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Structure of an Anthracene Derivative

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Abstract. 7-Methoxy-2-methyl-4,5-dihydroxy-9,10-anthracenedione, physcion, $C_{16}H_{12}O_5$, $M_r = 284 \cdot 27$, orthorhombic, $P2_12_12_1$, $a = 3 \cdot 850$ (1), $b = 23 \cdot 73$ (3), $c = 13 \cdot 667$ (9) Å, $V = 1249$ (2) Å^3, $Z = 4$, $D_m = 1 \cdot 50$ (2), $D_x = 1 \cdot 51$ Mg m^{-3}, λ(Cu $K\alpha$) $= 1 \cdot 54178$ Å, $\mu = 0 \cdot 903$ mm^{-1}, $F(000) = 592$, $T = 293$ K, final $R = 0 \cdot 0594$ for 1190 unique reflections with $F > 4\sigma(F)$. The crystal structure consists of planar molecules which are situated in the bc plane and form a densely packed arrangement. The structure of physcion differs from both unsubstituted and 1-acetyl-2,4,5,7-tetrahydroxy-9,10-substituted anthracenedione.

Introduction. The compound investigated, trivially named physcion, belongs to the anthraquinone derivatives which are known to be secondary metabolites of various microscopic fungi and plants. It is isolated from the filtrate of *mycelia Eurotium (Aspargillus) ropeus,* cultured under stable conditions (Podojil, Sedmera, Vokoun, Betina, Baráthová, Ďuráčková, Horáková & Nemec, 1979).

Experimental. Transparent orange, very thin single crystals were obtained from chloroform; the size of the crystal used was $0 \cdot 5 \times 0 \cdot 5 \times 0 \cdot 06$ mm. D_m was measured by flotation. Systematically absent reflections, $h00$ for h odd, $0k0$ for k odd and $00l$ for l odd, were determined from Weissenberg and precession photographs. Accurate unit-cell parameters were obtained by a least-squares fit of 15 reflections ($15 < 2\theta < 45°$). Intensity data were measured at 193 K on a Syntex $P2_1$ diffractometer using graphite-monochromated Cu $K\alpha$ radiation; θ–2θ scan mode with $(2\theta)_{max} = 126°$ and the index range h 0/4, k 0/27, l −14/15. Three standard reflections (060, 1$\bar{1}$1, 1$\bar{1}\bar{1}$) were measured every 47 reflections, no significant systematic fluctuation was found. 1936 reflections were measured, 1190 of which with $F_o \geq 4\sigma(F_o)$ were considered observed; $R_{int} = 0 \cdot 073$ for 890 unique reflections before absorption correction. Corrections for absorption effects were made using *DIFABS* (Walker & Stuart, 1983) after isotropic refinement; the maximum and minimum corrections were 1·433 and 0·652, respectively. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1990) and least-squares refined on F by *SHELX*76 (Sheldrick, 1976). A difference map of the partially refined structure gave the positions of all H atoms. Refinement continued on all 235 positional and thermal parameters, anisotropic for non-H atoms and isotropic for H atoms. In the final cycle $R = 0 \cdot 059$ and $wR = 0 \cdot 061$ were reached, for 1190 observed reflections with weights, w, $w^{-1} = k|\sigma^2(F) + gF^2|$, $k = 0 \cdot 8294$, $g = 0 \cdot 00023$; $S = 0 \cdot 9033$, max. $\Delta/\sigma = 0 \cdot 039$ and max. and min. heights in final $\Delta\rho$ map $+ 0 \cdot 23$ and $− 0 \cdot 26$ e Å^{-3}. The scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Table 1. *Final atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\mathring{A}^2 \times 10^3$) *with e.s.d.'s in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	5383 (18)	989 (3)	8572 (5)	52 (3)
C(2)	5060 (20)	457 (3)	8176 (5)	56 (3)
C(3)	3650 (18)	373 (3)	7272 (5)	52 (3)
C(4)	2440 (19)	824 (3)	6723 (6)	54 (3)
C(5)	1331 (18)	1850 (3)	6510 (5)	53 (3)
C(6)	793 (18)	2879 (3)	6318 (5)	52 (3)
C(7)	1212 (18)	3437 (3)	6654 (5)	55 (3)
C(8)	2685 (21)	3530 (4)	7558 (6)	61 (3)
C(9)	3791 (18)	3075 (3)	8138 (5)	53 (3)
C(10)	4562 (17)	2040 (3)	8397 (5)	50 (3)
C(11)	4200 (19)	1467 (3)	8025 (5)	52 (3)
C(12)	2699 (18)	1360 (3)	7108 (5)	51 (3)
C(13)	1836 (18)	2428 (3)	6889 (5)	51 (3)
C(14)	3394 (18)	2516 (3)	7805 (5)	52 (3)
O(15)	6881 (15)	1043 (3)	9458 (4)	66 (2)
O(16)	3565 (14)	−172 (2)	6956 (4)	70 (2)
C(17)	2205 (28)	−295 (5)	5999 (8)	73 (4)
O(18)	−145 (15)	1758 (2)	5731 (4)	71 (2)
C(19)	74 (26)	3929 (4)	6037 (7)	67 (3)
O(20)	5292 (15)	3203 (2)	9016 (4)	66 (2)
O(21)	5885 (13)	2123 (2)	9240 (4)	67 (2)

