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Structures of 3,8-Dimethoxy-1,4-phenanthrenequinone (1) and 3,7,8-Trimethoxy-1,4-phenanthrenequinone (2)

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Abstract. (1) $C_{16}H_{12}O_4$, $M_r = 268{\cdot}27$, monoclinic, $P2_1/c$, $a = 8{\cdot}278\,(1)$, $b = 23{\cdot}328\,(1)$, $c = 6{\cdot}511\,(1)$ Å, $\beta = 95{\cdot}91\,(1)°$, $V = 1250{\cdot}6\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}425$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}755$ mm^{-1}, $F(000) = 560$, $T = 296$ K, final $R = 0{\cdot}060$ for 1241 observed reflections. (2) $C_{17}H_{14}O_5$, $M_r = 298{\cdot}30$, triclinic, $P\bar{1}$, $a = 4{\cdot}128\,(1)$, $b = 13{\cdot}163\,(1)$, $c = 13{\cdot}918\,(1)$ Å, $\alpha = 65{\cdot}30\,(1)$, $\beta = 84{\cdot}54\,(1)$, $\gamma = 88{\cdot}80\,(1)°$, $V = 683{\cdot}8\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}450$ Mg m^{-3}, Cu $K\alpha$, $\mu = 0{\cdot}795$ mm^{-1}, $F(000) = 312$, $T = 296$ K, final $R = 0{\cdot}087$ for 940 observed reflections. Both of the molecular skeletons show small distortions from planarity with maximum out-of-plane deviations of 0·119 (5) Å for C(5) and 0·133 (5) Å for C(6) in (1) and 0·38 (1) Å for C(6) and 0·35 (1) Å for C(7) in (2). The distances and angles of the quinonoid rings agree well with those observed in other *p*-quinone structures. The C(17) methyl group in (2) is twisted out of the plane of the ring system, the torsion angle C(7)—C(8)—O(8)—C(17) being 77 (1)°, while the C(16) methyl is nearly planar with C(6)—C(7)—O(7)—C(16) = 4 (1)°. Intramolecular hydrogen bonds of the form C(5)—H(5)···O(4) are observed in (1) and (2). The structures are stabilized by weak intermolecular C—H···O interactions and van der Waals forces.

Introduction. The first naturally occurring 1,4-phenanthrenequinone (PQ) with sensitizing potency, separated from the orchid *Cypripedium calceolus* L., has been identified by X-ray analysis as 7-hydroxy-2,8-dimethoxy-1,4-PQ (Schmalle & Hausen, 1979) and named cypripedin. Its two independent molecules show slightly different conformations in the crystalline state (Bartsch, Schmalle, Jarchow, Hausen & Schulz, 1986). In order to study their allergenic properties and cross reactivities, a series of cypripedin-related PQ's have been synthesized by Diels–Alder reactions (Krohn & Loock, 1985) and used for sensitizing experiments in guinea pigs. As it was not possible to localize the methoxy group at position C(2) or C(3) by spectroscopic methods, X-ray structure determinations have been performed for the title compounds. Further X-ray analyses were made on 3,5,8-trimethoxy-1,4-PQ and 9-hydroxy-5,8-dimethoxy-1,4-PQ, which were identified as by-products of the syntheses of the PQ's (Schmalle, Jarchow, Hausen, Schulz, Krohn & Loock, 1986). In this paper the results of the structure determinations of (1) and (2) are presented.

Experimental. Compounds crystallized from dichloromethane (CH_2Cl_2). Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Cu $K\alpha$ radiation, θ–2θ scan method, variable scan rate 0·22 to 20·0° min^{-1}. Both structures solved using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and difference Fourier calculations by *SHELX*76 (Sheldrick, 1976). Anisotropic full-matrix least-squares refinements based on F_{hkl}, atomic scattering factors from *SHELX*. Additional computer programs: *XANADU* (Roberts & Sheldrick, 1975); *ORTEP* (Johnson, 1971); *ORFFE* (Busing, Martin, Levy, Brown, Johnson & Thiessen, 1971). (1) Ledge-shaped red crystal (0·09 × 0·03 × 0·31 mm). Cell dimensions from least-squares refinement of 19 reflections in interval $7 < \theta < 39°$. Max. $\sin\theta/\lambda = 0{\cdot}562$ Å^{-1}, $-9 \le h \le 9$, $-26 \le k \le 26$, $0 \le l \le 7$. 4098 reflections measured. Two standard reflections checked every two hours, no loss of intensity. Orientation controlled every 300 reflections using four standard reflections. Data reduction with the program of the CAD-4 structure

