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## Structures of 9-Hydroxy-5,8-dimethoxy-1,4-phenanthrenequinone, (1), and 3,5,8-Trimethoxy-1,4-phenanthrenequinone, (2)

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**Abstract.** (1)  $C_{16}H_{12}O_5$ ,  $M_r = 284.27$ , triclinic,  $P\bar{1}$ ,  $a = 7.221$  (1),  $b = 10.071$  (19),  $c = 10.474$  (1) Å,  $\alpha = 64.46$  (1),  $\beta = 68.97$  (1),  $\gamma = 80.85$  (1)°,  $V = 641.5$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.472$  Mg m<sup>-3</sup>, Cu  $K\alpha$  radiation,  $\lambda = 1.5418$  Å,  $\mu = 0.823$  mm<sup>-1</sup>,  $F(000) = 296$ ,  $T = 296$  K, final  $R = 0.048$  for 1507 observed reflections. (2)  $C_{17}H_{14}O_5$ ,  $M_r = 298.30$ , monoclinic,  $P2_1/n$ ,  $a = 8.442$  (1),  $b = 25.129$  (1),  $c = 6.717$  (1) Å,  $\beta = 98.18$  (1)°,  $V = 1410.4$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.405$  Mg m<sup>-3</sup>, Cu  $K\alpha$  radiation,  $\mu = 0.771$  mm<sup>-1</sup>,  $F(000) = 624$ ,  $T = 296$  K, final  $R = 0.052$  for 1861

observed reflections. The structures of (1) and (2) exhibit helical distorted molecules of optical antipodes which are located across centres of symmetry. The deviations of atoms O(4) and O(5) from the plane C(9) to C(12) are similar for both compounds: 1.108 (4) and -0.811 (4) Å for (1), and -1.075 (3) and 0.849 (3) Å for (2). The molecules in the crystal are held together by weak intermolecular C–H...O interactions and van der Waals forces.

**Introduction.** The naturally occurring phenanthrenequinone (PQ) cypripedin has been shown to possess a sensitizing capacity (Hausen, 1982). To obtain more information on relationships between chemical structure and allergenic properties of PQs, some 30 mono-,

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di- and trimethoxylated PQs were synthesized (Krohn & Loock, 1986) and examined experimentally for their sensitizing potency and cross reactivities. The X-ray structure determinations of the title compounds (1) and (2) were done in order to establish whether the hydroxy group was at C(9) or C(10) in compound (1) and to determine whether the methoxy group was at C(2) or C(3) in PQ (2). This was not possible by spectroscopic methods at the beginning of the investigations.

**Experimental.** (1) and (2) recrystallized from dichloromethane. Enraf-Nonius CAD-4 diffractometer, graphite-monochromatized Cu K $\alpha$  radiation,  $\theta$ - $2\theta$  scan method, variable scan rate 0.26 to 20.0° min<sup>-1</sup>. The structures were solved with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Anisotropic full-matrix least-squares refinement based on  $F_{hkl}^2$ ; neutral-atom scattering factors from Cromer & Mann (1968) used in *SHELX76* (Sheldrick, 1976). Additional computer programs: *XANADU* (Roberts & Sheldrick, 1975), *ORTEP* (Johnson, 1971), *ORFFE* (Busing, Martin, Levy, Brown, Johnson & Thiessen, 1971). (1) Dark-red ledge-shaped crystal (0.43 × 0.11 × 0.06 mm). Unit cell: 23 reflections in the interval  $8 < \theta < 26^\circ$ . Max.  $\sin\theta/\lambda = 0.562 \text{ \AA}^{-1}$ ,  $-8 \leq h \leq 8$ ,  $-11 \leq k \leq 11$ ,  $-11 \leq l \leq 0$ . No loss of intensity during measurement, orientation controlled every 400 reflections (four standard reflections). 2028 reflections measured. Lorentz-polarization correction, no absorption correction.  $R_{\text{int}} = 0.018$ , 1907 unique reflections, 1507 with  $I > 3\sigma(I)$ , 400 unobserved. All 12 H-atom positions from difference Fourier synthesis, refined with fixed isotropic temperature parameters  $B_{\text{iso}} = 3.16 \text{ \AA}^2$ . Number of reflections in final refinement cycle,  $m = 1507$ ; parameters refined,  $n = 226$ ; unit weight,  $R = 0.048$ . ( $\Delta/\sigma$ ) max = 0.09 in final refinement cycle. Max. and min. heights in final difference Fourier synthesis 0.18 and  $-0.26 \text{ e \AA}^{-3}$ . The final atomic parameters are given in Table 1.\*

