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# Structures of 4,5-Dimethoxyphenanthrene (I) and 1,8-Dimethoxynaphthalene (II). Deformation in Strained Aromatic Systems and Anomalous Internuclear Distances

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## Abstract

(I) $C_{16}H_{14}O_2$, $M_r = 238{\cdot}3$, triclinic, $P\bar{1}$, $a = 14{\cdot}844\,(3)$, $b = 14{\cdot}960\,(3)$, $c = 15{\cdot}464\,(3)$ Å, $\alpha = 59{\cdot}34\,(2)$, $\beta = 62{\cdot}84\,(2)$, $\gamma = 62{\cdot}00\,(2)^\circ$, $V = 2499{\cdot}3$ Å$^3$, $Z = 8$, $D_x = 1{\cdot}266$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}46$ cm$^{-1}$, $F(000) = 1008$, $T = 294$ K, final $R = 0{\cdot}043$ for 5118 reflections. (II) $C_{12}H_{12}O_2$, $M_r = 188{\cdot}2$, monoclinic, $C2/c$, $a = 12{\cdot}297\,(6)$, $b = 18{\cdot}849\,(4)$, $c = 11{\cdot}816\,(7)$ Å, $\beta = 119{\cdot}06\,(4)^\circ$, $V = 2394{\cdot}0$ Å$^3$, $Z = 8$, $D_x = 1{\cdot}044$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}51$ cm$^{-1}$, $F(000) = 800$, $T = 294$ K, final $R = 0{\cdot}034$ for 1103 reflections. Methoxy substitution of phenanthrene at the 4 and 5 positions and of naphthalene in the 1 and 8 positions results in the two O atoms being brought into very close proximity [average O···O 2·534 (7) Å (I); 2·543 (4), 2·547 (4) Å (II)]. These interactions result in severe deformation of the phenanthrene core but negligible deformation of the naphthalene core. Comparison of the deformation in (I) with that observed in other 4,5-disubstituted phenanthrenes reveals that the methoxy compound is more highly deformed than expected from the calculated overlap of the substituents, evidently as a consequence of the interaction between the methyl of the methoxy group and the phenanthrene core. Bond lengths in the phenanthrene core show no variation with the degree of deformation. The similarity of the O···O separations in (I) and (II) is counter-intuitive; a smaller separation is expected for the phenanthrene. This anomaly is interpreted as being possible evidence for anisotropy in the O···O interactions.

## Introduction

We recently reported the structures of a number of 4,5-disubstituted phenanthrenes and 9,10-dihydrophenanthrenes (Cosmo, Hambley & Sternhell, 1987*a*). A correlation was established between the apparent overlap of the substituents and various measures of deformation of the phenanthrene moiety. We have now determined the structure of the 4,5-dimethoxyphenanthrene (I) and report it herein along with a comparison with the structures of other phenanthrenes. Comparison of the separation between the substituents in these compounds with the separation between the same substituents in 1,8-disubstituted naphthalenes revealed that with relatively bulky substituents such as Cl, Br and $CH_3$, the former separation is greater than the latter (Cosmo, Hambley & Sternhell, 1987*b*). This counter-intuitive result has two possible explanations: (i) the phenanthrene nucleus is more deformable than that of naphthalene and a greater separation can be achieved or (ii) it is energetically less costly to bring the substituents into close proximity in a side-by-side fashion as in the *peri* positions of naphthalene than it is in a head-to-head fashion as in the *bay* positions of phenanthrene. While the former explanation will always be a contributing factor we concluded that the evidence supported the latter explanation (Cosmo, Hambley & Sternhell, 1987*b*). To investigate this problem further we have determined the structure of 1,8-dimethoxynaphthalene (II) for comparison with that of (I).

## Experimental

The preparation of 4,5-dimethoxyphenanthrene was reported by Cosmo & Sternhell (1987*b*). 1,8-Dimethoxynaphthalene was synthesized by procedures previously described by Buu-Hoi & Lavit (1956). Sublimation followed by recrystallization from ethanol gave pure 1,8-dimethoxynaphthalene, m.p. 430–432 K (reported m.p. 430 K). $^1$H NMR spectrum (400 MHz in $CDCl_3$): $\delta$ 3·97, *s*, 2 × $OCH_3$, 6H; 6·85, *dd*, $H_2$ and $H_7$, $J_{2,4} = 1{\cdot}6$ Hz, $J_{2,3} = 7{\cdot}0$ Hz, 2H; 7·37, *dd*, $H_3$ and $H_6$, $J_{3,2} = 7{\cdot}2$ Hz, $J_{3,4} = 8{\cdot}4$ Hz, 2H; 7·39, *dd*, $H_4$ and $H_5$, $J_{4,2} = 1{\cdot}6$ Hz, and $J_{4,3} = 8{\cdot}2$ Hz, 2H. For X-ray crystallography, 1,8-dimethoxynaphthalene was recrystallized by diffusion using dimethyl sulfoxide and water. Crystals were mounted on glass fibres with cyanoacrylate resin. Cell dimensions were determined by a least-squares fit to the setting parameters of 25 independent reflections in the range $10 < \theta < 12^\circ$, measured and refined on an Enraf–Nonius CAD-4F

