organic papers

3,3'-(3,6-Dihydroxy-*p*-phenylene)bis(4,7-dihydroxy-2*H*-chromen-2-one) dimethylformamide trisolvate

Qiong Shen,[a] **Ming-Hua Zeng**[a] **and Seik Weng Ng**[b*]

[a]Department of Chemistry, Guangxi Normal University, Guilin 541000, Guangxi, People's Republic of China, and [b]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail: seikweng@um.edu.my

The two chromen-3-yl substituents at the 2- and 3-positions of the 1,4-dihydroxybenzene in the title dimethylformamide (DMF) trisolvate, $C_{24}H_{14}O_{10}\cdot 3C_3H_7NO$, are aligned at 67.1 (1) and 69.8 (1)° with respect to the central aromatic ring. The 1-hydroxy group serves as a hydrogen-bond donor to a DMF whereas the substituent at the 3-position functions as a hydrogen-bond donor to two DMF molecules. The other three hydroxy groups interact with donor sites of adjacent molecules, generating a three-dimensional network architecture.

Comment

The 4-hydroxy-2-oxo-2*H*-chromen-3-yl group is an organic unit commonly found in natural products as well as in compounds that are synthesized for their biological activities. The C atom at the 3-position of 4-hydroxycoumarin is acidic, and the compound is capable of undergoing a Michael addition across the carbon–carbon double bond of *p*-benzoquinone (Rani & Darbarwar, 1987). When the reaction is performed in the presence of pyridine, the product is a 1,4-dihydroxybenzene whose 2-position bears the chromen-3-yl substituent; as there is a pyridinium group in the 3-position, the compound is a zwitterionic inner salt (Zhang *et al.*, 2004). For the reaction of 4,7-dihydroxycoumarin and *p*-benzoquinone, the product is not a disubstituted *p*-benzoquinone as postulated (Rani & Darbarwar, 1987), but is a disubstituted *p*-dihydroxyphenol. The compound crystallizes from dimethylformamide (DMF) as a trisolvate, (I) (Fig. 1).

(I)
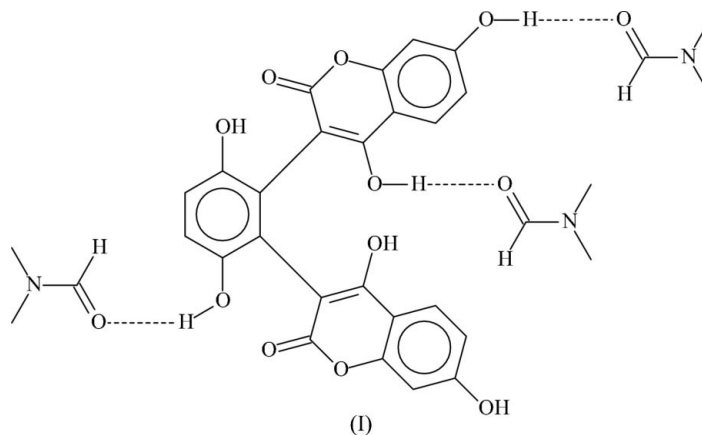
One of the chromen-3-yl groups engages in hydrogen bonding with two DMF molecule whereas the other forms hydrogen bonds with a symmetry-equivalent molecule. As a result of the hydrogen bonds, a three-dimensional network is formed.

Experimental

4,7-Dihydroxycoumarin (1.76 g, 10 mmol) and *p*-benzoquinone (0.50 g, 5 mmol) were dissolved in 50% aqueous acetone (50 ml). The solution was refluxed for 10 h. The solvent was removed and the residue was purified by silica-gel chromatography (cyclohexane/ acetone 1:4 *v*/*v*) to yield the pure title compound. Crystals were grown from DMF as solvent.

Crystal data

$C_{24}H_{14}O_{10} \cdot 3C_3H_7NO$	$Z = 4$
$M_r = 681.64$	$D_x = 1.390$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 11.3725$ (6) Å	$\mu = 0.11$ mm^{-1}
$b = 14.0520$ (8) Å	$T = 123$ (2) K
$c = 20.535$ (1) Å	Block, brown
$\beta = 97.058$ (1)°	$0.35 \times 0.25 \times 0.20$ mm
$V = 3256.7$ (3) Å^3	

Data collection

Bruker SMART area-detector diffractometer	6956 independent reflections
φ and ω scans	4883 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{int} = 0.043$
25715 measured reflections	$\theta_{max} = 27.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0791P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.062$	$+ 1.3446P]$
$wR(F^2) = 0.164$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
6956 reflections	$\Delta\rho_{max} = 0.31$ e Å^{-3}
510 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Figure 1
The asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level and H atoms as spheres of arbitrary radii. Only one of the two disordered DMF components is shown. Dashed lines represent hydrogen bonds.

behaviour. Carbon-bound H atoms were placed at calculated positions (C—H = 0.95–0.98 Å) and were included in the refinement in the riding-model approximation, with $U(H) = 1.2$–1.5 times $U_{eq}(C)$. The methyl groups were rotated to fit the electron density. The hydroxy H atoms were located in a difference Fourier and were refined with a distance restraint of O—H = 0.85 (1) Å; their displacement parameters were freely refined.

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXL97*.

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots$A	D—H	H$\cdots$A	$D\cdots$A	D—H$\cdots$A
O3—H3o$\cdots$O12	0.86 (1)	1.72 (2)	2.540 (2)	161 (3)
O4—H4o$\cdots$O11	0.85 (1)	1.79 (1)	2.638 (3)	172 (3)
O5—H5o$\cdots$O8^i	0.85 (1)	1.88 (1)	2.718 (2)	170 (3)
O6—H6o$\cdots$O13	0.85 (1)	2.04 (1)	2.883 (6)	172 (4)
O6—H6o$\cdots$O13'	0.85 (1)	1.72 (2)	2.532 (5)	159 (4)
O9—H9o$\cdots$O11^{ii}	0.86 (1)	1.84 (2)	2.642 (2)	156 (3)
O10—H10o$\cdots$O2^{iii}	0.85 (1)	1.87 (2)	2.666 (2)	155 (4)

Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $-x + 1, -y + 1, -z + 1$.

One of the three DMF molecules is disordered over two positions; as the site occupancy factors refined to almost 50:50, they were set to exactly 0.5. For the disorder components, the C—O distance was restrained to 1.25 (1) Å, the N—C$_{carbonyl}$ distance to 1.35 (1) Å and the N—C$_{methyl}$ distance to 1.45 (1) Å. Each component was restrained to be approximately planar. The displacement ellipsoids of the disordered atoms were restrained to approximately isotropic

References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Bruker (2004). *SMART* (Version 6.36A) and *SAINT* (Version 6.36A). Bruker AXS Inc., Madison, Wisconsin, USA.
Rani, B. S. U. & Darbarwar, M. (1987). *J. Indian Chem. Soc.* **64**, 38-41.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Zhang, S.-L., Huang, Z.-S., An, L.-K., Bu, X.-Z., Ma, L., Li, Y.-M., Chan, A. S. C. & Gu, L.-Q. (2004). *Org. Lett.* **6**, 4853–4855.