(2) Dark-red plate-shaped crystal (0.43 × 0.34 × 0.06 mm). Cell dimensions from least-squares refinement of 23 reflections in the interval  $17 < \theta < 29^\circ$ . Max.  $\sin\theta/\lambda = 0.562 \text{ \AA}^{-1}$ ,  $0 \leq h \leq 9$ ,  $-28 \leq k \leq 28$ ,  $-7 \leq l \leq 7$ . 4516 reflections measured. Two standard reflections checked every two hours, 0.2% loss of intensities. Orientation controlled every 500 reflections using four standard reflections. Data reduction with the program of the CAD-4 structure determination package. Lorentz-polarization correction, no absorption correction.  $R_{\text{int}} = 0.019$ , 2145 unique reflections, 1861

with  $I > 3\sigma(I)$ , 284 unobserved. All 14 H-atom positions from difference Fourier syntheses, refined with fixed isotropic temperature parameters  $B_{\text{iso}} = 3.16 \text{ \AA}^2$ . Number of reflections in final refinement cycle,  $m = 1861$ ; parameters refined in 2 separate blocks,  $n_1 = 127$ ,  $n_2 = 115$ ; unit weight,  $R = 0.052$ . ( $\Delta/\sigma$ ) max. = 0.48 (0.15 for nonhydrogen atoms) in final refinement cycle. Max. and min. heights in final difference Fourier synthesis 0.18 and  $-0.27 \text{ e \AA}^{-3}$ . The final atomic parameters are listed in Table 2.

Table 1. Final atomic coordinates ( $\times 10^4$ ) and  $U_{\text{eq}}$  values for 9-hydroxy-5,8-dimethoxy-1,4-phenanthrenequinone (1) with e.s.d.'s in parentheses

$U_{\text{eq}}$  values are given in the form  $\frac{1}{3}\sum_i\sum_k U_{ik}a_i^*a_k^*(\mathbf{a}_i, \mathbf{a}_k)$ .

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
O(1)	1253 (5)	4902 (3)	11029 (3)	0.083 (6)
O(4)	6871 (4)	1779 (3)	9030 (3)	0.073 (5)
O(5)	6747 (4)	2420 (3)	6336 (3)	0.068 (5)
O(8)	7560 (4)	8469 (3)	3760 (3)	0.065 (4)
O(9)	5181 (5)	8571 (3)	6180 (3)	0.073 (5)
C(1)	2323 (6)	4155 (4)	10398 (4)	0.058 (6)
C(2)	2188 (7)	2548 (5)	11080 (5)	0.074 (7)
C(3)	3558 (7)	1747 (5)	10493 (5)	0.071 (6)
C(4)	5304 (6)	2446 (4)	9160 (4)	0.056 (6)
C(5)	7177 (5)	3889 (4)	5694 (4)	0.045 (6)
C(6)	8328 (6)	4602 (4)	4239 (4)	0.054 (6)
C(7)	8516 (6)	6126 (4)	3584 (4)	0.055 (6)
C(8)	7508 (5)	6947 (4)	4366 (4)	0.049 (6)
C(9)	5131 (6)	7078 (4)	6740 (4)	0.049 (6)
C(10)	3851 (6)	6380 (4)	8153 (4)	0.055 (6)
C(11)	3790 (5)	4851 (4)	8856 (4)	0.048 (6)
C(12)	5063 (5)	3990 (4)	8158 (4)	0.046 (6)
C(13)	6226 (5)	4684 (4)	6610 (4)	0.041 (6)
C(14)	6314 (5)	6263 (4)	5897 (4)	0.043 (6)
C(15)	7959 (7)	1528 (5)	5605 (5)	0.068 (7)
C(16)	8159 (9)	9222 (5)	2154 (5)	0.084 (8)

