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Structure of (Phenyl)bis(4-hydroxybenzo-2H-pyran-2-one-3-yl)methane*

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Abstract. A derivative of dicoumarol, $C_{25}H_{16}O_6$, $M_r = 412.41$, orthorhombic, $P2_12_12_1$, $a = 7.959(2)$, $b = 12.865(3)$, $c = 18.606(6)$ Å, $V = 1905.3(22)$ Å³, $Z = 4$, $D_x = 1.44$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.965$ cm⁻¹, $F(000) = 856$, $T = 293$ K, final $R = 0.042$ for 2031 observations. The 4-hydroxycoumarins are intramolecularly hydrogen bonded between hydroxyls and carbonyls, O...O separations are 2.624(3) and 2.718(3) Å, a scheme which imparts a dissymmetry to the otherwise achiral molecule and underlies packing in a polar space group.

Introduction. During screening of a variety of coumarin compounds capable of H bonding, the title compound, which was not inherently chiral, was found to crystallize in a polar space group and have an unusually high density. Conveniently named phenyldicoumarol, in our hands the molecule was identified as a byproduct of the condensation of 4-hydroxycoumarin with 4-phenyl-3-buten-2-one (Bush & Traeger, 1983) although the original authors do not mention having isolated this molecule.

Experimental. Colorless blocks from 2-propanone, specimen: 0.51 × 0.38 × 0.54 mm, CAD-4 diffractometer, cell from 25 accurately centered higher-order intensities. Data measured to $2\theta = 60^\circ$ ($h: 0-10$, $k: 0-18$, $l: 0-21$), 2986 unique after elimination of systematic absences ($h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; $00l$, $l \neq 2n$), were corrected for coincidence, polarization; no decay noted, no absorption correction. An extinction

correction was applied later and refined, $g = 3.2(11) \times 10^{-7}$ (Zachariasen, 1963). Structure discovered with MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Non-H atom positions were refined with their U_{iso} 's by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$, then with their U_{ij} 's. Hydroxy H's located in difference Fourier map and positions refined with B_{iso} 's, other H's fixed at 1.0 Å from their adjacent atoms with B 's fixed at 1.3 B_{eq} for the attached carbon. Scattering factors were from *International Tables for X-ray Crystallography* (1974) except for H (Stewart, Davidson & Simpson, 1965). Final agreement factors: $R = 0.042$, $wR = 0.053$, $GOF = 1.401$ for the 2031 intensities with $I > 2.5\sigma_I$. Least-squares weights were taken as $4F_o^2/\sigma^2(I)$ where $\sigma^2(I) = \sigma^2(I)_c + 0.05(I)_c^2$; and the differences in structure factors were minimized for the 289 variables; maximum final $|\Delta\rho|$ excursions were less than +0.25 and -0.19 e Å⁻³; maximum Δ/σ in the final cycle 0.01. All programs were from the locally modified SDP package (Frenz, 1987). Positions and B_{eq} 's for the non-H atoms in phenyldicoumarol are given in Table 1.†

Discussion. A plot (Johnson, 1976) of the molecular structure of phenyldicoumarol is given in Fig. 1. The structure is closely related to those of dicoumarol

† Lists of H-atom positions, anisotropic vibrational amplitudes and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51613 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* IUPAC name: 3,3'-benzylidenedi-4-hydroxycoumarin.

