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Structure of 6,7-Dimethoxy-9-phenyl-1,4-phenanthrenequinone

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Abstract. $C_{22}H_{16}O_4$, $M_r = 344{\cdot}366$, triclinic, $P\bar{1}$, $a = 10{\cdot}490\,(1)$, $b = 11{\cdot}907\,(1)$, $c = 14{\cdot}902\,(1)$ Å, $\alpha = 98{\cdot}91\,(1)$, $\beta = 97{\cdot}83\,(1)$, $\gamma = 110{\cdot}36\,(1)^\circ$, $V = 1687{\cdot}3\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}356$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 7{\cdot}19$ cm^{-1}, $F(000) = 720$, $T = 295$ K, $R = 0{\cdot}048$ for 4587 observed unique reflections. The carbon skeletons of the rings are planar with maximum deviations of 0·033 (4) and −0·033 (4) Å for the quinonoid rings of the discrete molecules *A* and *B*. The carbonyl oxygens O(1*A*), O(1*B*) and O(4*A*), O(4*B*) deviate 0·109 (3), 0·038 (3) and 0·127 (3), 0·153 (3) Å, respectively, from the quinonoid rings. The maximum inclinations of adjacent ring planes are 1·8° in molecule *A* and 3·8° in molecule *B*. The methoxy groups at C(6) and C(7) in molecule *A* and at C(6) in molecule *B* are almost coplanar with the attached ring systems, the methoxy group at O(7*B*) twisting out of the adjacent ring by −0·118 (4) Å. The aromatic skeletons of the independent molecules are inclined at 14 (1)° to each other. The phenyl rings turn away from the phenanthrene moieties by 52·7 (5) and 56·1 (5)°. The molecules in the crystal are packed together by weak intermolecular C—H···O interactions and van der Waals forces.

Introduction. In the course of the identification of the constituents of commercial timbers the title compound was prepared as a by-product during the synthesis of latinone [Fig. 1, compound (I)]. The phenanthrenequinone latinone from *Dalbergia latifolia* Roxb. (East Indian rosewood) and melatinone [Fig. 1, compound (II)] from the African blackwood *Dalbergia melanoxylon* Guill. & Perr have been isolated by O'Criodain, O'Sullivan, Meegan & Donnelly (1981). These tropical wood species are known for their sensitizing properties (Hausen, 1984), and phenanthrenequinones with no substitution at C(2) and/or C(3), like the title compound or latinone, are suspected as the possible contact allergens. The present X-ray structure analysis has been carried out in order to compare the molecular shape and dimensions with other allergenic substituted phenanthrenequinones (Schmalle, Jarchow, Hausen, Schulz, Krohn & Loock, 1986, 1987; Bartsch, Schmalle, Jarchow, Hausen & Schulz, 1986; Krohn, Loock, Kiesele, Hausen & Schmalle, 1991).

Experimental. The crystal structure of the title compound was determined by X-ray diffraction using a CAD-4 diffractometer with graphite-mono-

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chromated Cu $K\alpha$ radiation (λ = 1·5418 Å), and was confirmed by ^{1}H and ^{13}C NMR measurements. Single crystals were synthesized by the following procedure: $AlCl_3$ (8 g) was added to an ice-cold solution of 1,2-dimethoxybenzene (6 g) and freshly distilled benzyl chloride in carbon disulfide (40 ml). After stirring at room temperature for 15 h the reaction mixture was refluxed for 5 h. The mixture was poured onto ice–HCl (10%) and extracted with chloroform. The organic layer was washed with aqueous sodium hydroxide solution (10%), water, brine and dried. Evaporation of the solvent yielded a solid which afforded 3,4-dimethoxybenzophenone [Fig. 1, compound (III)] (10·4 g) as needles from ethanol (m.p. 374 K).

To a mixture of magnesium (1·25 g) and dry diethyl ether (3 ml) was added a solution of methyl iodide (4·3 ml) in dry diethyl ether (10 ml) over a period of 15 min. The mixture was stirred for 20 min. A solution of 3,4-dimethoxybenzophenone (4 g) in dry diethyl ether (80 ml) was added dropwise over 30 min. The reaction mixture was stirred at room temperature for 16 h, then treated with ice–sulfuric acid (10%). The mixture was extracted with diethyl ether. The organic layer was washed successively with aqueous sodium hydroxide (10%), water, brine and dried. Evaporation yielded 1-(3,4-dimethoxyphenyl)-1-phenylethylene [Fig. 1, compound (IV)] (3·83 g) as a solid which crystallized as lustrous plates from methanol, m.p. 365–366 K.