Table 2. Final atomic coordinates ( $\times 10^4$ ) and  $U_{\text{eq}}$  values for 3,5,8-trimethoxy-1,4-phenanthrenequinone (2) with e.s.d.'s in parentheses

$U_{\text{eq}}$  values are given in the form  $\frac{1}{3}\sum_i\sum_k U_{ik}a_i^*a_k^*(\mathbf{a}_i, \mathbf{a}_k)$ .

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
O(1)	3224 (3)	4586 (1)	1927 (4)	0.092 (2)
O(3)	8822 (2)	4641 (1)	3703 (3)	0.054 (1)
O(4)	8413 (2)	3753 (1)	5633 (3)	0.052 (1)
O(5)	8162 (2)	3901 (1)	9441 (3)	0.052 (1)
O(8)	2461 (3)	2847 (1)	9651 (3)	0.061 (1)
C(1)	4446 (4)	4461 (1)	3037 (5)	0.056 (2)
C(2)	5982 (4)	4680 (1)	2737 (5)	0.052 (2)
C(3)	7316 (3)	4500 (1)	3840 (4)	0.044 (2)
C(4)	7273 (3)	4051 (1)	5304 (4)	0.040 (2)
C(5)	6870 (3)	3571 (1)	9436 (4)	0.041 (2)
C(6)	6706 (4)	3218 (1)	10925 (4)	0.052 (2)
C(7)	5258 (4)	2950 (1)	11002 (5)	0.053 (2)
C(8)	3951 (4)	3060 (1)	9625 (4)	0.047 (2)
C(9)	2729 (4)	3544 (1)	6586 (5)	0.050 (2)
C(10)	2856 (4)	3892 (1)	5068 (5)	0.054 (2)
C(11)	4357 (3)	4093 (1)	4764 (4)	0.044 (2)
C(12)	5720 (3)	3955 (1)	6062 (4)	0.037 (2)
C(13)	5587 (3)	3648 (1)	7823 (4)	0.037 (2)
C(14)	4078 (3)	3414 (1)	8009 (4)	0.041 (2)
C(15)	9058 (5)	5034 (2)	2199 (5)	0.061 (2)
C(16)	9652 (4)	3715 (2)	10449 (6)	0.066 (2)
C(17)	2237 (5)	2534 (2)	11359 (6)	0.070 (3)

\* Lists of structure factors, anisotropic thermal parameters of C and O atoms, coordinates and temperature factors for H atoms and selected torsion angles for both structures have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43290 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Discussion.** The bond distances and atom-numbering schemes of (1) and (2) are presented in the *ORTEP* drawings of Figs. 1 and 2. The bond angles are given in Table 3. The bond lengths and angles agree well with those values observed in 3,8-dimethoxy-1,4-PQ and 3,7,8-trimethoxy-1,4-PQ (Schmalle, Jarchow, Hausen, Schulz, Krohn & Loock, 1986). These molecules are approximately planar with maximum out-of-plane deviations of 0.133 (5) and 0.38 (1) Å for C(6). However, the title compounds are chiral as a result of intramolecular steric repulsions similar to that observed in *n*-helicene structures and form left- and right-handed screws. The carbonyl O atom at position 4 and the methoxy group at position 5 are displaced from the plane C(9) to C(12) by 1.108 (4) and -0.811 (4) Å in (1) and by -1.075 (3) and 0.849 (3) Å in (2). Similar observations have been made for 4,5,8-trimethyl-1-phenanthrylacetic acid (Newman & Hussey, 1947) and hexahelicene (Newman & Lednicer, 1956). Table 4 shows the deviations of atomic positions from the reference plane C(1) to C(4) of the quinonoid ring systems of the title compounds compared with the values of 3,8-dimethoxy-1,4-PQ, 3,7,8-trimethoxy-1,4-PQ (Schmalle *et al.*, 1986) and of the independent molecules of cypridin (Bartsch, Schmalle, Jarchow, Hausen & Schulz, 1986). The values for (1) correspond to a left-handed screw (Fig. 3) and those for (2) to a right-handed helix, defined after Cahn, Ingold & Prelog (1966). Since both structures are centrosymmetric, enantiomorphically related molecules are present in equal amounts in the two structures. The *ab* projection of the unit cell of (2) shows the different forms of the molecules (Fig. 4).