Discussion. Final atomic coordinates and equivalent isotropic temperature factors for the title compounds are given in Table 1.* The list of the bond lengths arranged in groups of similar type and corresponding bond angles (Nardelli, 1983) are given in Table 2. The molecular structure with atomic numbering is shown in Fig. 1 (*ORTEP*II; Johnson, 1971). The arrangement of the molecules in the crystal structure is schematically depicted in Fig. 2, in projection onto the *bc* plane. The packing is not the closest one: molecules are situated in the *bc* plane in pairs, their relative positions within these pairs corresponding to the given symmetry $P2_12_12_1$. Along the *c* axis, the molecules are arranged into zigzag chains.

The structural results obtained for the title compound have been compared with those of unsubstituted anthraquinone (I) (Prakash, 1967) and 1-acetyl-2,4,5,7-tetrahydroxy-9,10-anthracenedione (II) (Ulický, Kettmann, Soldánová & Betina, 1987). As in (II), the C(5)—O(18) bond length [1·226 (7) Å] is within the typical C=O double-bond range. On the other hand, the formal double bond C(10)—O(21) [1·274 (7) Å] is approximately 0·05 Å longer than C(5)—O(18), obviously due to a polarization of the π electrons of this bond towards O(18) as a result of two strong intramolecular hydrogen bonds, O(20)—H···O(21)···H—O(15). Analogous findings have been reported for (II). Within the central

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* Lists of structure factors, anisotropic displacement parameters, H-atom parameters and hydrogen-bond details have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53933 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

C(1)—C(2)	1·378 (7)	C(7)—C(8)	1·378 (9)	
C(1)—C(11)	1·434 (7)	C(7)—C(19)	1·506 (10)	
C(1)—O(15)	1·347 (5)	C(8)—C(9)	1·405 (9)	
C(2)—C(3)	1·365 (8)	C(9)—C(14)	1·412 (9)	
C(3)—C(4)	1·398 (8)	C(9)—O(20)	1·367 (7)	
C(3)—O(16)	1·363 (7)	C(10)—C(11)	1·459 (9)	
C(4)—C(12)	1·380 (9)	C(10)—O(21)	1·274 (7)	
C(5)—C(12)	1·516 (9)	C(10)—C(14)	1·461 (10)	
C(5)—C(13)	1·478 (8)	C(11)—C(12)	1·403 (8)	
C(5)—O(18)	1·226 (7)	C(13)—C(14)	1·404 (8)	
C(6)—C(7)	1·411 (9)	O(16)—C(17)	1·439 (9)	
C(6)—C(13)	1·383 (9)			

