Table 3. *Torsion angles* (°) *in metal-free* 1,4,8,11-*tetraazacyclotetradecanes*

Torsion angles	(1)	(2)	(3)	(4)
N(1)–C(2)–C(3)–N(4)	67·0 (1)	66·3	63·7	49·3
C(2)–C(3)–N(4)–C(5)	−168·8 (1)	−171·3	−174·6	59·3
C(3)–N(4)–C(5)–C(6)	179·4 (1)	−176·0	−179·8	−166·7
N(4)–C(5)–C(6)–C(7)	−71·3 (1)	−72·5	−66·7	177·1
C(5)–C(6)–C(7)–N(1ⁱ)	57·9 (1)	68·5	67·0	−59·4
C(6)–C(7)–N(1ⁱ)–C(2ⁱ)	−166·3 (1)	−164·2	−171·1	−74·2
C(7)–N(1ⁱ)–C(2ⁱ)–C(3ⁱ)	−171·1 (1)	176·1	170·5	179·1

References: (1) this work; (2) dihydrate of 5,5,7,12,12,14-hexamethyl compound (Gluziński, Krajewski & Urbańczyk-Lipkowska, 1980); (3) diperchloric acid salt of the unsubstituted macrocycle (Nave & Truter, 1974); (4) 1,4,8,11-tetrakis(diphenylphosphinomethyl) compound (Hope, Viggiano, Moezzi & Power, 1984).

Compound (4) in Table 3 is the only one in this group with substituents at the four N atoms and the effect of substitution on the torsion angles is clearly demonstrated. The corresponding angles of the first three compounds agree to a remarkable extent, considering that compound (2) is not protonated at all while compound (3) is the parent macrocycle without the six methyl groups. These angles do not seem to change very much even in the case of the nickel complex (Drew & Mok, 1987).

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7,8-Dimethoxybenzo[*j*]fluoranthene

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Abstract. $C_{22}H_{16}O_2$, $M_r = 312\cdot4$, monoclinic, $P2_1/c$ (No. 13), $a = 9\cdot488$ (3), $b = 6\cdot586$ (2), $c = 25\cdot71$ (1) Å, $\beta = 105\cdot09$ (2)°, $V = 1550\cdot6$ Å³, $Z = 4$, D_m(NaI flotation) = 1·33 (1), $D_x = 1\cdot34$ Mg m⁻³, $\lambda = 0\cdot7107$ Å, μ(Mo $K\alpha$) = 0·047 mm⁻¹, $F(000) = 656$, $T = 298$ K, final $R = 0\cdot042$ for 1952 observed reflections. C atoms within individual rings are coplanar within 0·1 Å but the benzo ring *E* is inclined at about 3·5° to the plane of the naphthalenic *B* ring. In the methoxy groups, with mean dimensions $C-O = 1\cdot380$ (2), $O-C = 1\cdot415$ (3) Å and $C-O-CH_3 = 114\cdot4$ (3)°, the methyl C atoms are each about 1·1 Å out of, and on opposite sides of, the molecular plane, in contrast to the planar arrangement in 5,10-dimethoxybenzo[*j*]fluoranthene.

Introduction. Rather few structural determinations are available for methoxy-substituted non-alternant polycyclic hydrocarbons (Day, Day, Fuerniss & Wheeler, 1975; Briant, Edwards, Jones & McDonald, 1984). When a benzo ring is added to fluoranthene, which is only slightly active carcinogenically (Jones & Matthews, 1974), carcinogenic activity is appreciably increased; the resulting compound, benzo[*j*]fluoranthene (B[*j*]F) (LaVoie, Amin, Hecht, Furuya & Hoffman, 1982), possesses a 'pseudo *K* region' analogous to the phenanthrenic *K* region in benz-[*a*]anthracenes (Briant & Jones, 1983; Briant, Jones & Shaw, 1985). Following an X-ray and neutron study of the structure of fluoranthene (Hazell, Jones & Sowden, 1977) and an X-ray analysis of 5,10-dimethoxybenzo-[*j*]fluoranthene (5,10-DMBF) (Briant *et al.*, 1984), we report here the structure of 7,8-dimethoxybenzo[*j*]-fluoranthene (I) derived from B[*j*]F by chromate oxidation followed by reductive methylation of the 7,8-quinone.
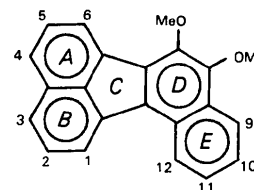
(I)