In spite of the fact that the standard deviations of the positional parameters of the H atoms are underestimated, a tendency to helical displacements is observed in the relatively planar molecules of 3,8-dimethoxy-1,4-PQ and of 3,7,8-trimethoxy-1,4-PQ (Schmalle *et al.*, 1986), as is indicated by the opposite signs of deviations from the quinonoid plane of atoms O(4) and H(5) in Table 4; the same observations for corresponding atoms and planes were made on the independent molecules of cypridin (Bartsch *et al.*, 1986). This effect has also been discussed for the phenanthrene molecule itself (Kay, Okaya & Cox, 1971).

A common feature of the most potent sensitizing PQs is no substitution at C(2) and C(3): 7,8-dimethoxy-, 8-methoxy-, 5,8-dimethoxy-, 7-methoxy-, 6-methoxy- and 1,4-PQ itself belong to this group. Moderate sensitizers are 3,6-dimethoxy-, 3,8-dimethoxy-, 3,5,8-trimethoxy-, 6,7-dimethoxy- and 3,7,8-trimethoxy-1,4-PQ. In contrast 3,6,7-trimethoxy-1,4-PQ is nonallergenic.

The intramolecular hydrogen bond O(9)—H(9)...O(8) of (1) is shown in Fig. 1. The corresponding angle is 146 (1)°. Intermolecular distances for (1) and (2)

were calculated up to 3.6 Å with *ORFFE*. The C—H...O interactions for (1) are indicated by dashed lines between neighbouring molecules in Fig. 3. The distances and angles are: C(6)...O(1<sup>b</sup>) 3.18(1), H(6)...O(1<sup>b</sup>) 2.51(2) Å, C(6)—H(6)...O(1<sup>b</sup>) 130(5)°; C(16)...

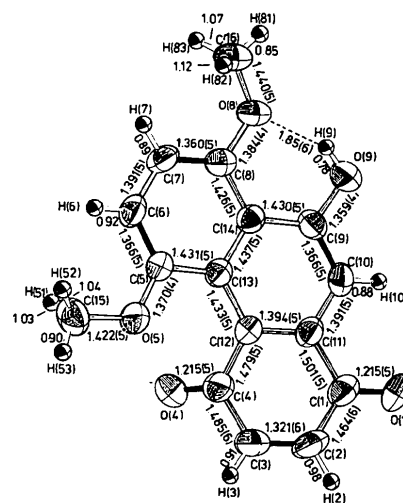


Fig. 1. *ORTEP* drawing of 9-hydroxy-5,8-dimethoxy-1,4-PQ (1) with atom-numbering scheme and bond distances (Å). The standard deviations for all C—H distances are 0.04 Å. C and O atoms are shown with 65% probability ellipsoids. H atoms are shown as spheres of arbitrary size. Blackened bond lines indicate C=C and C=O double bonds.

