planarity is significant for all the rings at the significance level of 1% (χ^2 test). Moreover, the consecutive ring planes are considerably bent (δ in Table 3). Each bond length in the naphthalene and phenanthrene units, however, agrees rather well with the corresponding one in naphthalene (Cruickshank, 1957) and phenanthrene (Kay, Okaya & Cox, 1971) which are almost planar.

The angles τ (torsion), φ_1, φ_2, and $\Delta\varphi$ (bending) as defined in Fig. 3 and the positions of the centers of the respective rings represented in cylindrical coordinates (Table 2) were calculated to describe the helical structure. The former three angles are related to the dihedral angle, δ, as $\cos\delta = \cos\tau\sin\varphi_1\sin\varphi_2 + \cos\varphi_1\cos\varphi_2$. In Table 3, these angles are compared with those calculated for hexahelicene (de Rango, Tsoucaris, Declercq, Germain & Putzeys, 1973). Some of the non-bonded contacts found in the inner core of the helix are shorter than the usual van der Waals distances (Table 4).

Comparison of the energies calculated for the optimal structures of (2) and (3) using the program *MMPI* showed that (3) was more stable than (2), though the energy difference was not sufficient to account for the complete conversion of (2) to (3) observed previously [5·1 kJ mol⁻¹; the items are −1·4

(non-bonded), −0·2 (stretching), −3·4 (bending), 10·2 (torsional) and −0·1 kJ mol⁻¹ (dipole)]. The reason for the lability of (2) is revealed by inspection of the optimized forms of (2) and (3) as follows. The cyclopentadiene (C) rings in both diastereomers were found to be puckered almost into envelope forms (Fig. 4), but the flap of the envelope was C(21) for (3), in contrast to C(19) for (2) (both atoms deviated upwards, in conformity with the helicity of each molecule). The deviation of C(21) is accompanied by a twist of the phenanthrene unit around the C(9)–C(20) axis, which most effectively relieves the repulsion due to the helical structure. This agrees with the structure of (3) found by X-ray analysis. However, the con-

Table 3. *Angles of δ, τ, φ_1, φ_2, and $\Delta\varphi$ ($=\varphi_1 - \varphi_2$) (°) between adjacent ring planes for (3) (upper) and hexahelicene (lower) (de Rango et al., 1973)*

The angles are defined in Fig. 3. The vectors normal to the respective ring planes are taken in the direction of the z axis in the cylindrical coordinates as described in Table 2. The angle τ indicated in Fig. 3 has the plus sign.

Rings	$A-B$	$B-C$	$C-D$	$D-E$	$E-F$
δ	8·7	10·9	15·6	14·3	11·9
	10·0	15·2	15·2	14·8	11·4
τ	4·0	4·1	14·3	9·8	2·0
	2·2	11·0	15·2	12·3	3·7
$\Delta\varphi$	7·7	10·1	6·3	−10·4	−11·8
	9·8	10·6	0·6	−8·4	−10·7
φ_1	93·7	93·7	92·9	83·5	83·2
	94·1	94·8	89·6	85·1	84·1
φ_2	86·0	83·6	86·6	93·9	95·0
	84·3	84·2	89·0	93·5	94·8

Table 4. *Short intramolecular non-bonded distances (Å) with e.s.d.'s in parentheses*

C(1)–C(15)	3·067 (6)	H(8)–H''(29)	2·29 (6)
H(1)–C(15)	2·86 (5)	H(8)–H(32)	2·32 (7)
H(1)–C(16)	2·66 (5)	H(10)–C(33)	2·75 (5)
H(1)–C(18)	2·53 (5)	H(10)–H(33)	2·14 (8)
H(1)–C(20)	2·67 (5)	H(15)–C(1)	2·70 (5)
H(8)–C(29)	2·39 (5)	H(15)–C(20)	2·92 (5)
H(8)–C(32)	2·84 (5)	H(15)–C(22)	2·77 (5)
H(8)–H'(29)	2·16 (6)	H(15)–C(24)	2·56 (5)

Table 2. *Positions of the centers of the rings $A-F$ represented in the cylindrical coordinates (ρ, θ, z)*

The origin is placed at the center of gravity of the whole molecule. The z axis lies parallel to the normal of ring A in the direction of the pitch of the helix passing through A to F.