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determination package. Lorentz–polarization correction, no absorption correction. $R_{\rm int} = 0{\cdot}033$, 1859 unique reflections, 1241 with $I > 3\sigma(I)$, 618 unobserved. All 12 H-atom positions from difference Fourier syntheses, refined with isotropic temperature parameters. The C—H bond lengths were constrained at 1·08 Å within an e.s.d. of 0·015 Å. 1241 reflections in final refinement cycle; 217 parameters refined ($B_{\rm iso}$ for the H atoms fixed); unit weight, $R = 0{\cdot}060$. $(\Delta/\sigma)_{\rm max} = 0{\cdot}06$ in final refinement cycle. Max. and min. heights in final difference Fourier synthesis 0·24 and –0·25 e Å^{-3}. The final atomic parameters are listed in Table 1.*

(2) Extremely thin dirty aggregates, ledge-shaped red crystal (0·36 x 0·08 x 0·02 mm). Unit cell: 24 reflections in interval $6 < \theta < 28°$. Max. $\sin\theta/\lambda = 0{\cdot}531$ Å^{-1}, range of h,k,l: 0–4, $\bar{1}\bar{3}$–13, $\bar{1}\bar{4}$–14. 9·2% loss of intensity in standard reflections $01\bar{3}$ and $1\bar{2}\bar{1}$ monitored initially and then every two hours. 2025 reflections measured. Lorentz–polarization correction, no absorption correction. $R_{\rm int} = 0{\cdot}065$, 1731 unique reflections, 947 with $I > 3\sigma(I)$, 784 unobserved. $\langle {\rm mod}(E)\rangle$, $\langle E^n\rangle$ and $N(Z)$ cumulative probability distribution values showed strong hypercentricity of the data. The solution of the structure was obtained after several trials with *MULTAN* in combination with weighted Fourier calculations using different molecular fragments in the space group $P1$. The centre of symmetry was found and the molecules were shifted to the correct position according to the space group $P\bar{1}$. In spite of the poor data set all 14 H-atom positions were found by difference Fourier syntheses; their isotropic temperature parameters were fixed at $B = 3{\cdot}2$ Å^2; two C—H bond lengths were constrained at 1·08 Å within an e.s.d. of 0·015 Å in the final refinement cycles. Reflections $\bar{1}10$, $\bar{1}11$, $\bar{1}21$, $\bar{1}12$, and $\bar{1}22$ omitted because secondary extinction was suspected; reflections 155 and $1\bar{1}6$ omitted because coincidence of intensities may have happened between the single crystal and another tiny individual that could not be removed. 940 reflections in final refinement cycle; separation of variables was necessary: 115 and 127 parameters refined alternately; unit weight, $R = 0{\cdot}087$. The rather poor agreement is believed to be due to the experimental difficulties. $(\Delta/\sigma)_{\rm max} = 1{\cdot}03$ (H-atom parameter) in final refinement cycle. Max. and min. heights in final difference Fourier synthesis 0·25 and –0·36 e Å^{-3}. The final atomic parameters are given in Table 2.*

Discussion. The atom-numbering schemes and bond distances of (1) and (2) are shown in the *ORTEP* drawings of Fig. 1 and Fig. 2. Bond angles for both of the structures are compared in Table 3. Their tricyclic conjugated ring systems each consist of a *p*-benzoquinone and a phenanthrenequinone moiety. The sp^2–sp^2 double- and single-bond distances and corresponding angles of the quinonoid part of (1) and (2) agree well with those values observed in *p*-benzoquinone structures (Schmalle, Jarchow, Hausen & Schulz, 1984). However, many different bond distances and angles are observed in nonsubstituted phenanthrene structures (*e.g.* Trotter, 1963; Kay, Okaya & Cox,