Experimental. Synthetic material (Edwards & Lockett, 1976) recrystallized from ethanol to yield fragile, yellow–brown needles. From oscillation and Weissenberg photographs, systematic absences *h0l* with *l* odd and *0k0* with *k* odd determined the space group as $P2_1/c$ with one molecule per asymmetric unit. Lattice parameters determined from 15 reflections, 2θ range 35–40°. Two data sets, *A* and *B*, collected with graphite-monochromatized Mo $K\alpha$ radiation by $\omega/2\theta$ scan on a Syntex $P2_1$ diffractometer (Department of Chemistry, Leeds University), standard reflection $1\bar{1}4$ checked every 49 reflections had intensity constant within 4%. Set *A*: $0.9 \times 0.45 \times 0.5$ mm crystal, 2θ range 4–45°, index ranges $h\,0$ to 7, $k\,0$ to 7, $l\,-26$ to 26, 2439 measured intensities yielded 1440 unique reflections with $I > 3\sigma(I)$. Set *B*: $0.5 \times 0.4 \times 0.3$ mm crystal, 2θ range 4–50°, index ranges $h\,0$ to 11, $k\,0$ to 7, $l\,-29$ to 29, 3192 measured intensities yielded 1952 unique reflections with $F_o > 5\sigma(F_o)$. Structure solution by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). All H atoms located by Fourier difference synthesis. Positional parameters of all atoms, anisotropic thermal parameters of non-H atoms, and different isotropic thermal parameters for methyl and aromatic H atoms were refined by full-matrix least squares (on *F*) for the two data sets separately. For set *A*, with *SHELX*76 (Sheldrick, 1976) weighting $w = [\sigma^2(F_o) + 5.84 \times 10^{-3}|F_o|^2]^{-1}$, final $R = 0.0376$, $wR = 0.0596$ over 1440 reflections. For set *B*, with $w = [\sigma^2(F_o) + 4.80 \times 10^{-3}|F_o|^2]^{-1}$, final $R = 0.0424$, $wR = 0.0700$ for 267 variables and 1952 reflections.* Max. $\Delta/\sigma = 0.05$, final $\Delta\rho$ excursions ≤ 0.2 e Å^{-3}. No corrections for secondary extinction or absorption. Atomic scattering factors from Stewart, Davidson & Simpson (1965) for H, and Cromer & Mann (1968) for C and O.

Discussion. Two data sets were obtained and refined, but results are given only from set *B* (slightly smaller e.s.d.'s than those from set *A*). Table 1 contains atomic coordinates, while bond lengths and angles not involving H atoms are given in Table 2 and Fig. 1. Fig. 2 shows the 50% probability thermal ellipsoids from set *B* and Fig. 3 the crystal packing. Half-normal probability analyses (Abrahams & Keve, 1971) for parameters derived from sets *A* and *B* are fairly linear with 10% underestimates of e.s.d.'s and no significant discrepancies except for U_{22}. Individual rings of C atoms are closely planar (r.m.s. deviations < 0.01 Å) but there

is slight twisting out of the mean molecular plane [much as in 5,10-DMBF (Briant *et al.*, 1984)] with the benzo *E* ring inclined at 3.5° to the naphthalenic *B* ring, although the fluoranthene moiety is as planar as in fluoranthene itself (Hazell *et al.*, 1977). Methyl C atoms are each displaced by 1.1 Å on opposite sides of the mean *ABCDE* molecular plane (or the *DE* naphthalene plane); deviations of the methoxy O atoms are much smaller (< 0.1 Å) and in the opposite sense to those of the corresponding methyl C atoms. As a result