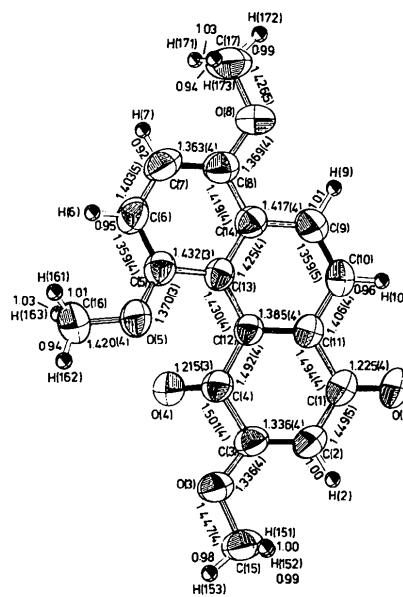


Fig. 2. *ORTEP* drawing of 3,5,8-trimethoxy-1,4-PQ (2) with atom-numbering scheme and bond distances (Å). The standard deviations for all C—H distances are 0.03 Å. C and O atoms are shown with 65% probability ellipsoids. H atoms are shown as spheres of arbitrary size. Blackened bond lines indicate C=C and C=O double bonds.

O(4<sup>ii</sup>) 3.49(1), H(82)...O(4<sup>ii</sup>) 2.41(2) Å, C(16)—H(82)...O(4<sup>ii</sup>) 163(5)° [symmetry code: (i)  $-1 + x, y, 1 + z$ ; (ii)  $2 - x, 1 - y, 1 - z$ ]. One C—H...O contact is observed in compound (2): C(17)...O(4<sup>i</sup>) 3.44(1), H(171)...O(4<sup>i</sup>) 2.49(2) Å, C(17)—H(171)...O(4<sup>i</sup>) 153(5)° [symmetry code: (i)  $\frac{1}{2} + x, \frac{1}{2} - y, -1.5 + z$ ]. The structures are both stabilized by these interactions and by van der Waals forces.

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Table 3. Bond angles (°) of 9-hydroxy-5,8-dimethoxy-1,4-phenanthrenequinone (1) and 3,5,8-trimethoxy-1,4-phenanthrenequinone (2)

E.s.d.'s are given in parentheses.

	(1)	(2)	(1)	(2)
C(5)—O(5)—C(x)*	117.7 (3)	116.9 (3)	C(7)—C(8)—C(14)	120.8 (3) 120.3 (3)
C(8)—O(8)—C(y)*	117.4 (3)	117.0 (3)	O(9)—C(9)—C(10)	116.6 (3) —
C(2)—C(1)—C(11)	117.2 (3)	119.2 (3)	O(9)—C(9)—C(14)	122.4 (3) —
O(1)—C(1)—C(2)	121.7 (4)	120.7 (3)	C(10)—C(9)—C(14)	120.9 (3) 120.9 (3)
O(1)—C(1)—C(11)	121.1 (4)	120.0 (3)	C(9)—C(10)—C(11)	120.7 (3) 120.6 (3)
C(1)—C(2)—C(3)	120.6 (4)	119.7 (3)	C(1)—C(11)—C(10)	118.0 (3) 118.8 (2)
C(2)—C(3)—C(4)	121.1 (4)	121.4 (3)	C(1)—C(11)—C(12)	120.9 (3) 121.0 (3)
O(4)—C(4)—C(3)	118.8 (4)	119.4 (3)	C(10)—C(11)—C(12)	121.1 (3) 120.3 (3)
O(4)—C(4)—C(12)	124.0 (4)	123.4 (3)	C(4)—C(12)—C(11)	115.5 (3) 115.9 (2)
C(3)—C(4)—C(12)	116.8 (4)	116.7 (2)	C(4)—C(12)—C(13)	124.9 (3) 123.1 (2)
O(5)—C(5)—C(6)	123.2 (3)	123.9 (2)	C(11)—C(12)—C(13)	119.0 (3) 120.0 (2)
O(5)—C(5)—C(13)	115.9 (3)	115.9 (2)	C(5)—C(13)—C(12)	123.2 (3) 124.0 (2)
C(6)—C(5)—C(13)	120.7 (3)	120.0 (3)	C(5)—C(13)—C(14)	117.6 (3) 117.9 (2)
C(5)—C(6)—C(7)	121.0 (4)	121.4 (3)	C(12)—C(13)—C(14)	118.9 (3) 118.1 (2)
C(6)—C(7)—C(8)	120.7 (4)	120.2 (3)	C(8)—C(14)—C(9)	122.9 (3) 121.3 (3)
O(8)—C(8)—C(7)	123.5 (3)	124.6 (3)	C(8)—C(14)—C(13)	118.7 (3) 119.5 (2)
O(8)—C(8)—C(14)	115.6 (3)	115.1 (2)	C(9)—C(14)—C(13)	118.3 (3) 119.3 (3)
C(3)—O(3)—C(15)	—	117.2 (2)	O(3)—C(3)—C(2)	— 127.4 (3)
O(3)—C(3)—C(4)	—	110.9 (2)		

