Refinement

Refinement on F^2
$R(F) = 0.055$
$wR(F^2) = 0.139$
$S = 0.891$
870 reflections
66 parameters
$w = 1/[\sigma^2(F_o^2) + (0.048P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.15$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.010 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (2)*

O1—C4	1.207 (3)	C4—C4'	1.483 (4)
C1—C4''	1.490 (4)	C4'—C4''	1.524 (3)
C1—C2	1.493 (4)	C4'—C4''^{i}	1.545 (3)
C2—C3	1.508 (4)	C4''—C4'^{i}	1.545 (3)
C3—C4	1.467 (4)		
C4''—C1—C2	112.3 (3)	C4—C4'—C4''	119.0 (2)
C1—C2—C3	109.9 (3)	C4—C4'—C4''^{i}	113.0 (2)
C4—C3—C2	112.3 (2)	C4''—C4'—C4''^{i}	90.22 (19)
O1—C4—C3	121.0 (3)	C1—C4''—C4'	116.6 (3)
O1—C4—C4'	119.8 (2)	C1—C4''—C4'^{i}	117.5 (2)
C3—C4—C4'	119.2 (2)	C4'—C4''—C4'^{i}	89.78 (19)

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

Variable scan rate, a θ–2θ scan mode with a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$ to a maximum 2θ value of 50°. H-atom positions were calculated using idealized geometry and constrained to this geometry.

For both compounds, data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1038). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1966–1968

6-Hydroxy-5,7-dimethoxy-4-methylcoumarin

AMARJIT SINGH,[a] RAJESH KUMAR,[a] VIRINDER S. PARMAR[a] AND WILLIAM ERRINGTON[b]

[a]*Department of Chemistry, University of Delhi, Delhi 110 007, India, and* [b]*Department of Chemistry, University of Warwick, Coventry CV4 7AL, England. E-mail: w.errington@warwick.ac.uk*

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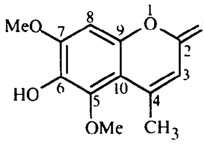
Abstract

The synthesis and structure of the title compound, $C_{12}H_{12}O_5$, are described. The molecule is approximately flat with the exception of the 5-methoxy group which is twisted at 70.1 (3)° with respect to the aromatic ring. The molecules pack together with intermolecular hydrogen bonding between the O4 and O2($x, y, z - 1$) atoms.

Comment

Coumarins constitute an important group of natural products and many of their analogues are found to be biologically active (Murray, Medez & Brown, 1982). 4-Methylcoumarins have been found to possess a wide range of biological activities *viz.* choleretic, analgesic, antispermatogenic and diuretic properties (Deana, 1983; Yang *et al.*, 1981). We have found that 18 4-methylcoumarins bearing different functionalities inhibit effectively the rat liver microsome mediated aflatoxin B_1-DNA binding *in vitro* (Raj *et al.*, 1996). Encouraged by these findings, we have synthesized a series of novel 4-methylcoumarins for structure–activity studies. This paper reports the synthesis and structure of a new coumarin in this series, namely, 6-hydroxy-5,7-dimethoxy-4-methylcoumarin, (I).



(I)

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The molecular structure of (I) is illustrated in Fig. 1. The bond lengths and angles are unremarkable and the C3—C4 distance of 1.355 (4) Å is clearly indicative of double bonding. The best plane through the aromatic ring shows an r.m.s. deviation of 0.016 Å; in contrast, the O1—C2—C3—C4—C10—C9 ring shows a much greater deviation from planarity, with an r.m.s. deviation of 0.028 Å. The angle between these two planes is 4.1 (1)°. The methoxy groups are not coplanar with the aromatic ring; the methoxy group attached to C7 deviates only slightly from planarity with a C13—O5—C7—C6 torsion angle of 172.3 (2)°, whilst the substituent at C5 is considerably twisted with respect to the plane, as indicated by the C12—O3—C5—C6 torsion angle of 70.1 (3)°.