Table 1. Positions and B_{eq} for phenyldicoumarol with $e.s.d.$'s in parentheses
$$B_{eq} = (1/3) \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
O1	0.4086 (3)	-0.0792 (1)	0.16216 (9)	3.91 (4)
O2	0.2882 (3)	-0.2043 (1)	0.1007 (1)	4.03 (4)
O3	0.2560 (3)	0.1424 (1)	0.0178 (1)	3.48 (4)
O4	0.3371 (2)	-0.0627 (1)	-0.18056 (9)	3.53 (4)
O5	0.2409 (3)	0.0614 (1)	-0.11145 (9)	3.58 (4)
O6	0.2297 (3)	-0.2878 (1)	-0.0312 (1)	4.64 (5)
C2	0.3099 (4)	-0.1106 (2)	0.1062 (1)	3.03 (5)
C3	0.2420 (3)	-0.0333 (2)	0.0579 (1)	2.61 (5)
C4	0.2942 (3)	0.0674 (2)	0.0645 (1)	2.75 (5)
C5	0.4370 (4)	0.2043 (2)	0.1379 (1)	3.80 (6)
C6	0.5323 (4)	0.2289 (2)	0.1974 (2)	4.75 (7)
C7	0.5850 (5)	0.1510 (3)	0.2443 (2)	4.91 (7)
C8	0.5437 (4)	0.0483 (3)	0.2328 (2)	4.54 (7)
C9	0.4464 (4)	0.0247 (2)	0.1728 (1)	3.36 (5)
C10	0.3926 (3)	0.0998 (2)	0.1250 (1)	3.02 (5)
C11	0.1232 (3)	-0.0755 (2)	0.0015 (1)	2.39 (4)
C12	0.2615 (3)	-0.0322 (2)	-0.1180 (1)	2.75 (5)
C13	0.2134 (3)	-0.1098 (2)	-0.0665 (1)	2.60 (4)
C14	0.2561 (4)	-0.2111 (2)	-0.0785 (1)	3.21 (5)
C15	0.3683 (5)	-0.3462 (2)	-0.1630 (2)	4.77 (7)
C16	0.4453 (5)	-0.3694 (3)	-0.2269 (2)	5.75 (8)
C17	0.4893 (5)	-0.2899 (3)	-0.2746 (2)	5.42 (8)
C18	0.4507 (4)	-0.1881 (3)	-0.2592 (2)	4.51 (7)
C19	0.3721 (4)	-0.1657 (2)	-0.1945 (1)	3.32 (5)
C20	0.3306 (4)	-0.2421 (2)	-0.1454 (1)	3.42 (5)
C21	-0.0349 (3)	-0.0106 (2)	-0.0140 (1)	2.58 (5)
C22	-0.0942 (4)	0.0630 (2)	0.0344 (2)	3.53 (5)
C23	-0.2447 (4)	0.1148 (2)	0.0221 (2)	4.47 (6)
C24	-0.3368 (4)	0.0936 (3)	-0.0386 (2)	5.16 (7)
C25	-0.2807 (4)	0.0199 (3)	-0.0857 (2)	4.76 (7)
C26	-0.1304 (4)	-0.0327 (2)	-0.0739 (2)	3.50 (6)

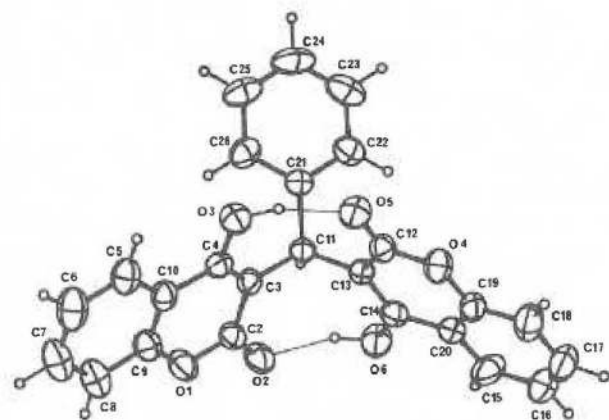


Fig. 1. A plot of phenyldicoumarol with 50% probability ellipsoids enclosing the non-H atoms, and showing the numbering scheme.

(Bravic, Gaultier & Hauw, 1968) and dibromodicycoumarol (Alcock & Hough, 1972). Two 4-hydroxycoumarin moieties are linked through a methylene bridge on which one H has been replaced with a phenyl group. Bond distances and angles are given in Table 2. Although most of the bond distances are of expected length the C(11)–C(21) distance of 1.539 (3) Å is longer than an unstrained C(sp³)–C(Ar) bond, but in the range characteristic of triphenylmethane and related sterically crowded structures (Bernardinelli & Gerdil, 1981; Destro, Pilati & Simonetta, 1980). Differences in exocyclic angles about the coumarin points of attachment to the methylene carbon are of note also. The exocyclic angles about C(3) [C(2)–C(3)–C(11) =

Table 2. Bonded distances (Å) and interbond angles (°)