A solution of 1-(3,4-dimethoxyphenyl)-1-phenylethylene (0·98 g) and 1,4-benzoquinone (1·76 g) in glacial acetic acid was heated on a steam bath for 90 min. The reaction mixture was poured into water and extracted with chloroform. The organic layer was washed successively with aqueous sodium hydroxide (10%), water, brine and dried. Evaporation of the solvent afforded a red oil which solidified after 10 h. Crystallization from ethanol yielded 6,7-dimethoxy-9-phenyl-1,4-phenanthrenequinone [Fig. 1, compound (V)] as red needles (0·78 g), m.p. 471–472 K. Composition found: C 76·74, H 4·65%; $C_{22}H_{16}O_4$ requires C 76·51, H 4·65%.

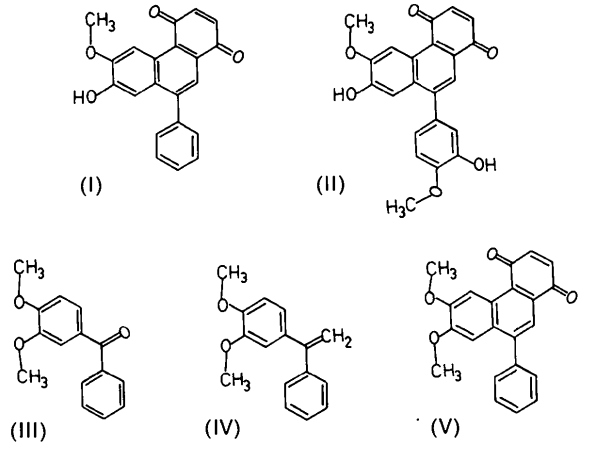

Fig. 1. Naturally occurring phenanthrenequinones latinone (I) and melatinone (II) and intermediates [(III), (IV)] in the synthesis of 6,7-dimethoxy-9-phenyl-1,4-phananthrenequinone (V).

A wedge-shaped platelet of approximate dimensions 0·25 × 0·33 × 0·34 mm was selected for data collection. The unit-cell parameters were determined by least-squares refinement of the setting angles of 25 automatically centred reflections in the range 17·8 < θ < 41·0°. Intensities of 5973 reflections (excluding 216 standards) in the interval $-12 < h < 12$, $-14 < k < 14$, $-17 < l < 0$ with θ between 2·0 and 65·0° ($\sin\theta_{\max}/\lambda$ = 0·588 Å^{-1}) were collected using the ω–2θ scan technique. The scan rate varied from 0·26 to 8·24° min^{-1}, the maximum measuring time was 300 s. Two standard reflections were monitored every 2 h of measuring time, no loss of intensities was noted. Orientation was controlled every 300 reflections using three standard reflections. No absorption correction (μ = 0·72 mm^{-1}) was carried out. The data were corrected for Lorentz and polarization effects. Data reduction led to 5481 unique reflections. 4587 reflections were considered observed with $I \geq 3\sigma(I)$, 894 reflections were unobserved.

Several trials to solve the phase problem in space group $P\bar{1}$ failed. Data statistics showed a tendency to hypercentricity for this structure. The structure was solved in space group $P1$ by direct methods with *SHELXS*84 (Sheldrick, 1985) using 438 E values and 257 negative quartets. The centre of symmetry was deduced from atomic positional parameters of the four phenanthrene nuclei. The refinement was started with *SHELX*76 (Sheldrick, 1976) in space group $P\bar{1}$ after shifting the atomic coordinates of the two independent molecules by x + 0·1947, y + 0·2273 and z + 0·2593. Refinements and subsequent difference Fourier syntheses revealed all H atoms for both of the independent molecules. The structure was finally refined by diagonal block-matrix least-squares calculations with the program *GX* (Mallinson & Muir, 1985), minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F_o)$ on F_{hkl} with anisotropic thermal parameters for the non-H atoms* using 598 variables and 4587 observed reflections; R = 0·048, wR = 0·056. The final maximum shift/e.s.d. ratio was 0·038. The maximum height in final difference Fourier synthesis was 0·16 e Å^{-3}. Scattering factors were used as in the *SHELX* and *GX* program systems. The refined