|				
C(2)—C(1)—C(11)	119·4 (4)	C(6)—C(13)—C(14)	120·8 (7)
C(1)—C(2)—C(3)	121·7 (7)	C(5)—C(13)—C(14)	120·4 (7)
C(2)—C(3)—C(4)	127·7 (7)	C(10)—C(14)—C(13)	120·7 (7)
C(3)—C(4)—C(12)	118·7 (7)	C(9)—C(14)—C(13)	118·3 (7)
C(12)—C(5)—C(13)	118·5 (6)	C(9)—C(14)—C(10)	121·0 (7)
C(13)—C(6)—C(7)	120·6 (7)		
C(6)—C(7)—C(19)	120·8 (7)		
C(6)—C(7)—C(8)	119·3 (8)	C(11)—C(1)—O(15)	122·0 (5)
C(8)—C(7)—C(19)	119·9 (8)	C(2)—C(1)—O(15)	118·6 (5)
C(7)—C(8)—C(9)	120·5 (8)	C(2)—C(3)—O(16)	115·8 (7)
C(8)—C(9)—C(14)	120·5 (7)	C(4)—C(3)—O(16)	123·5 (7)
C(14)—C(10)—C(11)	119·9 (6)	C(13)—C(5)—O(18)	122·0 (7)
C(10)—C(11)—C(1)	121·7 (6)	C(12)—C(5)—O(18)	119·5 (7)
C(10)—C(11)—C(12)	121·3 (7)	C(8)—C(9)—O(20)	117·0 (7)
C(1)—C(11)—C(12)	117·0 (7)	C(14)—C(9)—O(20)	122·6 (7)
C(11)—C(12)—C(5)	119·1 (7)	C(14)—C(10)—O(21)	120·3 (7)
C(4)—C(12)—C(11)	122·5 (8)	C(11)—C(10)—O(21)	119·8 (7)
C(4)—C(12)—C(5)	118·5 (7)	C(3)—O(16)—C(17)	119·3 (7)
C(5)—C(13)—C(6)	118·8 (7)		
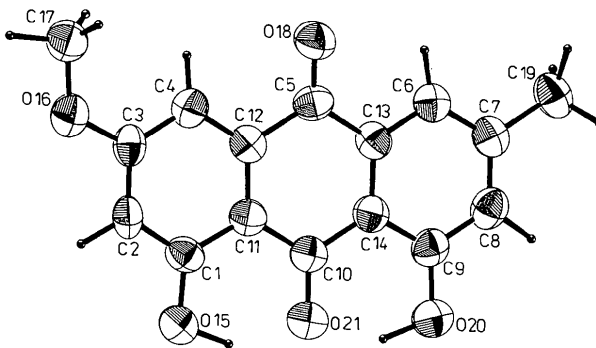
Fig. 1. The molecular structure of 2-methyl-7-methoxy-4,5-dihydroxy-9,10-anthracenedione with atomic numbering.
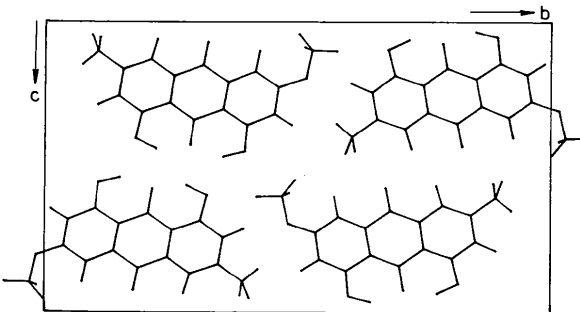

Fig. 2. Arrangement of the molecules in the crystal projected onto the *bc* plane.

ring of the anthraquinone moiety, C(10)—C(11) [1·459 (9) Å] and C(10)—C(14) [1·461 (8) Å] are, in accordance with the above, shorter than C(5)—C(12) [1·516 (9) Å] and C(5)—C(13) [1·478 (8) Å], the latter showing almost pure C(sp^2)—C(sp^2) single-bond character. Bond lengths C(6)—C(13), C(4)—C(12), C(4)—C(3), C(3)—C(2), C(2)—C(1) and C(7)—C(8) correspond to an average value of the C—C bond length in benzene (1·39 Å). C(13)—C(14) and C(11)—C(12) bond lengths are about 0·03 Å shorter than those in structure (II).