Table 1. *Final atomic coordinates* (×10^4) *and* U_{eq} (Å^2) *of* 3,8-*dimethoxy*-1,4-*phenanthrenequinone with e.s.d.'s in parentheses*

$$U_{\rm eq} = \sum_i \sum_k U_{ik} a_i^* a_k^* (\mathbf{a}_i.\mathbf{a}_k).$$

	x	y	z	$U_{\rm eq}$
O(1)	3134 (4)	4765 (2)	2295 (5)	0·066 (2)
O(3)	8619 (4)	4189 (2)	3115 (5)	0·060 (2)
O(4)	8004 (5)	3594 (2)	6224 (7)	0·106 (4)
O(8)	1363 (4)	3276 (2)	10805 (5)	0·063 (2)
C(1)	4260 (6)	4496 (2)	3216 (7)	0·047 (3)
C(2)	5864 (6)	4504 (2)	2526 (7)	0·047 (3)
C(3)	7073 (6)	4222 (2)	3572 (7)	0·048 (3)
C(4)	6854 (6)	3874 (2)	5459 (7)	0·053 (3)
C(5)	6145 (6)	3251 (2)	9345 (7)	0·046 (3)
C(6)	5731 (6)	2965 (2)	11049 (8)	0·052 (3)
C(7)	4136 (6)	2954 (2)	11610 (7)	0·052 (3)
C(8)	2962 (6)	3247 (2)	10444 (7)	0·048 (3)
C(9)	2072 (6)	3853 (2)	7428 (8)	0·050 (3)
C(10)	2406 (6)	4154 (2)	5703 (7)	0·049 (3)
C(11)	3987 (5)	4161 (2)	5119 (6)	0·040 (3)
C(12)	5243 (5)	3867 (2)	6239 (6)	0·040 (3)
C(13)	4941 (5)	3554 (2)	8080 (6)	0·041 (3)
C(14)	3311 (5)	3555 (2)	8641 (6)	0·041 (3)
C(15)	8989 (6)	4497 (3)	1287 (8)	0·062 (3)
C(16)	865 (8)	2939 (3)	12481 (9)	0·073 (4)

Table 2. *Final atomic coordinates and* U_{eq} (Å^2) *of* 3,7,8-*trimethoxy*-1,4-*phenanthrenequinone with e.s.d.'s in parentheses*

$$U_{\rm eq} = \sum_i \sum_k U_{ik} a_i^* a_k^* (\mathbf{a}_i.\mathbf{a}_k).$$

	x	y	z	$U_{\rm eq}$
O(1)	1·277 (2)	0·3438 (5)	0·5193 (5)	0·079 (8)
O(3)	1·151 (2)	0·6782 (5)	0·2153 (4)	0·071 (8)
O(4)	0·866 (2)	0·5648 (5)	0·1362 (5)	0·104 (9)
O(7)	0·315 (2)	0·1156 (5)	0·1182 (5)	0·085 (8)
O(8)	0·469 (2)	0·0283 (5)	0·3205 (5)	0·074 (8)
C(1)	1·176 (2)	0·3934 (7)	0·4305 (7)	0·06 (1)
C(2)	1·246 (3)	0·5137 (7)	0·3713 (7)	0·06 (1)
C(3)	1·134 (2)	0·5664 (7)	0·2772 (6)	0·06 (1)
C(4)	0·958 (3)	0·5096 (7)	0·2219 (7)	0·07 (1)
C(5)	0·668 (3)	0·3659 (7)	0·1269 (7)	0·07 (1)
C(6)	0·519 (3)	0·3007 (7)	0·0879 (7)	0·07 (1)
C(7)	0·464 (3)	0·1845 (7)	0·1520 (7)	0·06 (1)
C(8)	0·541 (2)	0·1416 (7)	0·2532 (6)	0·06 (1)
C(9)	0·780 (3)	0·1554 (7)	0·4028 (7)	0·07 (1)
C(10)	0·933 (3)	0·2164 (7)	0·4424 (7)	0·07 (1)
C(11)	1·003 (2)	0·3331 (7)	0·3802 (6)	0·06 (1)
C(12)	0·912 (2)	0·3847 (6)	0·2795 (6)	0·05 (1)
C(13)	0·757 (2)	0·3221 (6)	0·2325 (6)	0·06 (1)
C(14)	0·693 (2)	0·2047 (6)	0·2977 (6)	0·05 (1)
C(15)	1·301 (3)	0·7449 (9)	0·2595 (9)	0·08 (1)
C(16)	0·229 (4)	0·1603 (9)	0·0115 (8)	0·09 (1)
C(17)	0·690 (3)	–0·0443 (9)	0·2985 (9)	0·07 (1)