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and hydrogen-bonding parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53551 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and equivalent isotropic thermal parameters for* 6,7-*dimethoxy*-9-*phenyl*-1,4-*phenanthrenequinone*

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}(Å^2)
O(1*A*)	0·6197 (3)	0·9495 (2)	0·0105 (2)	0·071 (1)
O(4*A*)	0·2723 (3)	0·4924 (2)	−0·1397 (2)	0·064 (1)
O(6*A*)	0·1844 (3)	0·2238 (2)	0·0639 (2)	0·059 (1)
O(7*A*)	0·3077 (3)	0·2980 (2)	0·2346 (2)	0·056 (1)
C(1*A*)	0·5342 (4)	0·8460 (3)	−0·0209 (2)	0·051 (1)
C(2*A*)	0·4620 (4)	0·8072 (3)	−0·1187 (2)	0·059 (1)
C(3*A*)	0·3767 (4)	0·6931 (3)	−0·1537 (2)	0·056 (1)
C(4*A*)	0·3453 (3)	0·5972 (3)	−0·0992 (2)	0·047 (1)
C(5*A*)	0·2884 (3)	0·4241 (3)	0·0315 (2)	0·044 (1)
C(6*A*)	0·2671 (3)	0·3453 (3)	0·0888 (2)	0·044 (1)
C(7*A*)	0·3368 (3)	0·3863 (3)	0·1842 (2)	0·045 (1)
C(8*A*)	0·4233 (3)	0·5053 (3)	0·2162 (2)	0·043 (1)
C(9*A*)	0·5385 (3)	0·7166 (3)	0·1923 (2)	0·039 (1)
C(10*A*)	0·5619 (3)	0·7939 (3)	0·1324 (2)	0·043 (1)
C(11*A*)	0·4984 (3)	0·7543 (3)	0·0380 (2)	0·042 (1)
C(12*A*)	0·4077 (3)	0·6333 (3)	0·0024 (2)	0·040 (1)
C(13*A*)	0·3795 (3)	0·5493 (3)	0·0625 (2)	0·039 (1)
C(14*A*)	0·4471 (3)	0·5907 (3)	0·1581 (2)	0·039 (1)
C(15*A*)	0·6087 (3)	0·7675 (3)	0·2922 (2)	0·042 (1)
C(16*A*)	0·7509 (4)	0·8317 (3)	0·3152 (2)	0·047 (1)
C(17*A*)	0·8169 (4)	0·8819 (3)	0·4077 (3)	0·057 (1)
C(18*A*)	0·7424 (4)	0·8672 (3)	0·4760 (2)	0·064 (1)
C(19*A*)	0·6011 (4)	0·8056 (4)	0·4549 (3)	0·065 (1)
C(20*A*)	0·5333 (4)	0·7556 (3)	0·3625 (2)	0·052 (1)
C(21*A*)	0·1137 (4)	0·1766 (3)	−0·0316 (3)	0·063 (1)
C(22*A*)	0·3795 (4)	0·3325 (4)	0·3295 (3)	0·068 (1)
O(1*B*)	−0·0896 (3)	0·3392 (2)	0·0413 (2)	0·073 (1)
O(4*B*)	0·0266 (3)	0·2146 (2)	0·3602 (2)	0·077 (1)
O(6*B*)	0·2406 (3)	0·5431 (2)	0·6197 (2)	0·055 (1)
O(7*B*)	0·3101 (3)	0·7653 (2)	0·6019 (2)	0·064 (1)
C(1*B*)	−0·0655 (4)	0·3135 (3)	0·1156 (2)	0·053 (1)
C(2*B*)	−0·1134 (4)	0·1866 (3)	0·1259 (3)	0·062 (1)
C(3*B*)	−0·0856 (4)	0·1586 (3)	0·2060 (3)	0·062 (1)
C(4*B*)	−0·0036 (4)	0·2518 (3)	0·2916 (3)	0·053 (1)
C(5*B*)	0·1420 (3)	0·4619 (3)	0·4567 (2)	0·043 (1)
C(6*B*)	0·2061 (3)	0·5564 (3)	0·5315 (2)	0·045 (1)
C(7*B*)	0·2430 (4)	0·6795 (3)	0·5215 (2)	0·047 (1)
C(8*B*)	0·2125 (4)	0·7029 (3)	0·4364 (2)	0·045 (1)
C(9*B*)	0·1156 (3)	0·6302 (3)	0·2662 (2)	0·042 (1)
C(10*B*)	0·0522 (3)	0·5333 (3)	0·1915 (2)	0·046 (1)
C(11*B*)	0·0120 (3)	0·4117 (3)	0·2011 (2)	0·044 (1)
C(12*B*)	0·0397 (3)	0·3833 (3)	0·2870 (2)	0·042 (1)
C(13*B*)	0·1084 (3)	0·4821 (3)	0·3666 (2)	0·040 (1)
C(14*B*)	0·1447 (3)	0·6059 (3)	0·3563 (2)	0·040 (1)
C(15*B*)	0·1507 (3)	0·7566 (3)	0·2492 (2)	0·042 (1)
C(16*B*)	0·2286 (4)	0·7899 (3)	0·1819 (2)	0·051 (1)
C(17*B*)	0·2545 (4)	0·9028 (3)	0·1600 (3)	0·061 (1)
C(18*B*)	0·2046 (4)	0·9842 (3)	0·2036 (2)	0·062 (1)
C(19*B*)	0·1270 (4)	0·9521 (3)	0·2698 (3)	0·060 (1)
C(20*B*)	0·1018 (4)	0·8399 (3)	0·2928 (2)	0·053 (1)
C(21*B*)	0·2103 (4)	0·4202 (3)	0·6310 (3)	0·059 (1)
C(22*B*)	0·3357 (6)	0·8903 (4)	0·5991 (3)	0·087 (1)

