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The Crystal and Molecular Structure of *endo*-1,2,3,4,4a,9a-Hexahydro-1,4-(*peri*-naphthaleno)fluoren-9-one

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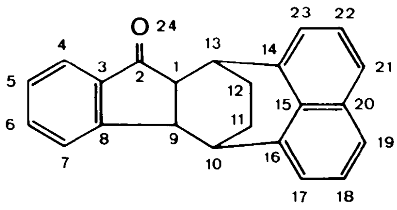
$C_{23}H_{18}O$ is orthorhombic with a = 7·501 (2), b = 12·128 (1), c = 17·225 Å; Z = 4; space group $P2_12_12_1$. The structure was solved by direct methods and refined to a final R of 0·038. H atoms were located from a difference synthesis and their positions refined. The unsaturated part of the hexahydrofluorenone ring system is quasi planar with the five-membered ring in a slightly puckered conformation and the saturated six-membered ring in a skew boat conformation. Calculation of overlap integrals on the basis of the present geometry points to a small 'through-space' interaction between the indanono and naphthaleno groups; therefore intramolecular transfer of electronic excitation energy between them is best explained in terms of 'through-σ-bond' interaction which is favoured by the structure of the title compound.

Introduction

The title compound is one of a series that were spectroscopically investigated to determine the influence of stereochemistry on intramolecular energy transfer (Amrein & Schaffner, 1975*b*). The present structure determination was carried out to ascertain the *endo* conformation deduced from NMR data, and to obtain the geometry of the relative orientation of the chromophoric groups. The atom numbering system used is shown below and should not be confused with the conventional nomenclature used in the title. The H atoms are labelled according to the numbering of the atoms to which they are bonded.



Experimental

The crystals form colourless elongated prisms and were supplied by Amrein & Schaffner (1975*a*). The sample selected was cut to 0·16 × 0·24 × 0·26 mm and sealed in a Lindemann capillary. Lattice parameters and diffracted intensities were measured at room temperature on an automatic four-circle Philips PW1100 diffractometer with a graphite monochromator and Mo $K\bar{\alpha}$ radiation (λ = 0·71067 Å).

Crystal data

$C_{23}H_{18}O$ (m.p. 254 °C). Orthorhombic; space group $P2_12_12_1$, a = 7·501 (2), b = 12·128 (1), c = 17·225 (3) Å; U = 1567·2 Å^3; Z = 4; D_m = 1·29, D_x = 1·316 g cm^{-3}; μ = 0·85 cm^{-1}.

Of the 1002 independent reflexions measured (θ–2θ scan; 0·02° s^{-1}; scan width 1°) out to a limit $\theta \leq$ 21·0°, 920 with $|F| > 2\sigma_F$ were considered observed. Three monitor reflexions measured at average intervals of 38 reflexions showed no significant signs of crystal degradation. Absorption corrections were not applied.

Structure determination and refinement

Preliminary attempts to solve the structure by Patterson search techniques with the $I(\theta,\varphi)$ function of Tollin & Cochran (1964) led to the determination of the general orientation of the two main molecular planes, but neither could specifically be assigned to the naphthalene or indanone ring. The phase problem was finally solved with *MULTAN* (Germain, Main & Woolfson, 1971). The best results were obtained with 250 normalized structure amplitudes (E > 1·27) and 1750 triple-phase relations between them. Four origin and enantiomorph-fixing reflexions were selected and the phases of three additional reflexions were varied, requiring the examination of 32 starting sets of phases. Three sets with the highest figures of merit revealed the location of all the non-hydrogen atoms with an accuracy better than 0·06 Å. At this stage R was 0·28. Positional parameters and anisotropic temperature factors were then refined by full-matrix least squares. When R had fallen to 0·085 all H atoms were located from a difference synthesis and included in the