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Table 1. *Summary of data-collection and processing parameters*

| | (I) | (II) |
|---|---|---|
| Crystal habit | Prismatic | Plates |
| Dimensions (mm) | 0·49 × 0·38 × 0·22 | 0·30 × 0·28 × 0·15 |
| Diffractometer | Enraf–Nonius CAD-4F, four circle | |
| Monochromator | Graphite | Graphite |
| Scan mode | $\omega$–1·67$\theta$ | $\omega$–0·67$\theta$ |
| $2\theta$ range (°) | 1·0–50·0 | 1·0–50·0 |
| Standards | 3 | 3 |
| Decomposition | < 2% | < 2% |
| Reflections measured | 9485 | 1896 |
| Unique reflections | 7167 | 1466 |
| $R_{\rm int}$ | 0·008 | 0·004 |
| Range of *hkl* | 0→16, − 16→16, − 16→16 | 0→14, 0→17, − 14→14 |
| Reflections used [$I > 2·5\sigma(I)$] | 5118 | 1103 |
| $R$ | 0·043 | 0·034 |
| $wR$ | 0·064 | 0·052 |
| Weighting constants $g, k$ [$w = g/(\sigma^2F_o + kF_o^2)$] | 1·0, 1·5 × $10^{-3}$ | 2·3, 5·0 × $10^{-4}$ |

four-circle diffractometer. No absorption corrections were applied. Details of the data collection and structure refinement are collected in Table 1.

(I). The structure was solved by direct methods (*SHELX*76) and refined by blocked-matrix least-squares methods. Of the four molecules in the asymmetric unit, two were found to be disordered over two sites (88:12 and 87:13). H atoms were fully refined with individual isotropic thermal parameters for molecule 1 and were included at calculated sites (C—H 0·97 Å) for the other molecules. Non-H atoms were refined anisotropically except in the case of the minor contributors to the disordered molecules. Refinement converged with all shifts less than 0·2$\sigma$. Maximum excursions in a final difference map were ±0·2 e Å$^{-3}$. Positional and equivalent isotropic thermal parameters are given in Table 2.*

(II). The structure was solved by direct methods (*MULTAN*) and refined by full-matrix least-squares methods. H atoms were fully refined with individual isotropic thermal parameters. Non-H atoms were refined anisotropically. Refinement converged with all shifts less than 0·05$\sigma$. Maximum excursions in a final difference map were ±0·2 e Å$^{-3}$. Positional and equivalent isotropic thermal parameters are given in Table 3.*

Programs used were *SUSCAD* (Guss, 1976) for data reduction, *SHELX*76 (Sheldrick, 1976) for solution and refinement, *MULTAN* (Germain, Main & Woolfson, 1971) for structure solution, and *ORTEP* (Johnson, 1965) for plotting. Scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974).

Table 2. *Positional parameters* (× 10$^4$) *for* (I)