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* Lists of structure factors, anisotropic thermal parameters of the C and O atoms and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42628 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1971; Wright, Yakushi & Kuroda, 1978; Evans & Robinson, 1977; Herbstein, Kapon, Rzonzew & Rabinovich, 1978) as well as in substituted phenanthrenes (*e.g.* Courseille, Castellan, Busetta & Hospital, 1975; Lu, Hseu & Lee, 1977; Hacker, McOmie, Meunier-Pieret & Van Meerssche, 1982). These few examples and others found in the literature show that bond distances and angles depend on the C atoms which carry substituents, which may affect π-electron delocalization over the whole ring system.

In spite of many differences in details concerning bond lengths and angles, the molecular skeletons of the title compounds show relatively small distortions from planarity, which may be favoured by the intramolecular hydrogen bonds of the form C(5)—H(5)···O(4). Contrary to this effect is the distortion from planarity in the phenanthrene molecule (Kay *et al.*, 1971) resulting from a short H(4)···H(5) distance of 2·04 Å. Much greater distortions of this kind are observed in the oxygen-substituted PQ's 9-hydroxy-5,8-dimethoxy-1,4-PQ and 3,5,8-trimethoxy-1,4-PQ (Schmalle *et al.*, 1986). A least-squares plane fitted to the atoms C(1) to C(4) of the quinonoid parts of the title compounds and cypripedin shows maximum out-of-plane deviations of 0·119 (5) and 0·133 (5) Å for C(5) and C(6) in (1) and of 0·38 (1) and 0·35 (1) Å for C(6) and C(7) in (2). The independent molecules of cypripedin have different conformations with maximum deviations from the same plane of 0·16 (1) and 0·18 (1) Å for C(7) and C(8) in molecule (I), and −0·75 (1) and −0·85 (1) Å for C(6) and C(7) in molecule (II).

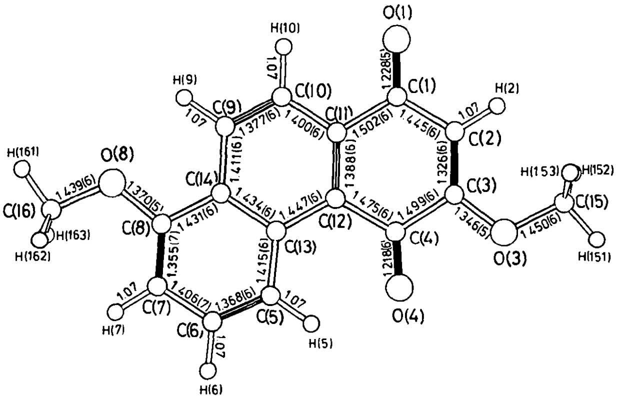

Fig. 1. *ORTEP* drawing of (1) with atom numbering scheme and bond distances (Å). The standard deviations for all C—H distances are 0·015 Å. Blackened bond lines indicate C=C and C=O double bonds.

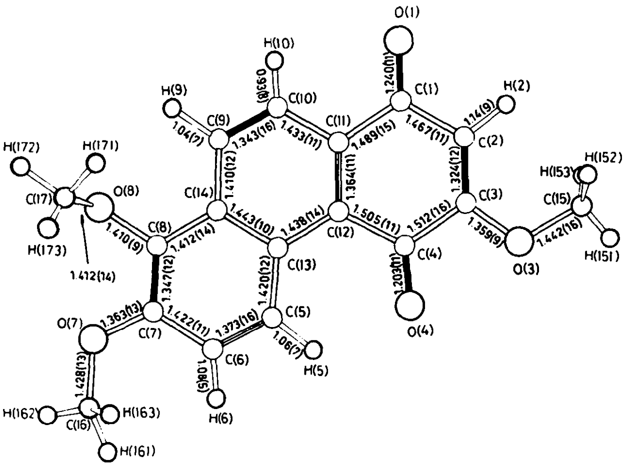

Fig. 2. *ORTEP* drawing of (2) with atom numbering scheme. Bond distances (Å) are shown with e.s.d.'s in parentheses. Blackened bond lines indicate C=C and C=O double bonds.