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Table 1. *Final positional parameters* ($\times 10^4$) *with standard deviation in parentheses*

	x	y	z
C(1)	6327 (6)	40 (3)	2334 (2)
C(2)	7422 (10)	−210 (5)	1612 (4)
C(3)	6190 (8)	−587 (5)	1005 (3)
C(4)	6592 (7)	−1008 (4)	264 (3)
C(5)	5196 (9)	−1360 (4)	−189 (3)
C(6)	3426 (8)	−1282 (4)	70 (3)
C(7)	3052 (6)	−859 (4)	798 (2)
C(8)	4433 (7)	−509 (4)	1262 (3)
C(9)	4341 (6)	−41 (4)	2075 (2)
C(10)	3390 (6)	1085 (3)	2125 (2)
C(11)	3441 (7)	1497 (4)	2969 (3)
C(12)	5296 (7)	1371 (4)	3345 (3)
C(13)	6767 (7)	1127 (4)	2750 (3)
C(14)	7100 (9)	2082 (5)	2197 (4)
C(15)	5810 (8)	2406 (4)	1628 (3)
C(16)	4085 (8)	1930 (4)	1558 (3)
C(17)	2942 (7)	2295 (4)	982 (3)
C(18)	3448 (10)	3144 (5)	461 (3)
C(19)	5069 (9)	3605 (4)	525 (3)
C(20)	6299 (7)	3270 (4)	1094 (3)
C(21)	7999 (8)	3776 (5)	1152 (3)
C(22)	9136 (7)	3473 (5)	1707 (4)
C(23)	8703 (6)	2622 (4)	2236 (3)
O(24)	9036 (5)	−122 (3)	1561 (2)

Table 2. *Observed positional parameters of the hydrogen atoms* ($\times 10^4$)

B is set equal to the isotropic thermal parameter of the carbon atom to which H is bonded.

	x	y	z	B(Å^2)
H(1)	6539	−664	2725	3·97
H(4)	7999	−1145	145	4·54
H(5)	5316	−1696	−711	4·32
H(6)	2338	−1640	−323	4·30
H(7)	1809	−718	981	3·40
H(9)	3685	−585	2419	2·97
H(10)	2090	967	2002	2·73
H(11)A	2508	1111	3321	4·39
H(11)B	3211	2357	3008	4·39
H(12)A	5074	792	3723	4·05
H(12)B	5618	2138	3678	4·05
H(13)	7859	1123	3079	3·93
H(17)	1743	1922	943	4·54
H(18)	2390	3359	38	5·30
H(19)	5521	4224	120	4·56
H(21)	8302	4341	666	4·66
H(22)	10281	3831	1756	5·09
H(23)	9694	2453	2595	4·58

structure model. Their coordinates were refined, maintaining B (Å^2) constant and equal to the isotropic thermal parameter of the bonded C atom. The conditions for inclusion of a reflexion in a cycle of refinement were: $|F_o| \geq 3\sigma(F_o)$; when $2\sigma(F_o) \leq |F_o| < 3\sigma(F_o)$ only if $|F_c| > |F_o|$. The final R based on 903 reflexions was 0·038 with the weighting scheme: $\omega = 1{\cdot}0$ for $3{\cdot}1 < |F_o| \leq 30{\cdot}8$, $\omega = 0{\cdot}5$ for $|F_o| \leq 3{\cdot}1$ and $|F_o| > 30{\cdot}8$. The final values of the positional parameters are listed in Tables 1 and 2.*

Discussion of the results

Bond distances and angles are shown in Fig. 1. The mean standard deviations are 0·008 Å and 0·5°, respectively. Some distances averaged over bonds of the same type are: C(sp^3)–C(sp^3) = 1·542 (8); C(sp^3)–C(sp^2) = 1·516 (6); C–C(phenylene) = 1·390 (14); C–C(naphthylene) = 1·399 (36) Å. C–H lengths are in the range 0·97–1·14, mean 1·04 (6) Å.

For the discussion three main ring systems can be arbitrarily singled out in the molecular frame. The naphthalene ring is planar within limits of error [absolute mean deviation 0·011 (6) Å]. C(10) is shifted by 0·122 Å from this plane, whereas C(13) is displaced 0·118 Å in the opposite direction. These shifts are inter-