$$B_{\rm eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{\rm eq}$(Å$^2$) |
|---|---|---|---|---|
| O(1) | 2049 (1) | 3458 (1) | 6206 (1) | 4·44 |
| C(2) | 1745 (2) | 3259 (2) | 7243 (2) | 3·69 |
| C(3) | 842 (2) | 3929 (2) | 7705 (2) | 4·53 |
| C(4) | 452 (2) | 3579 (2) | 8790 (2) | 5·53 |
| C(5) | 919 (2) | 2557 (2) | 9401 (2) | 5·50 |
| C(6) | 1851 (2) | 1871 (2) | 8953 (2) | 4·65 |
| C(7) | 2351 (2) | 2264 (2) | 7856 (1) | 3·68 |
| C(8) | 2277 (2) | 759 (2) | 9574 (2) | 5·35 |
| C(9) | 1552 (3) | 4465 (2) | 5525 (2) | 5·42 |
| O(11) | 3967 (1) | 3075 (1) | 6043 (1) | 4·69 |
| C(12) | 4158 (2) | 1972 (2) | 6495 (2) | 4·03 |
| C(13) | 5081 (2) | 1252 (2) | 6114 (2) | 4·94 |
| C(14) | 5333 (2) | 141 (2) | 6700 (2) | 5·67 |
| C(15) | 4692 (2) | − 249 (2) | 7681 (2) | 5·47 |
| C(16) | 3731 (2) | 457 (2) | 8085 (2) | 4·56 |
| C(17) | 3398 (2) | 1579 (2) | 7443 (2) | 3·76 |
| C(18) | 3121 (2) | 73 (2) | 9155 (2) | 5·39 |
| C(19) | 4703 (3) | 3520 (3) | 5127 (3) | 5·94 |
| O(21) | 8119 (1) | 1166 (1) | 4142 (1) | 5·20 |
| C(22) | 7714 (2) | 2216 (2) | 4071 (2) | 3·89 |
| C(23) | 7592 (2) | 2507 (2) | 4844 (2) | 4·47 |
| C(24) | 7318 (2) | 3598 (2) | 4667 (2) | 5·34 |
| C(25) | 7245 (2) | 4383 (2) | 3708 (2) | 4·86 |
| C(26) | 7359 (2) | 4111 (2) | 2905 (2) | 3·96 |
| C(27) | 7484 (1) | 3035 (2) | 3110 (2) | 3·59 |
| C(28) | 7452 (2) | 4899 (2) | 1856 (2) | 4·77 |
| C(29) | 8421 (3) | 329 (2) | 5047 (2) | 6·43 |
| O(31) | 6719 (1) | 1376 (1) | 3494 (1) | 5·96 |
| C(32) | 7214 (2) | 1915 (2) | 2486 (2) | 5·03 |
| C(33) | 7377 (2) | 1681 (3) | 1661 (2) | 6·68 |
| C(34) | 7680 (2) | 2393 (3) | 638 (2) | 8·20 |
| C(35) | 7772 (2) | 3351 (3) | 434 (2) | 6·86 |
| C(36) | 7651 (2) | 3592 (2) | 1256 (2) | 4·96 |
| C(37) | 7474 (2) | 2810 (2) | 2301 (2) | 4·13 |
| C(38) | 7649 (2) | 4636 (2) | 1063 (2) | 5·03 |
| C(39) | 6688 (4) | 326 (3) | 3783 (3) | 8·98 |
| O(41) | 8374 (2) | 3402 (2) | 6944 (2) | 6·67 |
| C(42) | 7345 (3) | 3374 (3) | 7347 (2) | 4·65 |
| C(43) | 6469 (4) | 4297 (4) | 7353 (3) | 6·02 |
| C(44) | 5502 (3) | 4293 (3) | 7528 (3) | 6·11 |
| C(45) | 5353 (3) | 3388 (4) | 7669 (3) | 5·38 |
| C(46) | 6211 (4) | 2418 (4) | 7703 (2) | 4·47 |
| C(47) | 7231 (2) | 2358 (3) | 7602 (2) | 3·69 |
| C(48) | 6039 (2) | 1521 (3) | 7761 (2) | 5·64 |
| C(49) | 8574 (4) | 4062 (4) | 7220 (4) | 10·17 |
| O(51) | 9045 (2) | 1584 (2) | 8344 (2) | 6·59 |
| C(52) | 9022 (2) | 994 (2) | 7911 (2) | 4·31 |
| C(53) | 9829 (3) | 57 (3) | 7822 (3) | 5·27 |
| C(54) | 9675 (3) | − 639 (3) | 7588 (2) | 5·52 |
| C(55) | 8747 (3) | − 461 (2) | 7521 (2) | 5·08 |
| C(56) | 7902 (2) | 510 (2) | 7606 (2) | 4·47 |
| C(57) | 8065 (2) | 1319 (2) | 7688 (2) | 3·82 |
| C(58) | 6869 (3) | 630 (2) | 7656 (2) | 5·75 |
| C(59) | 10006 (3) | 1343 (5) | 8509 (4) | 9·55 |
| C(41′) | 16850 (13) | 986 (14) | 8177 (14) | 7·01 |
| C(42′) | 16648 (39) | 2109 (34) | 7726 (32) | 6·73 |
| C(43′) | 15745 (33) | 2684 (34) | 7523 (25) | 6·21 |
| C(44′) | 15427 (23) | 3877 (29) | 7229 (23) | 5·70 |
| C(46′) | 16835 (38) | 3749 (42) | 7446 (35) | 7·17 |
| C(47′) | 17424 (25) | 2589 (33) | 7682 (27) | 5·17 |
| C(48′) | 17517 (17) | 4178 (17) | 7518 (16) | 5·11 |
| C(49′) | 16203 (26) | 486 (26) | 8242 (25) | 8·01 |
| O(51′) | 18797 (13) | 571 (12) | 7086 (12) | 5·97 |
| C(52′) | 19161 (19) | 853 (19) | 7326 (20) | 5·41 |
| C(53′) | 20090 (24) | 315 (26) | 7750 (23) | 4·69 |
| C(54′) | 20455 (22) | 732 (24) | 8124 (22) | 7·14 |
| C(55′) | 19831 (59) | 2005 (57) | 8034 (53) | 16·90 |
| C(56′) | 18801 (15) | 2391 (17) | 7880 (15) | 3·98 |
| C(57′) | 18449 (15) | 1905 (16) | 7680 (14) | 4·29 |
| C(58′) | 18613 (23) | 3375 (27) | 7831 (24) | 7·16 |
| O(61) | 2901 (3) | 2340 (3) | 1168 (3) | 6·45 |
| C(62) | 3440 (2) | 2818 (2) | 1208 (2) | 4·51 |
| C(63) | 4306 (2) | 3114 (2) | 402 (2) | 5·66 |
| C(64) | 4952 (3) | 3436 (4) | 531 (3) | 6·42 |
| C(65) | 4804 (3) | 3356 (3) | 1498 (4) | 7·34 |
| C(66) | 3907 (4) | 3080 (3) | 2342 (4) | 5·35 |
| C(67) | 3135 (3) | 2940 (2) | 2182 (3) | 4·58 |
| C(68) | 3836 (4) | 2855 (3) | 3374 (4) | 7·67 |
| C(69) | 3302 (5) | 2036 (4) | 304 (3) | 7·23 |
| O(71) | 1145 (2) | 3650 (2) | 1818 (2) | 6·20 |
| C(72) | 1171 (3) | 3113 (3) | 2826 (4) | 4·52 |
| C(73) | 301 (4) | 2933 (2) | 3664 (4) | 6·04 |
| C(74) | 338 (4) | 2577 (3) | 4685 (4) | 6·72 |

