

Piperidinium 3-[(4-hydroxy-5,7-dimethyl-2-oxo-2H-chromen-3-yl)-phenylmethyl]-5,7-dimethyl-2-oxo-2H-chromen-4-olate

L. Vijayalakshmi,^a V. Parthasarathi,^{a*} Vipul Vora,^b Bhavik Desai^b and Anamik Shah^b

^aDepartment of Physics, Bharathidasan University, Tiruchirappalli 620 024, India, and ^bDepartment of Chemistry, Saurashtra University, Rajkot 360 005, India

Correspondence e-mail: sarati@bdu.ernet.in

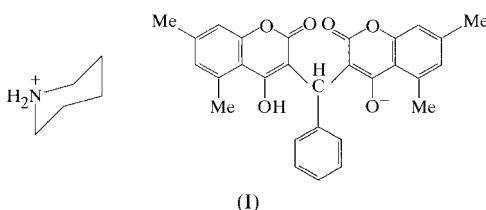
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In the title salt, $C_5H_{12}N^+ \cdot C_{29}H_{23}O_6^-$, both benzopyran systems are planar. Intermolecular N—H···O hydrogen bonds and a short O—H···O intramolecular hydrogen bond are observed in the structure.

Comment

The title compound, (I), is a derivative of 3,3'-benzylidene-bis(4-hydroxycoumarin), also known as dicoumarol. Dicoumarol itself has received attention recently due to its pronounced anti-HIV activity (Thaisrivongs, 1994; Hong *et al.*, 1996). In the present investigation, the X-ray structure analysis of (I) was carried out in order to study its molecular conformation and hydrogen-bond characteristics.



In the molecule of (I), both benzopyran systems are planar. The bond lengths C10—C4 1.464 (2), C4=C3 1.378 (2) and C3—C2 1.425 (2) Å in one ring system and the bond lengths C20—C14 1.469 (3), C14=C13 1.392 (2) and C13—C12 1.410 (2) Å in the other indicate conjugation (Alcock & Hough, 1972). A very short O4···O14 intramolecular hydrogen bond is observed (Table 2). As a result of this hydrogen bond, a chelate ring of eight atoms is formed comprised of O4, H4, O14, C14, C13, C21, C3 and C4. The plane of the phenyl ring is inclined at angles of 78.02 (7) and 77.2 (1)° to the benzopyran moieties; the dihedral angle between the two benzopyran moieties is 65.4 (1)°. The orientations of the benzopyran moieties about C21 may be described by the torsion angles C13—C21—C3—C4 of -88.7 (2)° and C3—C21—C13—C14 of 61.5 (2)°. The prin-

cipal bond angles about C21 [113.6 (1), 114.5 (2) and 115.2 (1)°] are widened in comparison with normal tetrahedral values. Steric crowding about the C21 atom may be responsible for this (Valente & Eggleston, 1989). The piperidinium cation is present in the structure in a chair conformation. N—H···O-type intermolecular hydrogen bonds stabilize the structure (Table 2).

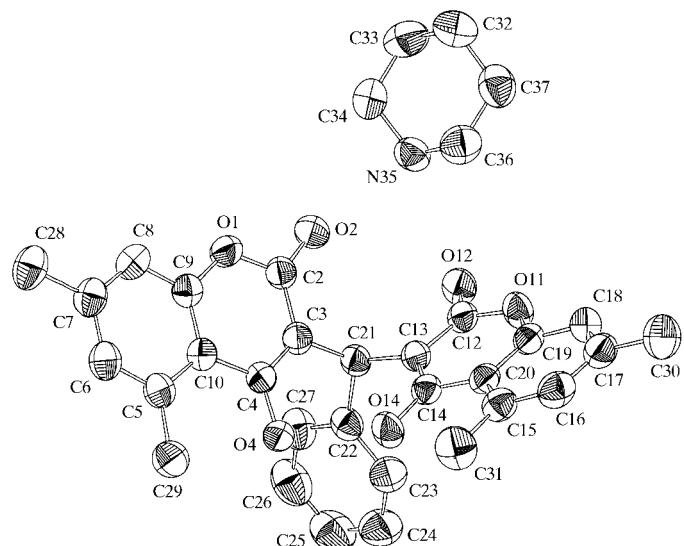


Figure 1

The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

4-Hydroxy-5,7-dimethylcoumarin (0.02 mol) in absolute ethanol (30 ml) was heated on a boiling water bath until a clear solution was obtained and this was then filtered. Benzaldehyde (0.01 mol) was added and the resulting solution was refluxed for 15 h. Piperidine (8 to 10 drops) was then added as a catalyst. Excess solvent was distilled off and the solution was cooled gradually whereupon the title compound was obtained. The product was filtered off, dried and purified in ethanol (m.p. 548 K; yield 62%).

Crystal data

$C_5H_{12}N^+ \cdot C_{29}H_{23}O_6^-$	$Z = 2$
$M_r = 553.63$	$D_x = 1.266 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.568 (2) \text{ \AA}$	Cell parameters from 25 reflections
$b = 11.567 (3) \text{ \AA}$	$\theta = 2-25^\circ$
$c = 14.010 (4) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$\alpha = 83.37 (2)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 80.69 (5)^\circ$	Plate, colourless
$\gamma = 72.08 (3)^\circ$	$0.25 \times 0.20 \times 0.12 \text{ mm}$
$V = 1452.3 (6) \text{ \AA}^3$	

Data collection

Enraf-Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.016$
$\omega-2\theta$ scans	$\theta_{\text{max}} = 25.7^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 11$
$T_{\text{min}} = 0.977$, $T_{\text{max}} = 0.993$	$k = -13 \rightarrow 14$
5659 measured reflections	$l = -16 \rightarrow 17$
5305 independent reflections	2 standard reflections every 60 reflections
4252 reflections with $I > 2\sigma(I)$	intensity decay: negligible

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.138$
 $S = 1.04$
5305 reflections
375 parameters
H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0654P)^2 + 0.4386P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\text{max}} = 0.001$$

$$\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$$

Extinction correction: *SHELXL97*
Extinction coefficient: 0.018 (2)

Table 1
Selected geometric parameters (\AA , $^\circ$).

O4—C4	1.309 (2)	O14—C14	1.283 (2)
C37—C32—C33—C34	55.0 (3)	C34—N35—C36—C37	−56.5 (3)
C32—C33—C34—N35	−54.5 (3)	N35—C36—C37—C32	56.7 (3)
C33—C34—N35—C36	55.1 (3)	C33—C32—C37—C36	−56.2 (3)

Table 2
Hydrogen-bonding geometry (\AA , $^\circ$).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O4—H4 \cdots O14	1.14	1.30	2.432 (2)	169
N35—H351 \cdots O2	0.90	1.92	2.765 (3)	155
N35—H352 \cdots O12 ⁱ	0.90	1.85	2.747 (2)	175

Symmetry code: (i) $-x, 2 - y, 1 - z$.

All H atoms were fixed and allowed to ride on their carrier atom ($C—H = 0.93\text{--}0.98 \text{ \AA}$). The O—H and N—H H atoms were located from difference Fourier maps and were included in the structure-factor calculations with isotropic displacement parameters equal to $1.1U_{\text{eq}}$ of the carrier atom and their parameters were not refined.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *MolEN* (Fair, 1990); data reduction: *MolEN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1122). Services for accessing these data are described at the back of the journal.

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