Table 1. *Fractional atomic positional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å^2), *set B, with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq} or U_{iso}
C(1)	6117 (2)	3237 (4)	1198 (1)	45 (1)
C(2)	7000 (3)	4942 (4)	1412 (1)	51 (1)
C(3)	6542 (3)	6435 (4)	1694 (1)	48 (1)
C(4)	4519 (3)	7679 (4)	2101 (1)	46 (1)
C(5)	3164 (3)	7309 (4)	2171 (1)	47 (1)
C(6)	2321 (3)	5594 (3)	1945 (1)	45 (1)
C(7)	1119 (2)	1249 (3)	1308 (1)	38 (1)
C(8)	909 (2)	−539 (3)	1024 (1)	39 (1)
C(9)	1766 (3)	−3135 (4)	481 (1)	47 (1)
C(10)	2786 (3)	−3809 (4)	237 (1)	56 (2)
C(11)	4074 (3)	−2717 (4)	278 (1)	53 (1)
C(12)	4330 (3)	−963 (3)	569 (1)	44 (1)
C(13)	3512 (2)	1626 (3)	1135 (1)	35 (1)
C(14)	4751 (2)	3078 (3)	1281 (1)	35 (1)
C(15)	4306 (2)	4616 (3)	1586 (1)	35 (1)
C(16)	2900 (2)	4243 (3)	1651 (1)	35 (1)
C(17)	2412 (2)	2336 (3)	1363 (1)	36 (1)
C(18)	5145 (2)	6305 (3)	1800 (1)	39 (1)
C(19)	1985 (2)	−1295 (3)	778 (1)	37 (1)
C(20)	3308 (2)	−190 (3)	829 (1)	35 (1)
C(21)	−164 (4)	1021 (6)	1978 (1)	73 (2)
C(22)	−1543 (3)	−986 (5)	565 (1)	64 (2)
O(1)	47 (2)	2046 (2)	1522 (1)	51 (1)
O(2)	−339 (2)	−1671 (2)	981 (1)	49 (1)
H(1)	6540 (26)	2179 (40)	1003 (10)	53 (2)
H(2)	7979 (29)	5076 (39)	1364 (9)	53 (2)
H(3)	7206 (27)	7629 (41)	1835 (9)	53 (2)
H(4)	5069 (27)	8968 (37)	2268 (9)	53 (2)
H(5)	2723 (27)	8246 (37)	2400 (10)	53 (2)
H(6)	1366 (29)	5345 (38)	2014 (9)	53 (2)
H(9)	912 (29)	−3923 (36)	479 (9)	53 (2)
H(10)	2593 (27)	−5093 (40)	51 (9)	53 (2)
H(11)	4810 (28)	−3111 (37)	92 (10)	53 (2)
H(12)	5219 (28)	−169 (39)	575 (9)	53 (2)
H(211)	−934 (42)	1661 (55)	2077 (14)	101 (5)
H(212)	769 (42)	1158 (52)	2292 (14)	101 (5)
H(213)	−282 (38)	−566 (62)	1909 (13)	101 (5)
H(221)	−2401 (40)	−1787 (59)	554 (13)	101 (5)
H(222)	−1205 (38)	−1424 (54)	194 (14)	101 (5)
H(223)	−1675 (39)	454 (63)	563 (14)	101 (5)

* Lists of structure factors, anisotropic thermal parameters of non-H atoms, intermolecular contacts, mutual inclinations of best planes, deviations of C atoms from best planes, and C—H bond lengths have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43588 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

C(1)—C(14)	1.372 (3)	C(12)—C(20)	1.409 (3)
C(6)—C(16)	1.372 (3)	C(19)—C(20)	1.427 (3)
C(1)—C(2)	1.423 (4)	C(8)—C(19)	1.424 (3)
C(5)—C(6)	1.418 (3)	C(9)—C(19)	1.418 (3)
C(2)—C(3)	1.358 (4)	C(7)—C(8)	1.372 (3)
C(4)—C(5)	1.366 (4)	C(9)—C(10)	1.358 (4)
C(3)—C(18)	1.424 (3)	C(7)—C(17)	1.395 (3)
C(4)—C(18)	1.418 (3)	C(10)—C(11)	1.398 (4)
C(15)—C(18)	1.394 (3)	C(13)—C(17)	1.404 (3)
C(14)—C(15)	1.411 (3)	C(11)—C(12)	1.363 (3)
C(15)—C(16)	1.409 (3)	C(7)—O(1)	1.380 (2)
C(13)—C(14)	1.486 (3)	O(1)—C(21)	1.412 (3)
C(16)—C(17)	1.470 (3)	C(8)—O(2)	1.379 (2)
C(13)—C(20)	1.416 (3)	O(2)—C(22)	1.421 (3)