O1–C2	1.366 (3)	C11–C13	1.521 (3)
O1–C9	1.384 (3)	C11–C21	1.538 (3)
O2–C2	1.222 (3)	C12–C13	1.436 (3)
O3–C4	1.333 (3)	C13–C14	1.365 (3)
O4–C12	1.368 (3)	C14–C20	1.435 (3)
O4–C19	1.379 (3)	C15–C16	1.371 (4)
O5–C12	1.221 (3)	C15–C20	1.412 (4)
O6–C14	1.339 (3)	C16–C17	1.398 (5)
C2–C3	1.445 (3)	C17–C18	1.376 (4)
C3–C4	1.365 (3)	C18–C19	1.387 (4)
C3–C11	1.513 (3)	C19–C20	1.381 (4)
C4–C10	1.434 (3)	C21–C22	1.390 (3)
C5–C6	1.380 (4)	C21–C26	1.378 (3)
C5–C10	1.410 (4)	C22–C23	1.390 (4)
C6–C7	1.394 (4)	C23–C24	1.374 (5)
C7–C8	1.379 (4)	C24–C25	1.366 (5)
C8–C9	1.391 (4)	C25–C26	1.392 (4)
C9–C10	1.382 (3)		
C2–O1–C9	121.4 (2)	O5–C12–C13	125.7 (2)
C12–O4–C19	121.6 (2)	C11–C13–C12	118.7 (2)
O1–C2–O2	115.9 (2)	C11–C13–C14	122.0 (2)
O1–C2–C3	119.1 (2)	C12–C13–C14	119.2 (2)
O2–C2–C3	125.1 (2)	O6–C14–C13	123.8 (2)
C2–C3–C4	118.9 (2)	O6–C14–C20	115.5 (2)
C2–C3–C11	114.7 (2)	C13–C14–C20	120.6 (2)
C4–C3–C11	126.4 (2)	C16–C15–C20	120.2 (3)
O3–C4–C3	124.0 (2)	C15–C16–C17	120.2 (3)
O3–C4–C10	115.1 (2)	C16–C17–C18	120.5 (3)
C3–C4–C10	120.9 (2)	C17–C18–C19	118.6 (3)
C6–C5–C10	119.5 (3)	O4–C19–C18	117.0 (2)
C5–C6–C7	120.2 (3)	O4–C19–C20	120.7 (2)
C6–C7–C8	121.3 (3)	C18–C19–C20	122.3 (2)
C7–C8–C9	117.8 (3)	C14–C20–C15	123.5 (2)
O1–C9–C8	116.6 (2)	C14–C20–C19	118.4 (2)
O1–C9–C10	121.0 (2)	C15–C20–C19	118.1 (2)
C8–C9–C10	122.4 (2)	C11–C21–C22	121.7 (2)
C4–C10–C5	123.2 (2)	C11–C21–C26	119.4 (2)
C4–C10–C9	118.1 (2)	C22–C21–C26	118.5 (2)
C5–C10–C9	118.7 (2)	C21–C22–C23	120.8 (3)
C3–C11–C13	112.7 (2)	C22–C23–C24	120.1 (3)
C3–C11–C21	116.5 (2)	C23–C24–C25	119.4 (3)
C13–C11–C21	112.8 (2)	C24–C25–C26	121.1 (3)
O4–C12–O5	115.3 (2)	C21–C26–C25	120.1 (3)
O4–C12–C13	119.1 (2)		

114.6 (2) and C(4)–C(3)–C(11) = 126.5 (2)°] differ by 11.9° whereas the corresponding angles about C(13) differ by only 3.3°. This asymmetry may arise from the effects of steric crowding within the molecule or from packing constraints. Likewise all principal bond angles about C(11) are widened over normal tetrahedral values, ranging from 112.7 (2) to 116.5 (2)°. Steric crowding about the methylene carbon may also be responsible for this feature.

The coumarin rings are planar with the two planes inclined at 121° to each other. The orientations of the coumarins about the methylene bridge may be described further by torsion angles C(4)–C(3)–C(11)–C(13) = 88.2 (3)° and C(3)–C(11)–C(13)–C(12) = -80.1 (3)°. The phenyl mean plane is inclined at 54° to one and 108° to the other 4-hydroxycoumarin.

Two intramolecular hydrogen bonds are found; each links a coumarin hydroxyl and carbonyl group. Unlike dibromodicycoumarol, in which the methylene group rests on a twofold axis and the H-bonding scheme is symmetrical, the H bonds in phenyldicoumarol are unsymmetrical. The O...O distances are 2.624 (3) Å between O(3) and O(5) and 2.720 (3) Å between O(2) and O(6); the angles subtended at the hydrogen between them are 161 (3) and 157 (3)°. In this respect,

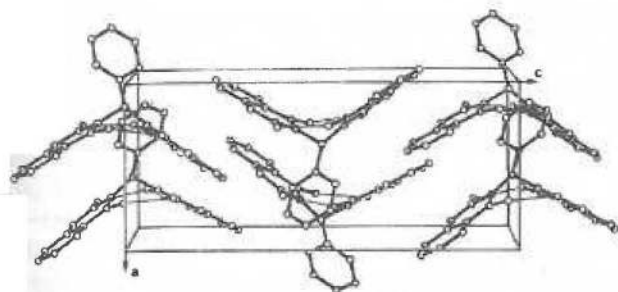


Fig. 2. A plot of a unit cell viewed nearly down the *b* axis.

phenyldicoumarol is similar to dicoumarol and to the flavones obtusifolin (Narayanan, Zeichmeister, Rohrl & Hoppe, 1971) and urarinol (Hufford, Lasswell, Hirotsu & Clardy, 1979), all of which also contain dissymmetric intramolecularly H-bonded molecules.

Packing in phenyldicoumarol is related partly to the arrangements found in both dicoumarol and dibromodicoumarol. A unit-cell drawing (Johnson, 1976) is given in Fig. 2. Coumarins on different molecules related by the screw axes along *a* (the short axis) pack at the nominal 3.5 Å separation, as in dibromodicoumarol ($P4_12_12$) where a similar intercoumarin spacing is found between screw-related molecules along one of the two short axes. In dicoumarol ($P2_1/c$), a similar intercoumarin spacing is found along the short axis but between glide-related molecules.

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