The structure of the anthraquinone nucleus in the physcion molecule cannot be expressed by a single canonical formula showing the electronic configuration (corresponding to the normal quinoid structure of anthraquinone):
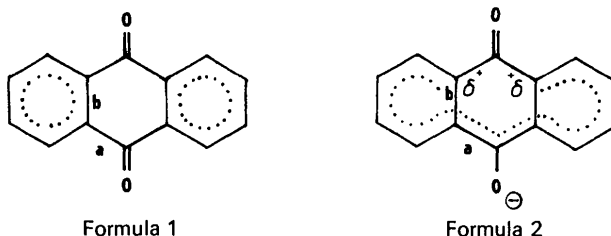
Formula 1   Formula 2

Formula 2 has been proposed as a second canonical form contributing to the electronic structure of the anthraquinone nucleus in the substituted anthracenedione derivatives (Ulický et al., 1987). This represents an extension of π-electron delocalization from the benzene rings to the C(11)—C(10)—C(14) bridge resulting in a shifting of one half of the central ring from a quinoid to a benzenoid structure. While the difference in the relevant C—C bond length averages, $\Delta = a - b$ [in our structure C(10)—C(11) = a and C(11)—C(12) = b], is 0·07 (1) Å for

anthracenedione (formula 1) and $\Delta \simeq 0$ Å for formula 2, in the present structure $\Delta = 0\cdot056$ (12) Å. Thus, the structure of the anthraquinone nucleus is closer to formula 1.

The rings composed of atoms C(1), C(2), C(3), C(4), C(11), C(12) (A) and C(13), C(6), C(7), C(8), C(9), C(14) (B) do not show any significant deviations from planarity. In contrast, the central ring (C) displays slight but significant deviation from planarity. This is a consequence of twisting around the C(5)—C(12) and C(5)—C(13) bonds, with the dihedral angles O(18)—C(5)—C(12)—C(4) = 4·22 and O(18)—C(5)—C(13)—C(4) = – 3·92°. As a result, the 14-membered ring system is also nonplanar. The angles between the planes of the individual rings are: AB 2·2 (3), C 3·3 (3), BC 1·6 (2)°.

Thus it may be concluded that the crystal and molecular structure of the present compound is different from those of (I) and (II). Despite the presence of strong intramolecular hydrogen-bond interactions, no intermolecular interactions, such as those observed in (II), have been identified. This fact results in a greater contribution of the 'quinoid' formula to the resonance structure and in a lack of charge-transfer effect, the latter being evident in (II).

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6,6-Dichloro-1-methyl-3,4,5-triphenylbicyclo[3.1.0]hex-3-en-2-one and 3-Chloro-2-methyl-4,5,6-triphenylphenol

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Abstract. (I) $C_{25}H_{18}Cl_2O$, $M_r = 405\cdot32$, monoclinic, $I2/a$, $a = 23\cdot95$ (2), $b = 6\cdot550$ (6), $c = 26\cdot59$ (2) Å, $\beta = 96\cdot4$ (1)°, $V = 4145\cdot2$ (10) Å^3, $Z = 8$, $D_x = 1\cdot298$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 2\cdot95$ mm^{-1}, $F(000) = 1680$, $T = 293$ K, $R = 0\cdot0735$ for 1700 reflexions. (II) $C_{25}H_{19}ClO$, $M_r = 370\cdot88$, monoclinic, $P2_1/n$, $a = 12\cdot211$ (8), $b = 26\cdot50$ (2), $c = 12\cdot477$ (9) Å, $\beta = 99\cdot12$ (1)°, $V = 3986\cdot4$ (8) Å^3, $Z =$