Table 3. *Bond angles* (°) *of* 3,8-*dimethoxy*-1,4-*phenanthrenequinone* (1) *and of* 3,7,8-*trimethoxy*-1,4-*phenanthrenequinone* (2)

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

	(1)	(2)		(1)	(2)
O(1)—C(1)—C(2)	121·2 (4)	118·9 (10)	O(8)—C(8)—C(14)	113·4 (4)	116·7 (7)
O(1)—C(1)—C(11)	119·9 (4)	121·8 (8)	C(8)—O(8)—C(*x**)	117·4 (4)	112·1 (7)
C(2)—C(1)—C(11)	119·0 (4)	119·2 (7)	C(10)—C(9)—C(14)	120·8 (4)	120·4 (7)
C(1)—C(2)—C(3)	120·2 (4)	118·6 (10)	C(9)—C(10)—C(11)	120·0 (4)	121·0 (8)
C(2)—C(3)—C(4)	122·8 (4)	124·4 (8)	C(10)—C(11)—C(12)	121·5 (4)	120·3 (9)
O(3)—C(3)—C(2)	126·8 (4)	126·8 (10)	C(1)—C(11)—C(10)	117·0 (4)	117·1 (7)
O(3)—C(3)—C(4)	110·4 (4)	108·8 (7)	C(1)—C(11)—C(12)	121·5 (4)	122·6 (7)
C(3)—O(3)—C(15)	116·1 (4)	115·5 (7)	C(11)—C(12)—C(13)	120·0 (4)	120·7 (7)
C(3)—C(4)—C(12)	118·6 (4)	116·5 (7)	C(4)—C(12)—C(11)	117·9 (4)	118·2 (9)
O(4)—C(4)—C(3)	118·1 (4)	119·5 (8)	C(4)—C(12)—C(13)	122·0 (4)	121·0 (7)
O(4)—C(4)—C(12)	123·3 (4)	124·0 (10)	C(12)—C(13)—C(14)	117·2 (4)	117·1 (7)
C(6)—C(5)—C(13)	119·7 (4)	121·9 (7)	C(5)—C(13)—C(12)	124·3 (4)	125·4 (7)
C(5)—C(6)—C(7)	122·7 (5)	120·0 (8)	C(5)—C(13)—C(14)	118·5 (4)	117·5 (9)
C(6)—C(7)—C(8)	118·9 (5)	119·0 (10)	C(9)—C(14)—C(13)	120·5 (4)	120·5 (9)
C(7)—C(8)—C(14)	121·3 (4)	123·3 (7)	C(8)—C(14)—C(9)	120·7 (4)	121·5 (7)
O(8)—C(8)—C(7)	125·4 (4)	120·0 (9)	C(8)—C(14)—C(13)	118·9 (4)	118·1 (7)
O(7)—C(7)—C(6)	—	122·8 (8)	O(7)—C(7)—C(8)	—	118·1 (7)
C(7)—O(7)—C(16)	—	119·7 (7)			

* *x* = 16 for (1), *x* = 17 for (2).

The methoxy methyl groups at C(3) in (1) and (2) are almost coplanar with the attached ring system with torsion angle C(2)—C(3)—O(3)—C(15) = 0·0 (6) and −2 (1)° respectively. Methoxy groups in the *ortho* position, however, show one methyl group twisting out of the plane of the aromatic ring system: the C(7)—C(8)—O(8)—C(17) torsion angle is 77 (1)° in compound (2); the corresponding values for cypripedin are −75 (1) and −71 (1)° (Bartsch *et al.*, 1986). This may be of interest with respect to hydrophobic methyl/π interactions between methyl groups of the allergenic phenanthrenequinone and ring systems (*e.g.* tyrosine, phenylalanine) of the receptor protein (surface antigen of Langerhans cells). The *ORTEP* stereo picture of Fig. 3 displays the superimposed structures of (1) and (2) on molecule (I) of cypripedin. The superimposition calculations (Liebman, 1982) have been made in order to show the free positions which they have in common for the postulated covalent bonding to the receptor in the skin (Schmalle & Hausen, 1984).