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* Lists of structure amplitudes, anisotropic thermal parameters of non-H atoms, positional and thermal parameters of H atoms, and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52732 (46 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2 (*cont.*)

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| C(75) | 1226 (4) | 2460 (3) | 4826 (3) | 5·95 |
| C(76) | 2188 (5) | 2596 (3) | 3993 (4) | 5·43 |
| C(77) | 2161 (3) | 2853 (2) | 2986 (2) | 4·46 |
| C(78) | 3032 (7) | 2502 (5) | 4243 (7) | 7·99 |
| C(79) | 359 (3) | 3610 (4) | 1553 (4) | 7·40 |
| O(61′) | 13698 (7) | 3721 (8) | 1162 (7) | 3·40 |
| C(62′) | 13717 (31) | 3165 (27) | 2099 (24) | 4·07 |
| C(63′) | 14488 (18) | 2919 (17) | 2576 (20) | 4·99 |
| C(64′) | 14237 (16) | 2472 (17) | 3712 (16) | 4·32 |
| C(65′) | 13058 (23) | 2701 (30) | 4085 (31) | 2·93 |
| C(66′) | 11805 (30) | 2569 (32) | 4276 (32) | 4·72 |
| C(67′) | 12679 (16) | 2847 (14) | 2889 (16) | 2·63 |
| C(69′) | 14611 (30) | 4052 (30) | 413 (29) | 9·40 |
| O(71′) | 13261 (14) | 2233 (20) | 1146 (18) | 4·04 |
| C(72′) | 12176 (11) | 2789 (10) | 1549 (10) | 2·13 |
| C(73′) | 11439 (10) | 3015 (10) | 1109 (10) | 2·80 |
| C(74′) | 10160 (24) | 3217 (23) | 2035 (25) | 6·49 |
| C(75′) | 10071 (11) | 3224 (12) | 2687 (12) | 3·35 |
| C(76′) | 10913 (26) | 2964 (20) | 3211 (22) | 3·00 |
| C(77′) | 11970 (13) | 2892 (11) | 2411 (11) | 2·54 |
| C(78′) | 10637 (17) | 2876 (17) | 4161 (20) | 4·19 |
| C(79′) | 13638 (42) | 2259 (44) | 11 (38) | 9·80 |

Table 3. *Positional parameters* ($\times 10^4$) *for* (II)

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| C(1) | 4263 (2) | 5 (1) | 6283 (2) | 2·98 |
| C(2) | 3579 (2) | − 500 (1) | 5180 (2) | 3·77 |
| C(3) | 3581 (2) | − 1440 (1) | 5218 (2) | 4·21 |
| C(4) | 4271 (2) | − 1888 (1) | 6340 (2) | 4·18 |
| C(5) | 5000 | − 445 (2) | 7500 | 2·99 |
| C(6) | 5000 | − 1408 (2) | 7500 | 3·47 |
| O(1) | 4267 (1) | 910 (1) | 6285 (1) | 3·47 |
| C(7) | 3532 (2) | 1351 (2) | 5076 (2) | 4·09 |
| C(11) | 739 (2) | 3 (1) | 7033 (2) | 2·93 |
| C(12) | 1408 (2) | − 495 (2) | 6608 (2) | 4·29 |
| C(13) | 1399 (2) | − 1433 (2) | 6633 (2) | 4·68 |
| C(14) | 723 (2) | − 1883 (1) | 7068 (2) | 3·93 |
| C(15) | 0 | − 438 (2) | 7500 | 2·76 |
| C(16) | 0 | − 1401 (2) | 7500 | 3·11 |
| O(11) | 762 (1) | 920 (1) | 7060 (1) | 4·27 |
| C(17) | 1484 (2) | 1357 (2) | 6584 (2) | 4·91 |

## Discussion

The structure of 4,5-dimethoxyphenanthrene (I) has four identical molecules in the asymmetric unit. Analysis of the metric symmetry of the reduced cell gives no evidence for a cell of higher symmetry. The molecules are packed with no intermolecular contact significantly shorter than the relevant van der Waals radii sum. Two of the molecules are disordered over two sites each. Discussion hereafter is limited to the molecules which are not disordered. Full tables of bond lengths and angles have been deposited. *ORTEP* plots of one of the molecules are shown in Fig. 1.

