Fig. 2. *ORTEP* drawing of (*a*) molecule *A* and (*b*) molecule *B*.
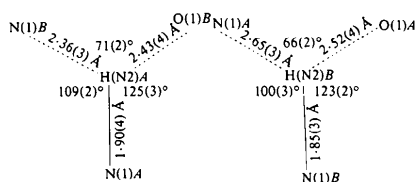

Fig. 3. Hydrogen bonding of H(N2)*A* and H(N2)*B*.

between the methoxycarbonyl group and the vicinal methyl group which appears to be shielded at 0·96 p.p.m. This result may be used as a criterion for the stereochemistry of some other analogous pyrazolidines where a methyl group in a *cis* position with respect to a methoxycarbonyl group is shielded.

Finally, we have considered the intramolecular and intermolecular contacts. This study shows that there are two symmetrical groups of hydrogen bridges between the two molecules in the asymmetric unit. The interactions, starting from atoms H(N2)*A* and H(N2)*B* respectively, are shown in Fig. 3 and Fig. 1(*a,b*). The similarity of the corresponding distances and angles can be noted. This may confirm the connexion of the two molecules in the asymmetric unit to form a hydrogen-bonded dimer in the crystalline state. The infrared spectroscopic data in the solid state (Le Fevre & Hamelin, 1980) also confirm this result.

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very comparable angles with the least-squares planes defined by C(1), C(2), N(1) and N(2) (39·2° for molecule *A* and 35·7° for molecule *B*).

^{1}H NMR spectra show a doublet at 1·38 p.p.m. for compound (3), and a doublet at 0·96 p.p.m. for epimer (3′) for the methyl group.

The X-ray analysis shows unambiguously that in compound (3), the methyl group is in the *trans* position with respect to the methoxycarbonyl group. Consequently in compound (3′) there is a *cis* relationship

Structure of 14-Methyl-7-phenylacenaphtho[1,2-*k*]fluoranthene

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Abstract. $C_{33}H_{20}$, $M_r = 416·5$, triclinic, $P\bar{1}$, $a = 12·184$ (7), $b = 12·507$ (6), $c = 8·542$ (3) Å, $\alpha = 97·64$ (4), $\beta = 104·45$ (4), $\gamma = 116·19$ (3)°, $V = 1085·86$ Å³, $D_x = 1·274$, $D_m = 1·26$ (3) Mg m⁻³, μ(Mo $K\alpha$) = 0·077 mm⁻¹, $Z = 2$, λ(Mo $K\alpha$) = 0·71069 Å, $F(000) = 436$. The structure was determined by direct methods. Final $R = 0·051$ for 2467 observed diffractometer data. The fluoranthene moiety is slightly non-planar; the phenyl ring is almost perpendicular to it and is essentially planar with normal

dimensions. Bond lengths and angles are in reasonably good agreement with those in other nonalternant hydrocarbons.

Introduction. The title compound was conveniently obtained by a one-step synthesis involving a Diels–Alder reaction between 1-chloroacenaphthylene and acecyclones (Banerjee & Bhattacharya, 1977). The crystal structure of fluoranthene, a medium-sized nonalternant hydrocarbon, has already been determined (Hazell, Jones & Sowden, 1977), as has that of 7,14-dibutylacenaphtho[1,2-*k*]fluoranthene (Seth & Chakraborty, 1981). The present X-ray structure investigation of the title compound was undertaken to establish how the phenyl and methyl groups are linked to the fluoranthene ring system, whether the fluoranthene system deviates from planarity and also to study the bonding in the molecule.

Yellow-brown crystals suitable for X-ray analysis were obtained on slow evaporation of a solution in a mixture of acetone and benzene at room temperature. D_m was determined by flotation in aqueous $ZnSO_4$ solution. Rotation and Weissenberg photographs showed the crystal to be triclinic and gave approximate lattice constants. Accurate cell parameters were determined by least squares from the 2θ values of 25 randomly chosen reflexions measured on an Enraf–Nonius CAD-4 diffractometer with graphite-mono-chromated Mo $K\alpha$ radiation from a crystal 0·35 × 0·25 × 0·18 mm. Intensity data, in the range $5 \le 2\theta \le 50°$, were collected at 298 K employing ω–2θ scans.