The values for the intramolecular hydrogen bonds in (1) and (2) are the following: C(5)–H(5) = 1·07 (2) and 1·06 (7) Å, C(5)···O(4) = 2·79 (1) and 2·82 (2) Å, H(5)···O(4) = 2·07 (2) and 2·24 (7) Å, the angle around the H atoms being 122 (2) and 112 (6)°.

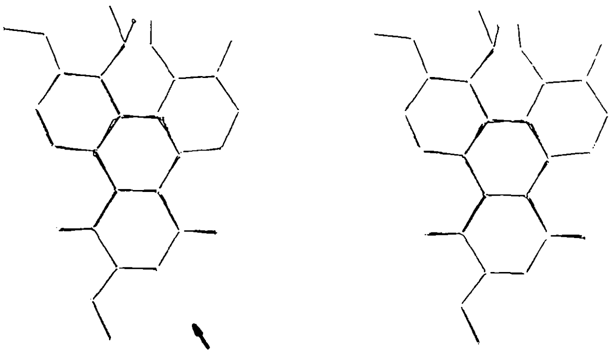

Fig. 3. Stereoscopic view (*ORTEP*) of the superimposed molecular skeletons of the title compounds on molecule (I) of the naturally occurring allergen cypripedin. The binding position to the receptor is marked with an arrow.

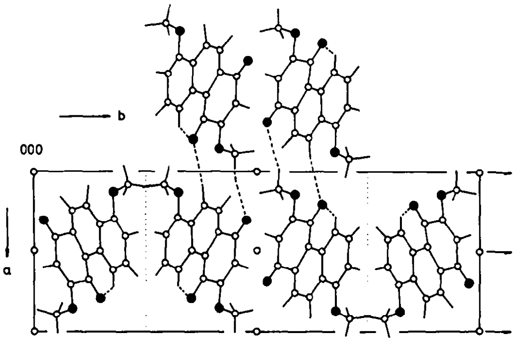

Fig. 4. *ab* projection of the structure of (1) showing C–H···O interactions. Filled circles of the molecular models indicate O atoms and open circles C atoms.

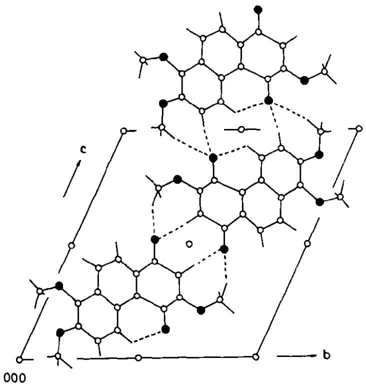

Fig. 5. *bc* projection of the structure of (2) with its C–H···O interactions. Filled circles of the molecular models indicate O atoms and open circles C atoms.

Intermolecular distances for (1) and (2) were calculated up to 3·6 Å with the program *ORFFE*. The weak C–H···O interactions for compound (1) are shown in the packing diagram of Fig. 4 as indicated by dashed lines between neighbouring molecules in the **a** direction. The distances are: C(9)···O(4) 3·43 (1), C(15)···O(1) 3·48 (1), O(4)···H(9) 2·50 (3), O(1)···H(151) 2·51 (2) Å, the C(9)–H(9)···O(4) and the C(15)–H(151)···O(1) angles being 145 (5) and 151 (5)° respectively. The *bc* projection of the unit cell for (2) with C–H···O interactions is shown in Fig. 5. The distances and angles are: C(2)···O(1) 3·48 (3), O(1)···H(2) 2·5 (1) Å; 176 (6)°; C(6)···O(4) 3·40 (3), O(4)···H(6) 2·3 (1) Å; 180 (6)°; C(15)···O(1) 3·44 (3), O(1)···H(153) 2·5 (1) Å; 148 (7)°; C(16)···O(4) 3·37 (3), O(4)···H(161) 2·4 (1) Å; 152 (7)°. These values are much greater than the typical distances of 3·2 and 2·3 Å for C–H···O interactions (Hamilton & Ibers, 1968) and thus may be considered as weak interactions.