It is clear from the figure and from measures of planarity that the methoxy substituents cause significant deformation of the phenanthrene moiety. One of the substituents is forced out of plane on one side of the plane and the other on the opposite side of the plane. Despite this deformation the O···O separation is 2·541 (3) and 2·527 (3) Å in molecules 1 and 2, significantly shorter than the van der Waals separation (3·04 Å; Bondi, 1964). Clearly the O···O interaction imposes a stress on the phenanthrene system. We have been interested in correlating the stress on a system with various manifestations of the strain (Bott, Field & Sternhell, 1980; Cosmo & Sternhell, 1987*a*; Cosmo, Hambley & Sternhell, 1987*a*). Apparent overlap ($\sum r^*$), which is the interpenetration of the van der Waals spheres calculated assuming idealized geometries, has been shown to be a useful measure of stress (Bott, Field & Sternhell, 1980). As a measure of strain we have previously considered a number of measures of deformation in 4,5-disubstituted phenanthrenes: the sum of the torsion angles in rings *A* and *C*, the sum of deviations from the least-squares planes through rings *A* and *C*, the distance between atoms C4 and C5, and the sum of pyramidalizations at all atoms in aromatic rings (Cosmo, Hambley & Sternhell, 1987*a*). The first three of these measures gave results which correlated very well with each other. The pyramidalizations, defined as the angle between one bond and the plane through the other two bonds, were not as consistent and showed more nonsystematic variation where there was more than one molecule in the asymmetric unit. The sum of the squares of the deviations from planarity should give a better estimate of the energy required to produce the observed deformations.

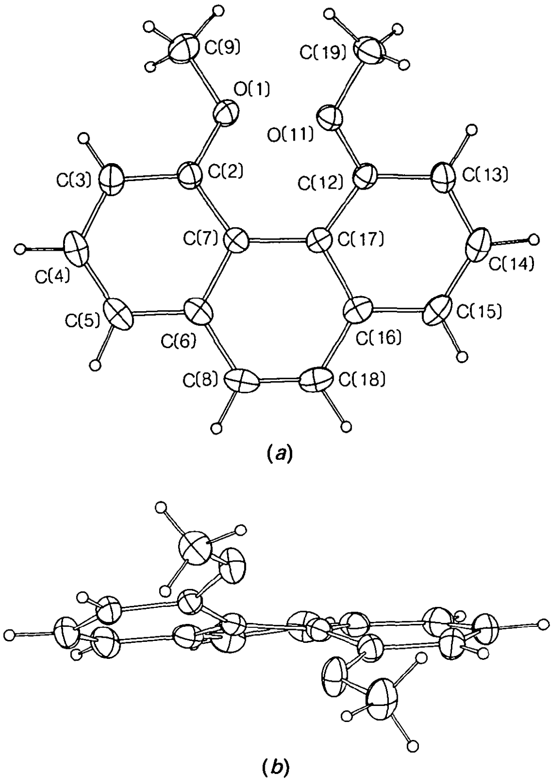

Fig. 1. (*a*), (*b*) *ORTEP* plots of (I) giving crystallographic atom numbering.

Therefore, this value is plotted against apparent overlap, as a measure of stress, in Fig. 2 for the title compound, other similarly substituted phenanthrenes and phenanthrene itself. These results show that 4,5-dimethoxyphenanthrene is highly deformed, even more so than the analogous methyl and chloro compounds. This is surprising since the O atom is sterically less demanding than either the methyl or chloro groups. The substituent with the most similar van der Waal's radius to O is F and we can see from Fig. 2 that the dimethoxy compound is deformed nearly twice as much as the difluoro compound.

The additional deformation of the methoxy compound is almost certainly a consequence of the interaction between the methyl group of the methoxy substituent and the ring to which it is connected. The methyl group lies almost in the plane of the aromatic ring to which it is connected as shown by the C3—C4—O—C(Me) torsion angles [0·6 (4)–22·2 (5)°]. The shortest interactions between the methyl group and C3 and H3 are in the ranges 2·788–2·833 Å (C—C), 2·451–2·535 Å (C—H) and 2·15–2·31 Å (H—H). These strong interactions lead to opening of the C3—C4—O angles [122·6 (3)–122·9 (3)°] and closing of the C4a—C4—O angles [116·2 (2)–116·6 (3)°] compared with values observed in other compounds in Table 4; C3—C4—*X*, 113·4 (2)–117·9 (3)° and C4a—C4—*X*, 119·5 (2)–125·0 (2)°. The consequence of this is that the O atoms are forced closer together and the phenanthrene core then deforms further to attempt to relieve the unfavourable O···O interaction.