During data collection crystal stability was monitored by periodically measuring three standard reflexions; there was no evidence of crystal deterioration. Of 3874 independent reflexions, 2468 were accepted as observed $[I \ge \sigma(I)]$ and were used for structure determination. Intensities were corrected for Lorentz and polarization effects but no correction was applied for absorption. The centrosymmetric space group was confirmed by the $N(Z)$ test (Howells, Philips & Rogers, 1950) and $|E|$ statistics.

The direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971) was used to calculate phases for the 300 $|E|$ values greater than 1·40. An E map computed with the phases obtained from the set with the highest combined figure of merit revealed the positions of 12 C atoms. Successive Fourier syntheses yielded the coordinates of the remaining C atoms.

Isotropic least-squares refinement gave $R \simeq 0.14$. The positions of 17 H atoms could be calculated (C—H = 0·95 Å) and the rest, belonging to the methyl group, were located from a difference Fourier synthesis. The structure was finally refined with block-diagonal-least squares techniques with anisotropic thermal parameters for C atoms and isotropic thermal parameters for H atoms. Refinement was discontinued when all the shifts were less than the corresponding e.s.d.'s. The

Table 1. *Final fractional coordinates with e.s.d.'s in parentheses and isotropic temperature factors B_{eq} for* C; B *for* H

$$B_{eq} = (B_{11} + B_{22} + B_{33})/3.$$

	x	y	z	B_{eq} or B (Å²)
C(1)	1·0331 (3)	−0·1271 (2)	0·2744 (4)	5·4
C(2)	0·9747 (2)	−0·0434 (2)	0·2639 (3)	3·6
C(3)	0·8566 (2)	−0·0742 (2)	0·2894 (3)	3·6
C(4)	0·7690 (2)	−0·1830 (2)	0·3334 (3)	3·8
C(5)	0·7701 (3)	−0·2866 (2)	0·3710 (3)	4·8
C(6)	0·6659 (3)	−0·3701 (2)	0·4151 (3)	5·4
C(7)	0·5627 (3)	−0·3544 (2)	0·4186 (3)	5·1
C(8)	0·5570 (2)	−0·2497 (2)	0·3802 (3)	4·3
C(9)	0·4595 (3)	−0·2172 (2)	0·3815 (3)	4·9
C(10)	0·4706 (3)	−0·1105 (2)	0·3453 (3)	4·9
C(11)	0·5791 (2)	−0·0270 (2)	0·3080 (3)	4·3
C(12)	0·6757 (2)	−0·0553 (2)	0·3063 (3)	3·7
C(13)	0·8004 (2)	0·0043 (2)	0·2766 (3)	3·6
C(14)	0·8638 (2)	0·1184 (2)	0·2441 (3)	3·6
C(15)	0·9812 (2)	0·1495 (2)	0·2178 (3)	3·6
C(16)	1·0680 (2)	0·2601 (2)	0·1759 (3)	3·8
C(17)	1·0672 (2)	0·3661 (2)	0·1497 (3)	4·8
C(18)	1·1695 (3)	0·4519 (2)	0·1055 (4)	5·7
C(19)	1·2703 (3)	0·4336 (2)	0·0912 (4)	5·2
C(20)	1·2740 (2)	0·3257 (2)	0·1180 (3)	4·4
C(21)	1·3709 (3)	0·2936 (3)	0·1084 (4)	5·2
C(22)	1·3604 (3)	0·1862 (3)	0·1400 (4)	5·6
C(23)	1·2548 (2)	0·1021 (2)	0·1807 (3)	4·9
C(24)	1·1585 (2)	0·1295 (2)	0·1905 (3)	3·7
C(25)	1·0353 (2)	0·0694 (2)	0·2266 (3)	3·6
C(26)	0·6619 (2)	−0·1674 (2)	0·3402 (3)	3·9
C(27)	1·1718 (2)	0·2422 (2)	0·1601 (3)	3·8
C(28)	0·8115 (2)	0·2059 (2)	0·2408 (3)	3·6
C(29)	0·7243 (2)	0·1983 (2)	0·0943 (3)	4·3
C(30)	0·6807 (2)	0·2837 (2)	0·0902 (3)	5·2
C(31)	0·7243 (3)	0·3770 (2)	0·2330 (4)	5·6
C(32)	0·8090 (3)	0·3852 (2)	0·3811 (4)	5·4
C(33)	0·8523 (2)	0·2988 (2)	0·3847 (3)	4·8
H(1)	0·969 (3)	−0·214 (3)	0·223 (4)	7·2 (9)
H(2)	1·072 (4)	−0·124 (3)	0·380 (5)	9·9 (10)
H(3)	1·091 (3)	−0·118 (3)	0·209 (5)	9·1 (10)
H(5)	0·846 (2)	−0·299 (2)	0·372 (3)	2·5 (5)
H(6)	0·670 (2)	−0·443 (2)	0·444 (3)	4·0 (6)
H(7)	0·492 (2)	−0·416 (2)	0·447 (3)	3·6 (6)
H(9)	0·382 (3)	−0·274 (2)	0·408 (3)	4·4 (6)
H(10)	0·402 (2)	−0·088 (2)	0·346 (3)	3·5 (6)
H(11)	0·585 (2)	0·054 (2)	0·288 (3)	2·0 (5)
H(17)	0·997 (2)	0·383 (2)	0·160 (3)	1·9 (5)
H(18)	1·166 (2)	0·528 (2)	0·079 (3)	3·9 (6)
H(19)	1·340 (3)	0·495 (2)	0·059 (3)	4·7 (7)
H(21)	1·443 (2)	0·350 (2)	0·075 (3)	3·0 (5)
H(22)	1·431 (2)	0·167 (2)	0·132 (3)	3·5 (6)
H(23)	1·254 (2)	0·025 (2)	0·202 (3)	3·0 (5)
H(29)	0·694 (2)	0·129 (2)	−0·007 (3)	3·8 (6)
H(30)	0·617 (3)	0·277 (2)	−0·020 (4)	4·6 (7)
H(31)	0·696 (2)	0·438 (2)	0·231 (3)	3·4 (6)
H(32)	0·841 (2)	0·458 (2)	0·490 (3)	3·6 (6)
H(33)	0·914 (3)	0·307 (2)	0·491 (3)	4·3 (6)