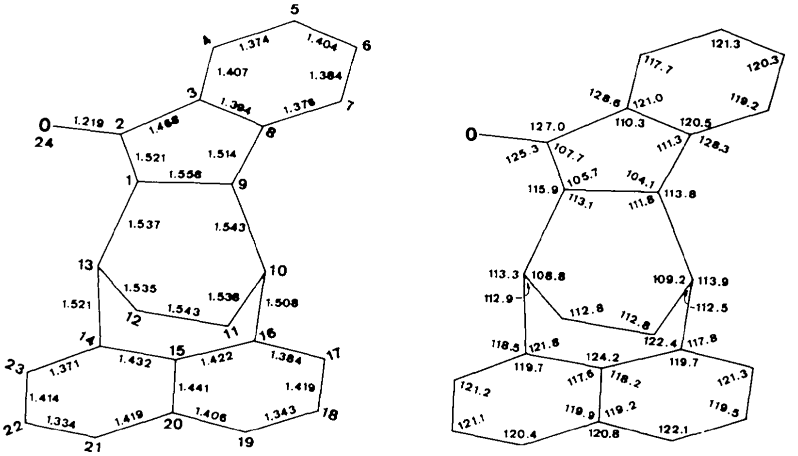

Fig. 1. Sketches of the molecule showing the numbering scheme, bond distances (Å) and angles (°).

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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 32568 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

related with the conformation of the six-membered ring defined by atoms 1–9–10–11–12–13. This ring assumes a slightly distorted skew boat conformation which is known to correspond to an energy minimum of the flexible form. In a somewhat idealized manner the observed form preserves a twofold axis perpendicular to the mean plane through atoms 1–9–11–12. The torsion angles averaged over pairs of 'equivalent' bonds are: 13·6° around C(1)–C(9) and C(11)–C(12); 45·5° around C(1)–C(13) and C(10)–C(11); −60·4° around C(9)–C(10) and C(12)–C(13). The conjugated part (atoms 2–3–4–5–6–7–8–24) of the indanone ring system is quasi planar [absolute mean deviation 0·013 (10) Å] with C(9) lying in the plane and C(1) at 0·182 Å above it and away from the naphthalene ring. Therefore, the five-membered ring is slightly puckered in an envelope form. C(1)–C(9) (1·558 Å) is long compared with its homologues in 2,2′-spirobiindan-1,1′-dione (Petersen & Danielsen, 1974) where the five-membered rings are much more puckered. The bond lengthening releases the angular strain at C(3) and C(8) and the steric repulsion between C(10) and C(13), separated by 2·753 Å. The mutual orientation of the indanono and naphthaleno groups is best seen in Fig. 2. The angle between their mean planes is 65·9° and intramolecular interaction between them only occurs through C(2)···C(14) and C(8)···C(16) at distances of 2·967 and 3·012 Å respectively. The O(24)···C(14) separation (3·233 Å) is larger than the sum of the van der Waals radii, whereas O(24) is in contact with C(13) at a distance of 3·064 Å.

A stereoscopic view of the contents of one unit cell is shown in Fig. 3. Most of the intermolecular interactions are van der Waals contacts with only a few distances shorter than the sum of interference radii. Along **a** the O atom is forced into close contact with H(7) of the neighbouring molecule related by one unit translation, with an O(24)···H(7) separation of only 2·42 Å. Another short contact is 2·67 Å between C(6)···H(21) of two molecules related by a screw diad parallel to **b**.

Through-space and through-bond interaction

Indanono naphthaleno compounds of the type studied here exhibit triplet energy transfer from the

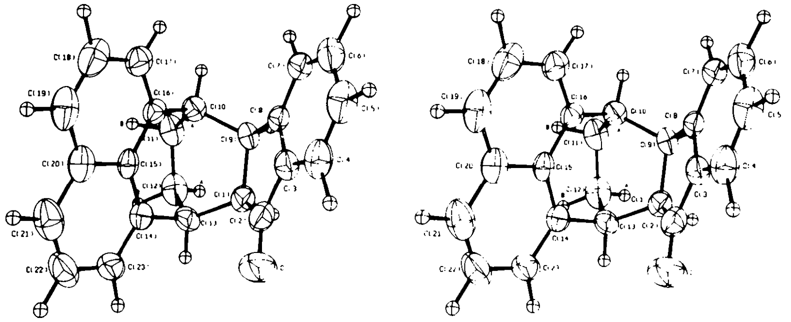


Fig. 2. Stereoscopic view of the molecular conformation.