of steric interaction with H(9) and H(6) (on C atoms in rings *A* and *E*), methoxy-group geometry in (I) conforms closely to the rare non-planar arrangement (Anderson, Kolleman, Domelsmith & Houk, 1979) in
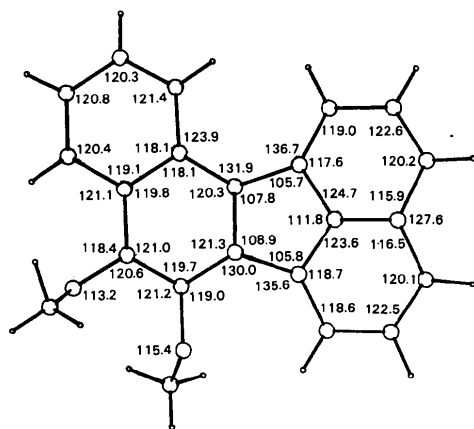

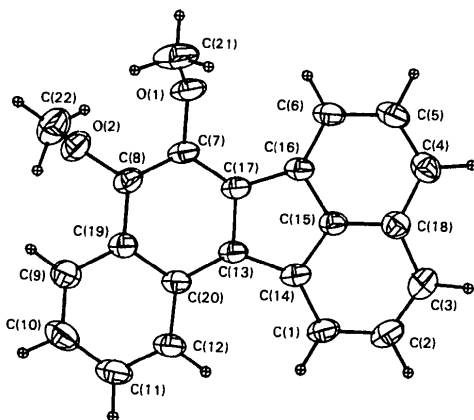
Fig. 1. Bond angles (°) from set *B* (e.s.d.'s 0·2°).

Fig. 2. Projection of the molecule showing 50% probability thermal ellipsoids and atom numbering. H atoms have 0·2 Å radii.
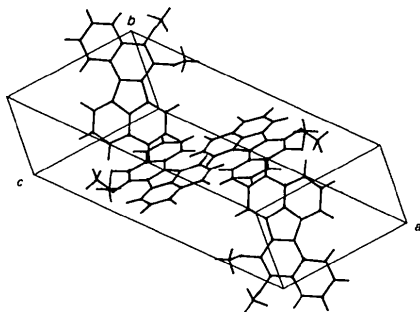

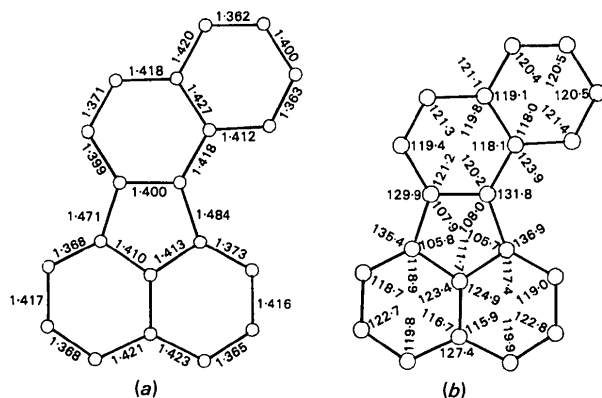Fig. 3. Projection of the unit-cell contents to show molecular packing.

Fig. 4. (*a*) Weighted mean bond lengths (Å) and (*b*) weighted mean bond angles (°) for benzo[*j*]fluoranthenes.

ortho-dimethoxybenzenes, whereas methoxy groups in 5,10-DMBF are of the coplanar type; means of angles C—O—CH$_3$ and inner bay C—C—O at 114·3 and 120·9° are appreciably different from the C—O—CH$_3$ and larger C—C—O angles in 5,10-DMBF, 117·4 and 124·9° (individual e.s.d.'s all 0·2°). From approximate repulsion-energy calculations with *MODEL* (Davies, 1980), the relatively large thermal vibrations of methyls C(21) and C(22) are appropriate for restricted rotation of 20° about their C$_{arom}$—O bonds.