atomic and equivalent isotropic displacement parameters are listed in Table 1. The standard deviations of U_{eq} were calculated after Schomaker & Marsh (1983).

Discussion. The asymmetric unit contains two molecules of the same chemical composition. The atom-numbering scheme is shown in the *ORTEP* (Johnson, 1971) drawing of Fig. 2 and bond distances and angles are given in Table 2. With the exception of C(6*A*)—C(7*A*) = 1·431 (4) and C(6*B*)—C(7*B*) = 1·417 (5) Å in the phenanthrene nuclei, and three distances of the phenyl rings, all comparable bond lengths of the molecules *A* and *B* are equivalent within 1σ. In general, the bond lengths are in good agreement with the values observed in other 1,4-phenanthrenequinone (PQ) structures, *e.g.* 7-hydroxy-2,8-dimethoxy-1,4-PQ with two discrete molecules in the asymmetric unit (Bartsch *et al.*, 1986), 3,8-dimethoxy- and 3,7,8-trimethoxy-1,4-PQ (Schmalle *et al.*, 1986), and 5-hydroxy-3,7-dimethoxy-1,4-PQ (Krohn *et al.*, 1991). When looking in detail, significant differences in bond distances and angles are observed between PQ's with different substituents at carbon atoms C(2), C(3) and C(5) to C(10), probably caused by π-electron delocalization at the phenanthrene ring system. Some examples show that unsubstituted C(9) corresponds to bond lengths C(9)—C(14) of 1·413 (8) and 1·422 (8) Å in cypripedin (Bartsch *et al.*, 1986), of 1·411 (6) and 1·41 (1) Å in 3,8-dimethoxy- and 3,7,8-trimethoxy-1,4-PQ (Schmalle *et al.*, 1986), of 1·417 (4) Å in 3,5,8-trimethoxy-1,4-PQ (Schmalle *et al.*, 1987), and of 1·411 (1) Å in 5-hydroxy-3,7-dimethoxy-1,4-PQ (Krohn *et al.*, 1991). Increasing C(9)—C(14) bond distances of about 0·02 Å are observed in PQ's with substitution at C(9), with lengths of 1·430 (5) Å in 9-hydroxy-5,8-dimethoxy-1,4-PQ (Schmalle *et al.*, 1987) and 1·434 (4) and 1·432 (5) Å in the title compound. The analogue of the effect given above can be observed by comparing bond lengths with substituted and non-substituted attached C atoms.