Table 4. *Bond lengths* (Å) *for phenanthrene and* 4,5-*disubstituted phenanthrenes averaged assuming* $C_2$ *symmetry*

| *X** | 3–4 | 4–4a | 2–3 | 1–2 | 1–10a | 4a–10a | 10–10a | 4a–5a | 9–10 |
|---|---|---|---|---|---|---|---|---|---|
| $OCH_3$ | 1·381 | 1·421 | 1·386 | 1·358 | 1·407 | 1·417 | 1·428 | 1·461 | 1·336 |
| $CH_3$ | 1·388 | 1·428 | 1·381 | 1·347 | 1·398 | 1·409 | 1·444 | 1·468 | 1·334 |
| F | 1·359 | 1·401 | 1·383 | 1·355 | 1·402 | 1·422 | 1·429 | 1·459 | 1·325 |
| Cl | 1·383 | 1·408 | 1·378 | 1·361 | 1·407 | 1·417 | 1·429 | 1·460 | 1·340 |
| Br | 1·381 | 1·416 | 1·380 | 1·383 | 1·395 | 1·424 | 1·433 | 1·452 | 1·338 |
| $CF_3$ | 1·383 | 1·425 | 1·385 | 1·348 | 1·423 | 1·421 | 1·427 | 1·469 | 1·343 |
| $H^a$ | 1·400 | 1·405 | 1·393 | 1·362 | 1·428 | 1·424 | 1·434 | 1·455 | 1·347 |
| $H^b$ | 1·392 | 1·404 | 1·378 | 1·366 | 1·422 | 1·408 | 1·441 | 1·457 | 1·335 |

* Data taken from this work ($OCH_3$); Cosmo, Hambley & Sternhell (1987*a*) ($CH_3$, F, Cl, $CF_3$); Hambley & Sternhell (unpublished results) (Br); Trotter (1963) ($H^a$); and Kay, Okaya & Cox (1971) ($H^b$). Standard deviations for all bonds are in the range 0·003–0·006 Å.

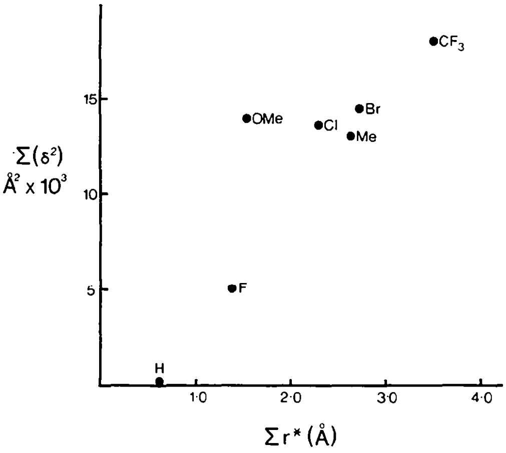

Fig. 2. Plot of the sum of the squares of the deviations from planarity of rings *A* and *C* [$\Sigma(\delta^2)$] against the apparent overlap ($\Sigma r^*$).

The observation that the methyl groups remain close to the plane of the ring to which they are attached, despite the strain this causes, suggests that the electronic barrier to rotation about the C4—O bond must be significant. This barrier is probably the result of delocalization of the $\pi$ electrons into the C4—O bond which is evidenced by the shorter length of the C4—O bond [1·360 (3) Å] compared with the O—C(Me) bond [1·406 (5) Å].

It is interesting that the deformation of the aromatic rings in the dimethoxy member of the 4,5-disubstituted 9,10-dihydrophenanthrenes is not significantly greater than that expected from the estimation of overlap, being similar to that observed for the difluoro analogue (Cosmo, Hambley & Sternhell, 1987*a*). The methyl groups of this compound are coplanar with the aromatic ring to which they are attached, as observed for the phenanthrene analogue, and the C4—O bond length is the same, indicating similar delocalization into this bond. Also, the C3—C4—O angle is opened and the C4a—C4—O angle closed as in the phenanthrene indicating a similarly unfavourable interaction between the methyl group and atoms C3 and H3. The hydrogenation at the 9 and 10 positions enables a greater O···O separation since rotation about C4a—C5a is more facile (Cosmo & Sternhell, 1987*a*) and consequently there is a greater angle between the O···O vector and the plane of the C4—O—C(Me) group. Thus, the movement of the O atoms away from C3, being constrained to the plane of the ring to which it is attached, is not as effective in forcing the O atoms closer to each other and so does not result in so great a deformation of the aromatic rings.