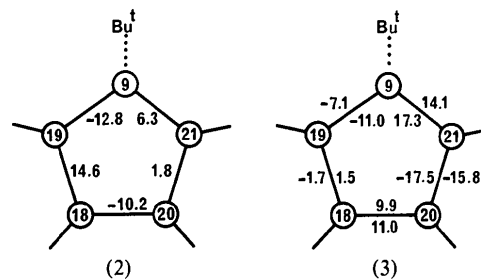|	ρ (Å)	θ (°)	z (Å)
A	3·174	0·0	−0·385
B	2·628	48·5	−0·543
C	1·830	104·5	−0·709
D	2·110	172·2	−0·859
E	2·701	223·9	0·305
F	2·198	259·0	2·191

Fig. 4. Torsion angles (°) in the optimal cyclopentadiene rings of (2) and (3) (inner). Those of (3) obtained by this X-ray work are also given (outer), of which e.s.d. values are 0·4°.

figuration of (2) is not suited for the deviation (downwards) of C(21), as it brings H(8) [buttressed by H(*tert*-Bu 7)] quite close to H(*tert*-Bu 9). In this case the second-best way to relieve the repulsion is by twisting the naphthalene unit around the C(9)–C(18) axis through the deviation of C(19), whereby the relief of the repulsion is not appreciably effective. The resulting increment of strain energy in (2) was found to be borne largely by the increased distortion of the phenanthrene unit from planarity, which was shown by the calculated torsional energy difference between (2) and (3) (8·9 and 1·4 kJ mol^{-1} for the phenanthrene and naphthalene unit, respectively).

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Crystallographic Studies of High-Density Organic Compounds. 1,4-Difluoro-1,1,4,4-tetranitro-2,3-dinitrooxybutane

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Abstract. $C_4H_2F_2N_6O_{14}$, $M_r = 396·1$, monoclinic, $P2_1/c$, $a = 7·6975$ (9), $b = 5·7890$ (8), $c = 14·722$ (3) Å, $\beta = 101·74$ (2)°, $D_{calc} = 2·05$ Mg m^{-3}, $Z = 2$; Cu $K\alpha$ ($\lambda = 1·5418$ Å) diffractometer data; 1045 unique intensities; $811 \geq 3\sigma$ above background; final $R = 0·054$. The molecule lies on a center of symmetry. The overall structure and conformation is similar to that of 1,4-difluoro-1,1,4,4-tetranitro-2,3-butanediol. The RO–NO_2 distance of $1·515$ (5) Å, which is substantially longer than other O–N single bonds, may account for the facile hydrolysis of the nitrate ester linkage. There are no short intermolecular contacts that would account for the exceptional crystal density.

Introduction. The fluorodinitromethyl group is of interest as a functional group for energetic materials such as explosives. We are currently investigating the structures of a number of high-crystal-density, polynitro-group-containing organic compounds as the first step in an investigation of the relationships between crystal density and structure in these types of com-

pounds. In this paper, the structure of the title compound (I) is reported, and compared with the structure of the diol (II) (Dickinson & Holden, 1979).

$$
\begin{array}{c}
\text{O--X} \\
| \\
(NO_2)FC\text{--}CH\text{--}CH\text{--}CF(NO_2)_2 \\
| \\
\text{O--X}
\end{array}
$$

(I)   X = NO₂, (II)   X = H
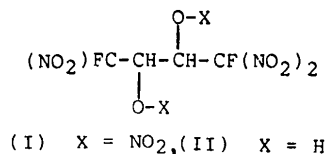
(I) was obtained from Dr H. Adolph, Naval Surface Weapons Center, Silver Spring, Maryland, as opaque white needles. The compound is moisture-sensitive, undergoing hydrolysis to the alcohol (II). A crystal with maximum dimensions of 0·3 mm was quickly transferred from its storage desiccator to a pre-dried capillary tube which was then sealed with dental wax.

The space group and approximate cell parameters were obtained from oscillation and Weissenberg photographs with Ni-filtered Cu radiation. Accurate cell parameters were determined and intensity measurements made with a Picker FACS-I diffractometer and graphite-monochromated Cu radiation (Cu $K\alpha$, $\lambda =$