Close similarity of molecular dimensions in (I) and 5,10-DMBF (Briant *et al.*, 1984) should provide a good model for deriving weighted molecular dimensions for unsubstituted B[*j*]F (Fig. 4); the presence of methoxy groups appears to have a negligible effect on bond lengths and angles at points of substitution. The C—C ring-bond lengths are in good agreement with SCF–MO calculations (Dewar & Trinajstic, 1970). Asymmetry (as a result of the benzo ring) of the fluoranthene moiety is slight but there is mild overcrowding in the pseudo bay region so that C(13)—C(20)—C(12) is as high as 123·9 (2)° in (I).

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Conformation of N-(p-Toluenesulfonyl)azacyclotridecane

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Abstract. $C_{19}H_{31}NO_2S$, $M_r = 337.56$, monoclinic, $P2_1/c$, $a = 21.284$ (2), $b = 5.541$ (1), $c = 15.992$ (2) Å, $\beta = 94.44$ (2)°, $V = 1880$ (1) Å³, $Z = 4$, $D_x = 1.19$ Mg m⁻³, $\lambda(Cu K\alpha) = 1.5418$ Å, $\mu = 1.55$ mm⁻¹, $F(000) = 736$, $T = 293$ K, $R = 0.043$ for 3112 independent observed reflections. The 13-membered ring adopts the [13333] conformation with C—C—C angles enlarged beyond tetrahedral, mean 114.3°. C(sp^3)—C(sp^3) bonds have a mean length of 1.523 Å. The sulfonamide N atom is distinctly pyramidal in character, with the N—S bond inclined at 28.5 (1)° to the C—N—C plane.

Introduction. The conformational properties of even-numbered medium-ring compounds (Dunitz, 1968; Anet, St. Jacques, Henrichs, Cheng, Krane & Wong, 1974) have been investigated to a greater extent than those of odd-numbered rings and only very limited information is available about the conformations of 13-membered rings (Dale, 1973; Anet & Rawdah, 1978). The unit cell of dimethyl 1-hydroxycyclotridecylphosphonate has two molecules in the asymmetric crystal unit, one with a well defined conformation and the other distinctly disordered (Samuel & Weiss, 1969); the ordered molecule has the [13333] conformation that Anet & Rawdah (1978) calculated to be the lowest-energy form of cyclotridecane. The predominant conformation of α,ω-bis(methyldodeca-1,12-diylammonio)hexane dibromide, which displays some conformational disorder in the solid, is also the [13333] form (Rubin, Williamson, Takeshita, Menger, Anet, Bacon & Allinger, 1984). Hexacosamethylcyclotridecasilane (Me₂Si)₁₃ adopts a conformation that does not correspond to any of the conformations considered for cyclotridecane (Shafiee, Haller & West, 1986).

An X-ray study of the title compound was undertaken to provide conformational details of the azacyclotridecane ring.

Experimental. Colourless crystal, dimensions 0.20 × 0.20 × 0.40 mm. Enraf–Nonius CAD-4 diffractometer, Cu Kα radiation. Cell dimensions from setting angles of 25 independent reflections with θ 18–25°. 4246 intensities surveyed in the range θ 2–72°; h −26–26, k 0–6, l 0–19; 3112 independent reflections with $I > 2.5\sigma(I)$, $R_{int} = 0.021$. Two reference reflections monitored periodically showed no significant variation in intensity. No absorption correction. Structure determined by direct phasing using *MITHRIL* (Gilmore, 1984). H atoms located in a difference Fourier synthesis. Full-matrix least-squares calculations on F with anisotropic thermal parameters for C, N and O atoms and isotropic for H atoms. Convergence at R 0.043, wR 0.056, S 2.72 for 332 parameters, $\Delta/\sigma < 0.35$ for C, N and O atoms, $w = 1/\sigma^2(|F_o|)$. Final $\Delta\rho$ max. 0.22, min. −0.46 e Å⁻³. Scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations on an SEL 32/27 computer with the *GX* system of programs (Mallinson & Muir, 1985).

Discussion. Atomic coordinates are listed in Table 1 and molecular dimensions in Table 2.* Fig. 1, drawn

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