final R values, omitting one reflexion because of obvious strong secondary extinctions, were: $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0.051$, and $R_w = [\sum w(|F_o| - |F_c|)^2/wF_o^2]^{1/2} = 0.051$ for 2467 reflexions. The weighting scheme based on $\sigma(F)$ was modified in

Table 2. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

C(1)—C(2)	1·504 (3)	C(2)—C(3)	1·398 (3)
C(2)—C(25)	1·397 (3)	C(3)—C(4)	1·479 (3)
C(3)—C(13)	1·424 (3)	C(4)—C(5)	1·382 (3)
C(4)—C(26)	1·415 (3)	C(5)—C(6)	1·420 (4)
C(6)—C(7)	1·363 (4)	C(7)—C(8)	1·418 (3)
C(8)—C(9)	1·417 (4)	C(8)—C(26)	1·400 (3)
C(9)—C(10)	1·366 (4)	C(10)—C(11)	1·421 (4)
C(11)—C(12)	1·374 (3)	C(12)—C(13)	1·474 (3)
C(12)—C(26)	1·414 (3)	C(13)—C(14)	1·397 (3)
C(14)—C(15)	1·393 (3)	C(14)—C(28)	1·490 (3)
C(15)—C(16)	1·480 (3)	C(15)—C(25)	1·422 (3)
C(16)—C(17)	1·377 (3)	C(16)—C(27)	1·413 (3)
C(17)—C(18)	1·418 (4)	C(18)—C(19)	1·375 (4)
C(19)—C(20)	1·416 (4)	C(20)—C(21)	1·421 (4)
C(20)—C(27)	1·395 (3)	C(21)—C(22)	1·361 (4)
C(22)—C(23)	1·417 (4)	C(23)—C(24)	1·378 (3)
C(24)—C(25)	1·486 (3)	C(24)—C(27)	1·414 (3)
C(28)—C(29)	1·385 (3)	C(28)—C(33)	1·383 (3)
C(29)—C(30)	1·388 (3)	C(30)—C(31)	1·373 (4)
C(31)—C(32)	1·377 (4)	C(32)—C(33)	1·396 (4)

Table 3. *Bond angles* (°)