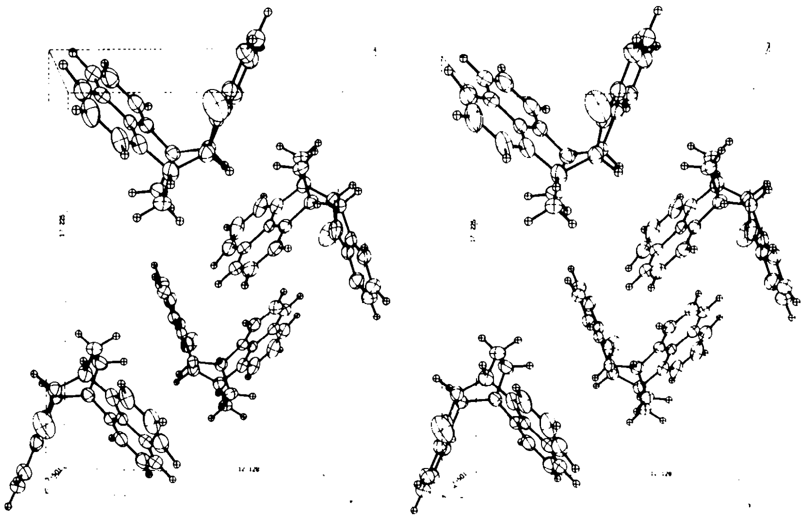
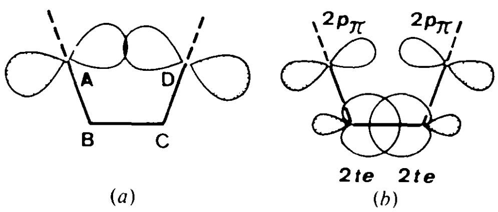


Fig. 3. Stereoscopic view of the contents of one unit cell. The origin and the basic molecule are in the rear, lower left corner.

ketone donor to the naphthalene acceptor which is more efficient in the *exo* than in the *endo* configuration (Amrein & Schaffner, 1975*a*,*b*). An explanation might be found in an efficient through-σ-bond exchange mechanism. To assess the relative extent of through-space and through-bond interaction between the indanone and naphthalene chromophores we follow the scheme originally proposed by Hoffmann, Imamura & Hehre (1968). Through-space interaction is essentially due to pairwise overlap between $2p_\pi$ atomic orbitals ($2p_{\pi,A}$ and $2p_{\pi,D}$, Fig. 4) centred on C(2), C(14) and C(8), C(16) respectively. Through-bond interaction arises from the interplay of the intervening σ-bonds, C(1)–C(13) and C(9)–C(10), whose associated localized bonding orbitals are formed by combinations of the type $(2te_B + 2te_C)/\sqrt{2}$. Through-bond interaction will occur only if each $2p_\pi$ orbital overlaps significantly with its vicinal $2te$ orbital. The overlaps were evaluated with a carbon Slater exponent of 1·625 and on the basis of the geometry determined by X-ray diffraction. Some values are reported in Table 3.

The vicinal $\langle 2p_\pi | 2te \rangle$ integrals are about four times larger than the $\langle 2p_\pi | 2p_\pi \rangle$ integrals; however, the latter are not negligibly small since they approximately correspond to the π-interaction of two *m*-carbon atoms in a benzene ring. Since we measure the extent of the interaction by the magnitude of the overlap we can state that the geometry of the title compound is more favourable to a through-bond coupling of the unsaturated moieties than to a direct through-space coupling.



(*a*) (*b*)

Fig. 4. Schematic picture and labelling of the carbon atomic orbitals used to represent pairwise interaction. The sp^3 hybrids directed along the B–C bond are denoted by the conventional $2te$ symbols. (*a*) Through-space interaction; (*b*) through-bond interaction.

Table 3. *Values of the overlap integrals for through-space and through-bond interactions*

	$\langle 2p_\pi \vert 2te \rangle$		$\langle 2p_\pi \vert 2te \rangle$
C(2), C(1)	0·161	C(8), C(9)	0·154
C(2), C(13)	0·026	C(8), C(10)	0·034
C(14), C(13)	0·135	C(16), C(10)	0·143
C(14), C(1)	0·057	C(16), C(9)	0·049
	$\langle 2p_\pi \vert 2p_\pi \rangle$		
C(2), C(14)	0·041		
C(8), C(16)	0·041		

A theoretical consequence of through-bond interaction in the ground state is the weakening of the B–C bond (see Gleiter, 1974, and references therein) relative to the A–B and C–D bonds. This effect is not detectable for the central bonds C(1)–C(13) and C(9)–C(10), whose lengths are within the range expected for normal C(sp^3)–C(sp^3) bonds; the same is true for the adjacent C(sp^3)–C(sp^2) bonds.

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