Bond lengths averaged over the two non-disordered molecules and assuming $C_2$ symmetry are given in Table 4. Similarly averaged values for other 4,5-disubstituted phenanthrenes and for phenanthrene itself are also given in Table 4 for comparison. There is little variation in these bond lengths as the substituents are varied, and no obvious correlation between any of the bond lengths and the degree of deformation of the phenanthrene core. This accords with the observation of Sternhell & Tansey (1987) that bond orders in the phenanthrene core do not vary with substituent. The only anomaly in the bond lengths is the C3—C4 bond in 4,5-difluorophenanthrene which is significantly shorter than the equivalent distance in all other compounds listed in Table 4. This anomaly is not crystallographic as the bond length occurs twice in this structure (Cosmo, Hambley & Sternhell, 1987*a*) and we therefore conclude that it is a consequence of the electronic properties of the F substituent. The other bond adjacent to the F atom in this compound, C4—C4a, is also the shortest for the compounds considered but the difference is barely significant.

The structure of 1,8-dimethoxynaphthalene (II) consists of two independent molecules, each lying on a twofold rotation axis at $x = \frac{1}{2}$, $z = \frac{3}{4}$. *ORTEP* plots of one of these molecules are shown in Fig. 3. The structures of the two independent molecules are not significantly different. Bond lengths and angles are given in Table 5.

The naphthalene core is close to being planar; the largest deviation from the plane through a single six-membered ring is 0·008 Å and the largest deviation from the plane through all ten atoms of a naphthalene is 0·017 Å. The methoxy groups lie close to these planes; the deviations of O and C from the plane through the six-membered ring are 0·01 and 0·05 Å respectively in molecule 1 and 0·04 and 0·03 Å in molecule 2. The coplanarity of the methoxy and the naphthalene moieties, despite the unfavourable intramolecular interactions which result [C(7)···C(2) 2·750, H(7*A*)···H(2) 2·217 Å], is similar to the situation observed in (I). The O(1)—C(1)—C(2) [122·6 (2), 122·5 (2)°] and O(1)—C(1)—C(5) [117·0 (1), 117·2 (1)°] angles reflect the strain resulting from these interactions. The suggestion, above, that the preference for a coplanar arrangement is a consequence of partial double-bond character in the C(1)—O(1) bond is supported by the naphthalene structure since this bond is shorter [1·359 (2), 1·362 (2) Å] than the O(1)—C(7) bond [1·425 (2), 1·419 (2) Å].

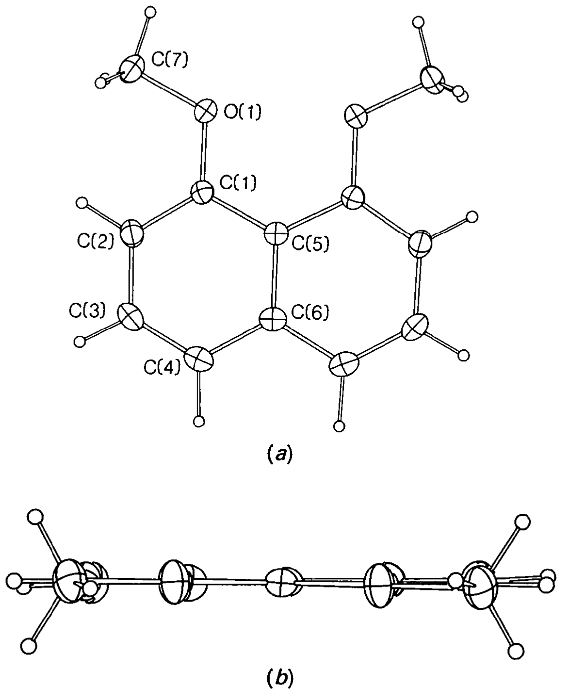

Fig. 3. (*a*), (*b*) *ORTEP* plots of (II) giving crystallographic atom numbering.

Table 5. *Bond lengths* (Å) *and angles* (°) *for* (II)

| | | | |
|---|---|---|---|
| C(2)—C(1) | 1·372 (2) | C(5)—C(1) | 1·431 (2) |
| O(1)—C(1) | 1·359 (2) | C(3)—C(2) | 1·396 (3) |
| C(4)—C(3) | 1·352 (3) | C(6)—C(4) | 1·413 (2) |
| C(6)—C(5) | 1·431 (3) | C(7)—O(1) | 1·425 (2) |
| C(12)—C(11) | 1·370 (2) | C(15)—C(11) | 1·430 (2) |
| O(11)—C(11) | 1·362 (2) | C(13)—C(12) | 1·393 (3) |
| C(14)—C(13) | 1·349 (3) | C(16)—C(14) | 1·416 (2) |
| C(16)—C(15) | 1·430 (3) | C(17)—O(11) | 1·419 (2) |
| | | | |
| C(5)—C(1)—C(2) | 120·4 (2) | O(1)—C(1)—C(2) | 122·5 (2) |
| O(1)—C(1)—C(5) | 117·0 (1) | C(1)—C(5)—C(1) | 125·7 (2) |
| C(3)—C(2)—C(1) | 121·0 (2) | C(4)—C(3)—C(2) | 121·0 (2) |
| C(6)—C(4)—C(3) | 120·2 (2) | C(4)—C(6)—C(4) | 119·4 (2) |
| C(6)—C(5)—C(1) | 117·1 (1) | C(5)—C(6)—C(4) | 120·3 (1) |
| C(7)—O(1)—C(1) | 117·2 (1) | C(15)—C(11)—C(12) | 120·2 (2) |
| O(11)—C(11)—C(12) | 122·6 (2) | O(11)—C(11)—C(15) | 117·2 (1) |
| C(11)—C(15)—C(11) | 125·6 (2) | C(13)—C(12)—C(11) | 121·3 (2) |
| C(14)—C(13)—C(12) | 121·1 (2) | C(16)—C(14)—C(13) | 119·8 (2) |
| C(14)—C(16)—C(14) | 119·2 (3) | C(16)—C(15)—C(11) | 117·2 (1) |
| C(15)—C(16)—C(14) | 120·4 (1) | C(17)—O(11)—C(11) | 117·3 (1) |