C(1)—C(2)—C(3)	122·0 (2)	C(1)—C(2)—C(25)	121·6 (2)
C(3)—C(2)—C(25)	116·3 (2)	C(2)—C(3)—C(4)	130·7 (2)
C(2)—C(3)—C(13)	122·0 (2)	C(4)—C(3)—C(13)	107·3 (2)
C(3)—C(4)—C(5)	136·2 (2)	C(3)—C(4)—C(26)	106·6 (2)
C(5)—C(4)—C(26)	117·2 (2)	C(4)—C(5)—C(6)	118·9 (3)
C(5)—C(6)—C(7)	123·1 (3)	C(6)—C(7)—C(8)	120·1 (3)
C(7)—C(8)—C(9)	127·7 (3)	C(7)—C(8)—C(26)	115·9 (2)
C(9)—C(8)—C(26)	116·4 (2)	C(8)—C(9)—C(10)	120·3 (3)
C(9)—C(10)—C(11)	122·5 (3)	C(10)—C(11)—C(12)	118·8 (2)
C(11)—C(12)—C(13)	135·7 (2)	C(11)—C(12)—C(26)	118·3 (2)
C(13)—C(12)—C(26)	106·0 (2)	C(3)—C(13)—C(12)	108·7 (2)
C(3)—C(13)—C(14)	121·2 (2)	C(12)—C(13)—C(14)	130·1 (2)
C(13)—C(14)—C(15)	117·1 (2)	C(13)—C(14)—C(28)	122·4 (2)
C(15)—C(14)—C(28)	120·5 (2)	C(14)—C(15)—C(16)	129·9 (2)
C(14)—C(15)—C(25)	121·4 (2)	C(16)—C(15)—C(25)	108·7 (2)
C(15)—C(16)—C(17)	135·6 (2)	C(15)—C(16)—C(27)	105·9 (2)
C(17)—C(16)—C(27)	118·6 (2)	C(16)—C(17)—C(18)	118·7 (3)
C(17)—C(18)—C(19)	122·0 (3)	C(18)—C(19)—C(20)	120·5 (3)
C(19)—C(20)—C(21)	127·3 (3)	C(19)—C(20)—C(27)	116·4 (3)
C(21)—C(20)—C(27)	116·3 (3)	C(20)—C(21)—C(22)	119·8 (3)
C(21)—C(22)—C(23)	122·9 (3)	C(22)—C(23)—C(24)	119·2 (3)
C(23)—C(24)—C(25)	136·4 (2)	C(23)—C(24)—C(27)	117·2 (2)
C(25)—C(24)—C(27)	106·3 (2)	C(2)—C(25)—C(15)	121·9 (2)
C(2)—C(25)—C(24)	130·7 (2)	C(15)—C(25)—C(24)	107·4 (2)
C(4)—C(26)—C(8)	124·9 (2)	C(4)—C(26)—C(12)	111·4 (2)
C(8)—C(26)—C(12)	123·7 (2)	C(16)—C(27)—C(20)	123·7 (2)
C(16)—C(27)—C(24)	111·7 (2)	C(20)—C(27)—C(24)	124·5 (2)
C(14)—C(28)—C(29)	121·2 (2)	C(14)—C(28)—C(33)	120·0 (2)
C(29)—C(28)—C(33)	118·8 (2)	C(28)—C(29)—C(30)	120·9 (2)
C(29)—C(30)—C(31)	119·7 (3)	C(30)—C(31)—C(32)	120·5 (3)
C(31)—C(32)—C(33)	119·6 (3)	C(28)—C(33)—C(32)	120·6 (3)

consideration of some systematic errors (Seal & Ray, 1981) in the following way: for $7·76 < |F_o| \le 10·22$, $\sigma(F) = 0·22|F_o|$; for $10·22 < |F_o| \le 12·69$, $\sigma(F) = 0·15|F_o|$; for $12·69 < |F_o| \le 15·51$, $\sigma(F) = 0·10|F_o|$; for $15·51 < |F_o| \le 19·39$, $\sigma(F) = 0·08|F_o|$; for $19·39 < |F_o| \le 23·62$, $\sigma(F) = 0·07|F_o|$; for $23·62 < |F_o| \le 38·78$, $\sigma(F) = 0·05|F_o|$ and for $|F_o| > 38·78$, $\sigma(F) = 0·03|F_o|$.

A difference synthesis after the final cycle showed random fluctuations of up to $\pm0·2$ e Å^{-3}. Atomic

scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Final atomic positional parameters are given in Table 1.* Bond distances and angles are given in Tables 2 and 3.

All computations were performed on the Burroughs B 6700 computer of the Regional Computer Centre, Jadavpur University Campus, Calcutta, with the program *XRAY ARC* (Vickery, Bright & Mallinson, 1971).