\*  $x = C(15)$  for (1),  $C(16)$  for (2);  $y = C(16)$  for (1),  $C(17)$  for (2).

Table 4. Deviation of atoms (Å) of the ring systems from the reference plane C(1) to C(4) for the title compounds (1), (2), 3,8-dimethoxy-1,4-PQ (3), 3,7,8-trimethoxy-1,4-PQ (4), and for the independent molecules of 7-hydroxy-2,8-dimethoxy-1,4-PQ (cypripedin) (5), (6)

	(1)	(2)	(3)	(4)	(5)	(6)
C(5)	-1.590	1.296	0.119	0.32	0.00	-0.54
C(6)	-2.019	1.466	0.133	0.38	0.05	-0.75
C(7)	-2.005	1.283	0.092	0.35	0.16	-0.85
C(8)	-1.600	0.993	0.062	0.18	0.18	-0.72
C(9)	-0.760	0.495	-0.002	-0.03	0.11	-0.36
C(10)	-0.437	0.309	-0.007	-0.05	0.05	-0.21
C(11)	-0.338	0.258	0.017	0.01	0.01	-0.13
C(12)	-0.530	0.453	0.039	0.09	0.01	-0.19
C(13)	-1.042	0.830	0.068	0.17	0.05	-0.40
C(14)	-1.118	0.768	0.044	0.10	0.10	-0.49
O(1)	0.205	-0.138	0.022	0.01	0.00	0.09
O(4), O(2)*	0.553	-0.527	-0.095	-0.03	0.01	0.17
O(5), H(5)†	-1.735	1.649	0.15	0.04	-0.14	-0.57
Max. e.s.d.	0.004	0.003	0.005	0.01	0.01	0.01
R.m.s.d. for the plane C(1) to C(4)	0.007	0.013	0.005	0.015	0.004	0.004

\* In cypripedin O(4) is labelled as O(2).

† In compounds (3), (4), (5), (6) position 5 is substituted by H atoms.

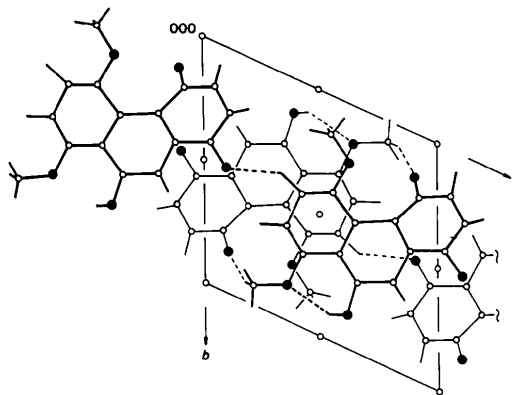


Fig. 3. The  $bc$  projection of the structure of (1). Filled circles of the molecular models indicate O atoms and open circles C atoms. The C—H...O interactions are indicated by broken lines.

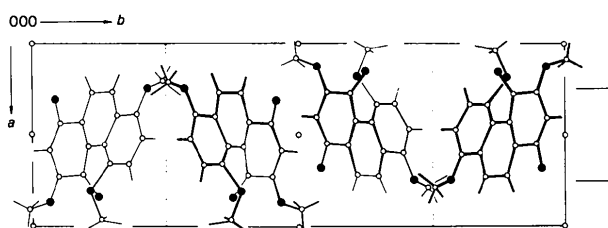


Fig. 4. The  $ab$  projection of the unit cell of (2) showing the distortions of the aromatic ring systems. Filled circles of the molecular models indicate O atoms and open circles C atoms.

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