The phenanthrene nuclei of both of the independent molecules in 6,7-dimethoxy-9-phenyl-1,4-PQ are essentially planar – reference least-squares plane C(1) to C(14) – with maximum out-of-plane deviations of 0·048 (4) for C(1*A*) and −0·075 (5) Å for C(2*B*). Assuming a slight helical distortion for the phenanthrene ring system, as discussed for other PQ's (Schmalle *et al.*, 1987), separate least-squares calculations were carried out for the three carbon rings of

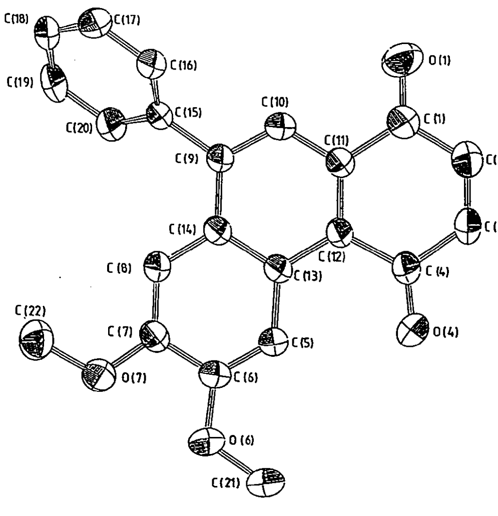

Fig. 2. A perspective view of molecule *A* with atom-numbering scheme and vibrational ellipsoids at the 50% probability level, drawn with *ORTEP* (Johnson, 1971).

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	Molecule *A*	Molecule *B*
C(1)—O(1)	1·217 (4)	1·211 (5)
C(1)—C(11)	1·485 (5)	1·499 (4)
C(3)—C(4)	1·473 (5)	1·482 (5)
C(4)—C(12)	1·496 (4)	1·486 (5)
C(5)—C(13)	1·423 (4)	1·420 (5)
C(6)—C(7)	1·431 (4)	1·417 (5)
C(7)—O(7)	1·359 (5)	1·366 (4)
C(9)—C(10)	1·364 (5)	1·371 (4)
C(9)—C(15)	1·496 (4)	1·491 (5)
C(11)—C(12)	1·391 (4)	1·392 (5)
C(13)—C(14)	1·428 (4)	1·427 (5)
O(7)—C(22)	1·432 (5)	1·426 (6)
C(16)—C(17)	1·391 (5)	1·376 (5)
C(18)—C(19)	1·371 (5)	1·379 (6)
C(15)—C(20)	1·392 (5)	1·385 (6)
C(1)—C(2)	1·469 (4)	1·457 (5)
C(2)—C(3)	1·314 (4)	1·310 (6)
C(4)—O(4)	1·218 (3)	1·221 (5)
C(5)—C(6)	1·347 (5)	1·357 (4)
C(6)—O(6)	1·362 (4)	1·363 (4)
C(7)—C(8)	1·355 (4)	1·360 (5)
C(8)—C(14)	1·415 (5)	1·426 (4)
C(9)—C(14)	1·434 (4)	1·432 (5)
C(10)—C(11)	1·402 (4)	1·397 (5)
C(12)—C(13)	1·426 (5)	1·434 (4)
O(6)—C(21)	1·437 (5)	1·428 (4)
C(15)—C(16)	1·383 (5)	1·396 (5)
C(17)—C(18)	1·362 (6)	1·373 (6)
C(19)—C(20)	1·393 (5)	1·376 (5)
C(6)—O(6)—C(21)	116·9 (3)	116·0 (3)
C(2)—C(1)—C(11)	117·5 (3)	117·5 (4)
O(4)—C(4)—C(12)	123·6 (3)	124·7 (4)
O(6)—C(6)—C(7)	114.3 (3)	114·9 (3)
C(6)—C(7)—C(8)	119·3 (3)	119·6 (3)
O(1)—C(1)—C(11)	121·4 (4)	121·0 (4)
O(4)—C(4)—C(3)	118·2 (3)	117·3 (4)
O(6)—C(6)—C(5)	125·5 (3)	124·6 (3)
O(7)—C(7)—C(8)	126·2 (3)	126·0 (3)
C(10)—C(9)—C(14)	119·4 (3)	118·9 (3)
C(1)—C(11)—C(10)	117·2 (3)	117·1 (3)
C(4)—C(12)—C(13)	123·0 (3)	123·3 (3)
C(10)—C(9)—C(15)	118·3 (3)	117·9 (3)
C(1)—C(11)—C(12)	122·5 (3)	121·6 (3)
C(4)—C(12)—C(11)	117·3 (3)	118·2 (3)
C(5)—C(13)—C(14)	117·8 (3)	118·0 (3)
C(8)—C(14)—C(13)	118·7 (3)	118·8 (3)
C(9)—C(15)—C(16)	119·4 (3)	118·8 (3)
C(9)—C(15)—C(20)	121·3 (3)	122·7 (3)
C(16)—C(17)—C(18)	120·3 (4)	120·7 (3)
C(18)—C(19)—C(20)	119·6 (4)	120·0 (4)
O(1)—C(1)—C(2)	121·1 (4)	121·5 (4)
C(2)—C(3)—C(4)	123·5 (4)	123·1 (4)
C(6)—C(5)—C(13)	122·0 (3)	121·7 (3)
O(7)—C(7)—C(6)	114·6 (3)	114·3 (3)
C(7)—O(7)—C(22)	117·0 (3)	117·3 (3)
C(1)—C(2)—C(3)	120·7 (4)	121·5 (4)
C(3)—C(4)—C(12)	118·2 (3)	117·9 (3)
C(5)—C(6)—C(7)	120·2 (3)	120·5 (3)
C(7)—C(8)—C(14)	122·0 (3)	121·4 (3)
C(14)—C(9)—C(15)	122·3 (3)	123·1 (3)
C(10)—C(11)—C(12)	120·3 (3)	121·3 (3)
C(5)—C(13)—C(12)	123·0 (3)	122·4 (3)
C(9)—C(10)—C(11)	122·0 (3)	121·9 (3)
C(11)—C(12)—C(13)	119·7 (3)	118·5 (3)
C(12)—C(13)—C(14)	119·2 (3)	119·7 (3)
C(8)—C(14)—C(9)	121·9 (3)	121·6 (3)
C(9)—C(14)—C(13)	119·4 (3)	119·6 (3)
C(16)—C(15)—C(20)	119·2 (3)	118·3 (3)
C(15)—C(16)—C(17)	119·9 (4)	120·2 (4)
C(17)—C(18)—C(19)	120·8 (4)	119·6 (4)
C(15)—C(20)—C(19)	120·2 (4)	121·1 (4)