Discussion. The molecule is shown in Fig. 1. The bond lengths and angles agree reasonably well with those in fluoranthene (Hazell *et al.*, 1977). The fluoranthene part of the title molecule deviates significantly from planarity although in 7,14-dibutylacenaphtho[1,2-k]-fluoranthene (Seth & Chakraborty, 1981) it is only slightly non-planar. The equation of the best plane through the fluoranthene ring atoms is $-0·0802X - 0·2158Y - 0·9731Z + 2·7471 = 0$, where X,Y,Z are referred to orthogonal axes. The atoms C(6) and C(10) show the greatest deviations from the least-squares plane [$-0·101$ (3) and $0·069$ (3) Å, respectively]. The phenyl ring is essentially planar; the least-squares plane fitted to this ring is $0·6790X + 0·6899Y - 0·2509Z - 6·3149 = 0$, the maximum deviation [$0·010$ (3) Å] involving C(31). The plane of the phenyl ring is almost perpendicular (87·7°) to the fluoranthene ring. The phenyl-ring bonds have a mean length of $1·384$ (8) Å. The central benzene ring is almost planar and the two
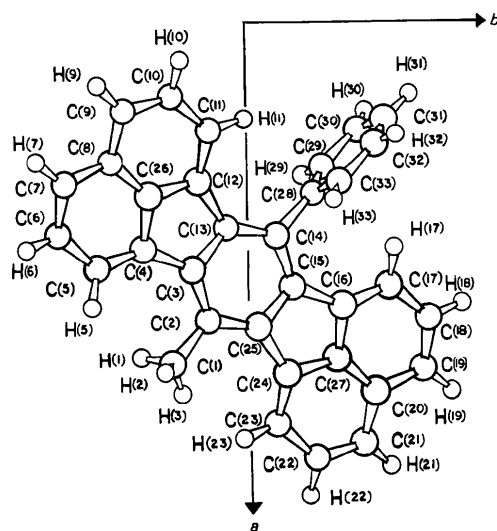
Fig. 1. The title compound projected along c' (c' lies in the plane of a and c, perpendicular to a, and b' is perpendicular to a and c').

five-membered rings are tilted slightly from the mean plane. The strain introduced by the presence of five-membered rings between the benzene and naphthalene nuclei is propagated throughout the molecule so that angles C(3)–C(2)–C(25) and C(13)–C(14)–C(15) are smaller than 120° and angles C(7)–C(8)–C(9) and C(19)–C(20)–C(21) are significantly larger than 120° [cf. 6b,10b-dihydrobenzo-[j]cyclobut[a]acenaphthylene (Hazell & Weigelt, 1976)].

Bond lengths and angles suggest that all bonds in the molecule are involved in resonance.

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Di-tert-butyl-3,5 Cyclohexanone-trans

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Abstract. $C_{14}H_{26}O$, $M_r = 210.4$, monoclinic, $C2/c$, $a = 25.136$ (12), $b = 6.284$ (3), $c = 18.864$ (9) Å, $\beta = 107.98$ (5)°, $Z = 8$, $D_c = 0.99$ g cm^{-3}. The final R is 0.075 for 2056 independent reflexions. The molecular structure shows that the ring has a twist conformation with a C_2 symmetry axis through C(1) and C(4).

Introduction. Pour les cycles à six chaînons de conformation chaise, un groupement tert-butyle axial développe généralement des interactions stériques si fortes que la conformation croisée devient tout à fait compétitive, sinon beaucoup plus stable.

Lorsque deux groupements tert-butyles sont trans dans une situation 1,3, on peut espérer que seule la conformation croisée sera présente. C'est ainsi que la première estimation expérimentale des différences d'enthalpie et d'entropie entre conformations chaise et flexible a été fondée sur cette hypothèse et sur les mises en équilibre des di-tert-butyl-1,3 cyclohexanone cis et trans (Allinger & Freiberg, 1960).

La di-tert-butyl-3,5 cyclohexanone-trans a été considérée a priori comme adoptant la conformation croisée; ce composé a été, de même que certaines cyclohexanones chaises substituées en position axiale β et β', considéré comme modèle dans des études de réactivité (Boyer, 1978). Une détermination de la structure de ce composé s'imposait donc.

Une étude préliminaire, effectuée sur chambre de Weissenberg, nous a permis de déterminer une première valeur des paramètres de la maille. Les conditions d'extinction systématique trouvées sont compatibles avec les groupes Cc et C2/c; compte tenu de la