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7,8-Benzochroman-4-one*

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Abstract. $C_{13}H_{10}O_2$, $M_r = 198{\cdot}2$, monoclinic, $C2/c$, $a = 37{\cdot}915\,(4)$, $b = 6{\cdot}2466\,(3)$, $c = 8{\cdot}367\,(1)$ Å, $\beta = 100{\cdot}418\,(5)^\circ$, $V = 1949{\cdot}0\,(3)$ Å^3, $Z = 8$, $D_m = 1{\cdot}33\,(2)$ (flotation), $D_x = 1{\cdot}350$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}64$ mm^{-1}, $F(000) = 832$, $T = 294$ K, $R = 0{\cdot}062$ for 1289 observed reflections. The molecular geometry is similar to that observed in comparable systems. The dihydropyran ring system is a modified half-chair distorted toward the *d,e*-diplanar arrangement. The two benzene rings in the naphthalene group are planar. The crystal packing is mainly stabilized by van der Waals interactions.

Introduction. Chromanones are potential synthons for the construction of many important oxygen heterocycles. The crystal structure of the title compound has been determined as an aid to understanding the conformation of the dihydropyran ring in heterocycles.

Experimental. Crystals from benzene–hexane mixture, CAD-4 diffractometer, crystal dimensions $0{\cdot}15 \times 0{\cdot}13 \times 0{\cdot}14$ mm, monochromatized Cu $K\alpha$ radiation, cell parameters from $\sin^2\theta$ values for 25 reflections (θ range 40–50°), intensity data for $0 < \theta < 75^\circ$, ω–$2(2/6)\theta$ scans, ω-scan angle $(1{\cdot}10 + 0{\cdot}24\tan\theta)^\circ$, extended by 25% in each direction for background, scan speeds 1 to 10° min^{-1}, horizontal aperture $(2{\cdot}0 + \tan\theta)$ mm, vertical aperture 4 mm, three standard reflections, <1% intensity variation, Lp but no absorption correction; 2234 reflections (h 0→47, k 0→7, l −10→10, 1289 (58%) with $I \geq 3\sigma(I)$, $\sigma^2(I) = C + 2B + [0{\cdot}04\,(C-B)]^2$, C = scan count, B = time-corrected background. Direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). An E map calculated from the set of phases with the highest figure of merit revealed the structure. Full-matrix least squares on F. Anisotropic temperature factors for C and O atoms, isotropic for H. H positions from difference map. $w = [\sigma^2(F_o) + 0{\cdot}0027\,F_o^2]^{-1}$, final $R = 0{\cdot}062$, $wR = 0{\cdot}072$ for 1289 observed reflections; $R = 0{\cdot}081$ for all 2234 reflections; $S = 1{\cdot}82$. $(\Delta/\sigma)_{\max} = 0{\cdot}52$, final ΔF map featureless, $\Delta\rho$ excursions $-0{\cdot}27$, $0{\cdot}29$ e Å^{-3}. No correction for secondary extinction, scattering factors as in *SHELX76* (Sheldrick, 1976). Calculations performed on an IBM 370 computer.

Discussion. Final atomic parameters are in Table 1.§ Bond distances and angles are given in Fig. 1. A perspective view of the molecule is shown in Fig. 2. The values of bond lengths and angles are similar to those observed in other comparable systems.

The ether oxygen O(1) shows a tendency to be coplanar with the benzene ring [C(7)—C(12)—C(13)—O(1), 178·5 (4); C(5)—C(4)—C(13)—O(1), −179·8 (4)°] causing an enlargement of the angle O(1)—C(13)—C(4), 123·5 (3)°, and a narrowing of the

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* IUPAC name: 2,3-dihydro-4*H*-naphtho[2,1-*b*]pyran-4-one.

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§ Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42826 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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