each molecule. The maximum out-of-plane deviation decreases to 0·033 (4) for C(1*A*) and −0·033 (4) Å for C(4*B*). As the carbonyl oxygens O(1*A*), O(1*B*) and O(4*A*), O(4*B*) deviate 0·109 (3), 0·038 (3) and 0·127 (3), 0·153 (3) Å, all towards the same direction of the quinonoid rings, both of the discrete molecules can be considered as belonging to a left-handed screw, defined according to Cahn, Ingold & Prelog (1966). As helicity is a special type of chirality, the unit cell of this centrosymmetric space group contains two left-handed screws and two right-handed screws. Up to now it was not possible to separate the different screws of allergenic phenanthrenequinones by crystallizing them in non-centrosymmetric space groups.

The methoxy groups at C(6) and C(7) for molecule *A* are almost coplanar with the attached ring system, with torsion angles C(5)—C(6)—O(6)—C(21) = −0·3 (4) and C(8)—C(7)—O(7)—C(22) = 2·8 (4)°, and O(6) and O(7) deviate 0·018 (3) and 0·014 (2) Å from the attached ring. For molecule *B*, however, the corresponding torsion angles are 2·4 (4) and 8·2 (4)°. Probably owing to packing forces between mol-

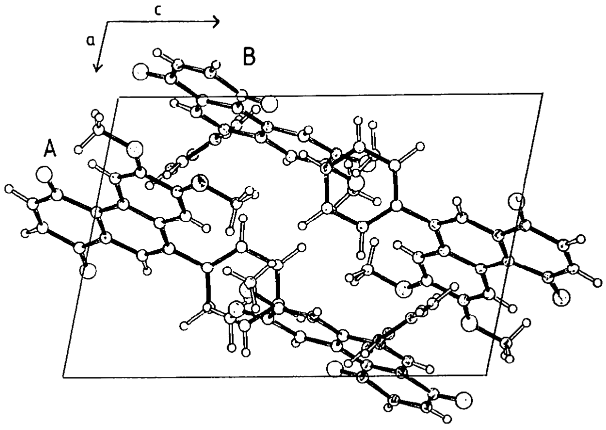

Fig. 3. Projection of the unit cell of 6,7-dimethoxy-9-phenyl-1,4-phenanthrenequinone on the *ac* plane. Independent molecules *A* and *B* are indicated.