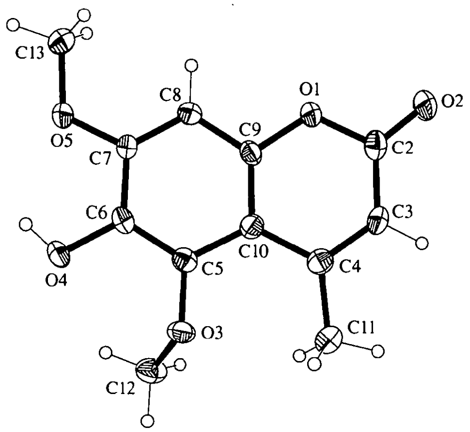

Fig. 1. View of the title molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

The molecules pack together in layers; there are short intermolecular contacts between the O4 and O5 atoms (at about 2.75 and 2.88 Å, respectively), and the O2 atom in an adjacent molecule. The O4· · ·O2(x, y, $z-1$) interaction involves hydrogen bonding with a calculated O—H· · ·O angle of about 158° and an O· · ·O separation of 2.752 (4) Å (*cf.* the sum of the van der Waals radii is 3.04 Å).

Experimental

A mixture of ethyl acetoacetate (8.91 ml, 0.07 mol), 4-hydroxy-2,6-dimethoxyphenol (11.9 g, 0.07 mol) and $POCl_3$ (6.5 ml, 0.07 mol) was refluxed in benzene (100 ml) for 10 h. The solvent was removed and the residue poured over crushed ice whereupon 6-hydroxy-5,7-dimethoxy-4-methylcoumarin, (I), precipitated out; it was recrystallized from ethanol as green needles (m.p. 476 K). IR (nujol) ν_{max}: 3300, 3000, 1700, 1620, 1560, 1510, 1440, 1380, 1360, 1320, 1260, 1180, 1150, 1100, 1080, 960, 910, 840 and 810 cm^{-1}. UV (MeOH) λ_{max}: 302 and 331 nm. ^1H NMR (250 MHz, DMSO-d_6): δ 2.52 (*d*, J = 1.24 Hz, 3H, C-4/CH_3), 3.83 (*s*, 3H, C-7/OCH_3), 3.90 (*s*, 3H, C-5/OCH_3), 6.07 (*q*, J = 1.24 Hz, 1H, H-3), 6.83 (*s*, 1H, H-8) and 8.92 (hump, 1H, C-6/OH). ^{13}C NMR (62.9 MHz, DMSO-d_6): δ 22.13 (C-4/CH_3), 56.20 (C-7/OCH_3), 60.33 (C-5/OCH_3), 95.79 (C-8), 107.30 (C-10), 112.17 (C-3), 136.41 (C-4), 144.92 (C-6), 147.47 (C-9), 152.06 (C-7), 153.44 (C-5) and 159.89 (C-2). EIMS m/z (relative intensity): 236 ([M^+], 100), 221 (10), 208 (25), 193 (35) and 165 (10).

Crystal data

$C_{12}H_{12}O_5$
$M_r = 236.22$
Triclinic
$P\bar{1}$
$a = 7.2909\,(8)$ Å
$b = 8.8019\,(10)$ Å
$c = 9.5696\,(11)$ Å
$\alpha = 66.754\,(2)°$
$\beta = 73.835\,(2)°$
$\gamma = 77.082\,(2)°$
$V = 537.44\,(10)$ Å^3
$Z = 2$
$D_x = 1.460$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 1458 reflections
$\theta = 2.37–25.00°$
$\mu = 0.115$ mm^{-1}
$T = 180\,(2)$ K
Needle
0.23 × 0.16 × 0.08 mm
Green

Data collection

Siemens SMART CCD area diffractometer
ω scans
Absorption correction: none
2742 measured reflections
1822 independent reflections