The other unfavourable interaction in the 1,8-dimethoxynaphthalene structure is between the two O atoms. Distances of 2·543 (4) and 2·547 (4) Å are observed, almost identical to the O···O separations observed for 4,5-dimethoxyphenanthrene and corresponding to a highly unfavourably interaction. This result is apparently counter-intuitive since from idealized models a much shorter interaction is expected in the phenanthrene compared with the naphthalene. Similar counter-intuitive results have been reported previously for chlorine and bromine substituents (Cosmo, Hambley & Sternhell, 1987*b*) and there we suggested two possible explanations. Firstly, that the phenanthrene nucleus is more deformable than the naphthalene nucleus and secondly that the head-to-head approach of atoms, as in the phenanthrene is more energetically unfavourable than side-to-side contact, as in the naphthalene. Of course, the first factor will always play some role since no two molecules are equally deformable and therefore it is difficult to establish the veracity of the second factor.

The coincidence of the O···O distances in the two compounds under study here may allow us to comment on whether there is a contribution from the second factor. If we start with the assumption that there is no difference in the energy cost associated with the O···O interactions in (I) and (II), then since the C(H)···methyl interactions are also similar, we must come to the conclusion that the energy required to further deform the phenanthrene and naphthalene cores is also similar. This, however, appears unlikely since the phenanthrene nucleus is grossly distorted yet the naphthalene nucleus is not significantly distorted. If we consider the energy profiles for deformation of these molecules as parabolas then in the phenanthrene case the observed structure would lie some way up the steep side of the curve and in the naphthalene case the structure lies close to the valley of the curve. Given that the O···O interaction in the naphthalene case is highly unfavourable then we would expect to see some distortion of the nucleus. Thus, we conclude that comparison of the present two structures indicates that it is easier to bring atoms close together side on, as in naphthalene, than more nearly head on, as in phenanthrene, unless the naphthalene nucleus is extraordinarily difficult to deform in the direction perpendicular to the aromatic rings.

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# Structure of Belladonna Mottle Virus: Cross-Rotation Function Studies with Southern Bean Mosaic Virus

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## Abstract

Belladonna mottle virus, which belongs to the tymovirus group of RNA plant viruses, crystallizes in rhombohedral space group $R3$ with $a = 295{\cdot}38$ Å and $\alpha = 59{\cdot}86°$. Cross-rotation function studies between belladonna mottle virus and southern bean mosaic virus reveal that the structure of this tymovirus is similar to those of sobemo viruses. A procedure for computing an icosahedrally averaged rotation function was developed as a general method for a more precise determination of the orientation of a symmetric molecule in an unknown cell. These studies suggest that it might be possible to obtain a high-resolution structure of belladonna mottle virus starting from phases derived from a model based on southern bean mosaic virus.

## 1. Introduction

Belladonna mottle virus (BDMV; Moline & Fries, 1974) belongs to the tymovirus group of monopartite RNA plant viruses. The type member of this group, turnip yellow mosaic virus (TYMV) has been extensively studied in terms of the forces stabilizing the particle structure (Kaper, 1971, 1975; Jacrot, Chauvin & Witz, 1977; Katouzian-Safadi, Favre & Haenni, 1980; Katouzian-Safadi & Berthet-Colominas, 1983; Katouzian-Safadi & Haenni, 1986; Keeling & Matthews, 1982). The integrity of the particle structure in these viruses is derived from strong hydrophobic association of protein subunits. Electron micrographs of TYMV particles prepared by the negative staining technique show 32 morphological units in an icosahedral arrangement (Nixon & Gibbs, 1960; Mellema & Amos, 1972). Neutron scattering experiments have revealed that there is little penetration of nucleic acid into the densely packed protein coat of TYMV (Jacrot *et al.*, 1977).

The amino-acid sequence of the coat proteins of three tymoviruses, TYMV (Peter, Stehelin, Reinbolt, Collot & Duranton, 1972), eggplant mosaic virus

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