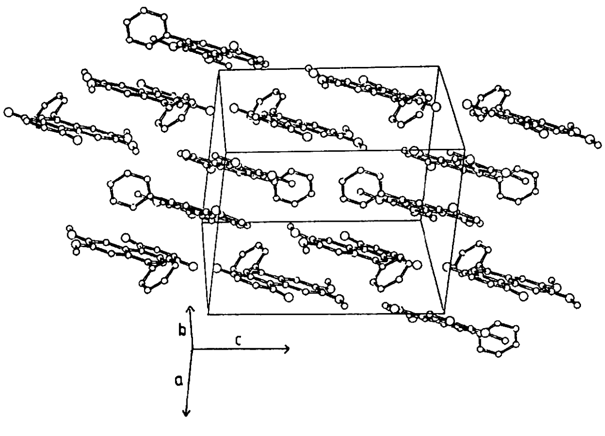

Fig. 4. Packing diagram of 6,7-dimethoxy-9-phenyl-1,4-phenanthrenequinone.

Table 3. *Hydrogen-bonding contacts* (Å) *and angles* (°) *in* 6,7-*dimethoxy*-9-*phenyl*-1,4-*phenanthrenequinone*

X—H···Y	X—H	H···Y	X···Y	X—H···Y	Symmetry operation
C(22*A*)—H(222*A*)···O(6*B*)	1·14 (4)	2·57 (4)	3·657 (5)	160 (3)	$1-x, 1-y, 1-z$
C(3*A*)—H(3*A*)···O(6*B*)	0·87 (3)	2·60 (3)	3·417 (4)	156 (4)	$x, y, 1+z$
C(2*B*)—H(2*B*)···O(1*A*)	0·92 (3)	2·48 (3)	3·233 (4)	138 (4)	$1+x, 1+y, z$
C(21*B*)—H(213*B*)···O(4*A*)	0·90 (4)	2·51 (4)	3·307 (4)	147 (4)	$x, y, -1+z$

ecules, the C(22) methyl group twists slightly [−0·118 (4) Å] out of the plane of the aromatic ring system. O(6*B*) and O(7*B*) deviate −0·007 (3) and 0·033 (2) Å from the ring C(5) to C(8), C(13) and C(14).

The phenyl rings are rotated from the phenanthrene rings by 52·7° in molecule *A* and 56·0° in molecule *B* (Fig. 3). Consequently, the packing of the molecules (Fig. 4) in this structure is less dense than in the PQ structures cited above; the calculated densities for those structures vary between 1·485 and 1·405 g cm^{-3}, compared to 1·356 g cm^{-3} for the title compound. The structure is stabilized by very weak C—H···O contacts (Table 3) and van der Waals forces.

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Structure of 2,2-Dimethyl-5-methylaminomethylene-1,3-dioxane-4,6-dione

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Abstract. $C_8H_{11}NO_4$, $M_r = 185{\cdot}2$, triclinic, $P\bar{1}$, $a = 5{\cdot}277\,(2)$, $b = 8{\cdot}872\,(3)$, $c = 10{\cdot}123\,(3)$ Å, $\alpha = 102{\cdot}86\,(2)$, $\beta = 90{\cdot}07\,(3)$, $\gamma = 102{\cdot}87\,(3)$°, $V = 449{\cdot}8\,(3)$ Å^3, $Z = 2$, $D_m = 1{\cdot}37$, $D_x = 1{\cdot}38$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}103$ mm^{-1}, $F(000) = 196$, $T = 300$ K, final $R = 0{\cdot}080$ for 765 independent observed reflections. Owing to the push–pull effect, the C═C bond distance is as long as 1·399 (10) Å and the torsion angles around this bond are 176·8 (10) and 0·5 (17)°. The 1,3-dioxane ring is in a half-boat conformation due to the equatorial substituents on C(4) and C(6), and also to the resonance system. The molecule has an intramolecular hydrogen bond between the amine and one carbonyl group. The molecules are linked by van der Waals forces.

Introduction. Our studies on the structural chemistry of compounds with push–pull effects have shown that the amine H atom H(1) has a strong proclivity to intramolecular hydrogen bonding. The driving force for such hydrogen bonding can be attributed to six-membered ring formation resulting from a preferred directionality of the sp^2 lone pairs associated with one carbonyl O atom.

A large number of substituted ethylenes are known where the C—C bond is significantly longer than in ethylene and the deviation from planarity is quite

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