1425 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 24.99°$
$h = -8 \rightarrow 6$
$k = -10 \rightarrow 10$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.138$
$S = 1.150$
1822 reflections
158 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0353P)^2 + 0.6439P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C2	1.368 (3)	O4—C6	1.362 (3)
O1—C9	1.383 (3)	O5—C7	1.362 (3)
O2—C2	1.222 (3)	O5—C13	1.428 (3)
O3—C5	1.377 (3)	C3—C4	1.355 (4)
O3—C12	1.446 (3)		
C2—O1—C9	121.3 (2)	C7—O5—C13	117.5 (2)
C5—O3—C12	114.7 (2)	O2—C2—O1	115.8 (3)
C9—O1—C2—O2	−175.9 (3)	C12—O3—C5—C6	70.1 (3)
C9—O1—C2—C3	6.7 (4)	C13—O5—C7—C6	172.3 (2)

The temperature of the crystal was controlled using an Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). Data were collected over a hemisphere of reciprocal space, by a combination of three sets of exposures. Each set had a different φ angle for the crystal and each exposure of

10 s covered 0.3° in ω. The crystal to detector distance was 5.01 cm. Coverage of the unique set was over 91% complete to at least 25° in θ. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analysing the duplicate reflections. H atoms were added at calculated positions and refined using a riding model. The hydroxyl H4 atom could not be located in a difference Fourier synthesis but it was added in the plane of the aromatic ring so as to maximize hydrogen bonding to the O5 atom. It is therefore not possible to comment on the significance of any O5···H4 interaction. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached.

Data collection: *SMART* (Siemens, 1994*a*). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL/PC* (Siemens, 1994*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury Laboratory (Fletcher, McMeeking & Parkin, 1996) for access to the Cambridge Structural Database (Allen & Kennard, 1993). AS and RK thank the Council for Scientific and Industrial Research (CSIR, New Delhi, India) for the award of research fellowships.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1185). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1968–1971

N^1,N^2-Diphenylacetamidine

PAUL R. PHILLIPS,[a] JAMES BARKER,[b] WILLIAM ERRINGTON[a] AND MALCOLM G. H. WALLBRIDGE[a]

[a]*Department of Chemistry, University of Warwick, Coventry CV4 7AL, England, and* [b]*Associated Octel Co. Ltd, Ellesmere Port, South Wirral L65 4HF, England. E-mail: w.errington@warwick.ac.uk*

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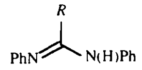
Abstract

The structure of the title compound, $C_{14}H_{14}N_2$, consists of amidine molecules hydrogen-bonded to form an alternating chain-like arrangement. Each molecule is bonded to two other molecules by N—H···N bonds. In each amidine N—C—N fragment, the C—N bond distances are different [1.281 (3) and 1.364 (3) Å], indicating some C═N imine character in one of the bonds.

Comment

The chemistry of amidines [R_2N—C(R)═NR] (R = H, alkyl, aryl) is becoming of increasing interest. This is because of the relevance of such species in the pharmaceutical and biological areas (Robert & Gagnon, 1994); for example, they are known to act as anti-pneumonia drugs in HIV therapy (Lowe, Sansom, Schwalbe & Stevens, 1989). In addition, amidines are versatile ligands and show a varied coordination chemistry towards both main group and transition metal elements (Barker & Kilner, 1994; Barker, Blacker *et al.*, 1996). As ligands they can bond either in the neutral form or, more usually, as the amidinate ion [RN—C(R)—NR]$^-$. Further structural information on amidine compounds is therefore desirable in order to understand better the relationship between their structure and reactivity. The N,N'-diphenyl-substituted amidines [H(Ph)NC(R)NPh] are of particular interest since they are often used as ligand species because of their availability and ease of handling, and their complexes involving the Group 13 elements have been shown to act as molecular precursors to useful electronic materials, such as gallium nitride, GaN (Barker, Blacker *et al.*, 1996). The structures of N,N'-diphenylformamidine (R = H), (I) (Anulewicz, Krygowski & Pniewska, 1987), and N,N'-diphenylbenzamidine (R = Ph), (II) (Alcock, Barker & Kilner, 1988), have already been



(I) R = H
(II) R = Ph
(III) R = Me

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