C(17)	0.0951 (2)	0.2629 (4)	−0.1066 (2)	0.0441 (15)
C(18)	0.0076 (3)	0.3419 (5)	−0.0336 (3)	0.0514 (18)
C(19)	0.0253 (3)	0.3431 (4)	0.0926 (3)	0.0490 (17)
C(20)	0.1364 (2)	0.2839 (4)	0.1491 (2)	0.0412 (15)
C(21)	0.1965 (3)	0.4622 (4)	0.3742 (2)	0.0445 (16)
C(22)	0.1322 (3)	0.5198 (5)	0.4718 (3)	0.0480 (18)
C(23)	0.1480 (3)	0.6812 (5)	0.5157 (3)	0.0548 (19)
C(24)	0.2276 (4)	0.7864 (5)	0.4611 (3)	0.0621 (21)
C(25)	0.2940 (4)	0.7311 (5)	0.3644 (3)	0.0693 (22)
C(26)	0.2790 (4)	0.5694 (5)	0.3221 (3)	0.0600 (21)

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

P—C(1)	1.815 (3)	P—C(20)	1.819 (3)
P—C(21)	1.835 (3)	C(1)—C(10)	1.391 (4)
C(10)—C(11)	1.479 (4)	C(11)—C(20)	1.391 (4)
H(8)· · ·H(13)	2.33 (5)		
P—C(1)—C(2)	125.7 (2)	P—C(1)—C(10)	112.5 (1)
P—C(20)—C(11)	111.6 (2)	P—C(20)—C(19)	125.9 (2)
P—C(21)—C(22)	119.8 (2)	P—C(21)—C(26)	121.7 (3)
C(1)—P—C(20)	89.4 (1)	C(1)—P—C(21)	100.9 (1)
C(20)—P—C(21)	103.2 (1)	C(2)—C(1)—C(10)	121.8 (3)
C(1)—C(10)—C(9)	117.9 (2)	C(1)—C(10)—C(11)	112.2 (2)
C(9)—C(10)—C(11)	129.6 (3)	C(10)—C(11)—C(12)	129.1 (3)
C(10)—C(11)—C(20)	112.6 (2)	C(12)—C(11)—C(20)	118.1 (2)

Table 3. *Dihedral angles (°) between least-squares planes*

Plane 1: P, C(1), C(10), C(11), C(20). Plane 2 C(1)-C(4), C(9), C(10). Plane 3: C(4)-C(9). Plane 4: C(11), C(12), C(17)-C(20). Plane 5: C(12)-C(17). Plane 6: C(21)-C(26). Napl 1: C(1)-C(10). Napl 2: C(11)-C(20).

Plane 1—Plane 2	6.67 (9)	Plane 1—Plane 4	12.03 (9)
Plane 1—Plane 6	92.9 (2)	Plane 2—Plane 3	12.2 (2)
Plane 2—Plane 4	18.7 (2)	Plane 3—Plane 5	38.2 (2)
Plane 4—Plane 5	9.6 (1)	Napl 1—Napl 2	28.7 (1)

The positional parameters for all non-H atoms were determined by direct methods (Sheldrick, 1985). The refinements were carried out by full-matrix least-squares techniques (Imoto, 1990). All H atoms were located in a difference Fourier map. The $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included in the calculation for the P atom (Cromer & Ibers, 1974). The refined structure showed *P* helicity. On the other hand, the enantiomeric structure gave *R* and *wR* values of 0.0494 and 0.0601. Thus, we decided that the title compound has the absolute configuration *P*. All calculations were carried out on an NEC ACOS 930S computer at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71696 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1077]

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5,6-Dihydroxy-7-methoxyflavone

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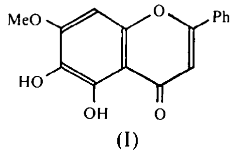
Abstract

The 5-hydroxy group of the title compound, 5,6-dihydroxy-7-methoxy-2-phenyl-4*H*-1-benzopyran-4-one, $C_{16}H_{12}O_5$, forms a cyclic intramolecular hydrogen bond O(3)—H···O(2), H···O = 1.71 (3) Å, with the carbonyl group. The heterocyclic ring is not coplanar with the phenyl ring. The C(7) methoxy group is in the plane of the γ-benzopyrone ring with the torsion angle C(11)—O(4)—C(7)—C(8) = 2.9 (3)°.

Comment

The dihedral angle of 12.2 (2)° between the phenyl ring and the γ-benzopyrone portion of the molecule (I) is significantly different from those of two related structures, 5-hydroxy-7-methoxyflavone (Shoja, 1989) and 5-hydroxyflavone (Shoja, 1990), with dihedral angles of 24.8 (2) and 5.7 (7)°, respectively. Given the wide range of dihedral angles and the fact that all three of these molecules contain hydrogen bonding, it is unlikely that any planarity is solely a



(I)

result of the 5-hydroxy intramolecular hydrogen bond. Perhaps the planarity of these molecules is a result of the crystal packing rather than stabilization of the negative charge on the carbonyl O atom due to hydrogen bonding as claimed by Rossi, Rickles & Halpin (1986).

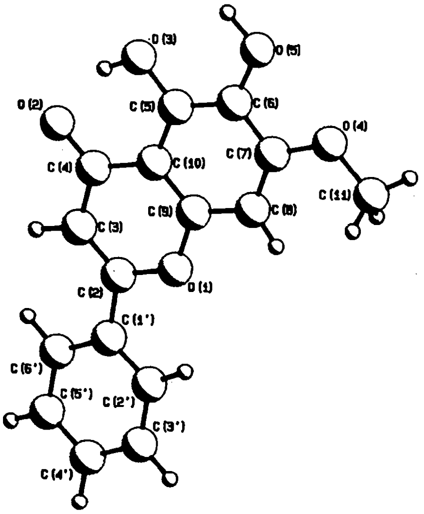


Fig. 1. Numbering of atoms and conformation of the molecule.

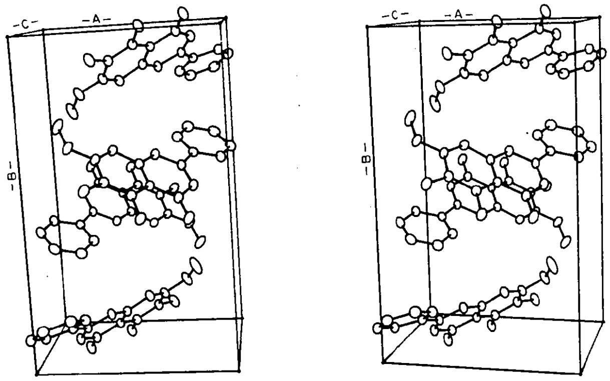


Fig. 2. Stereoview of the unit cell.

Experimental

Crystal data

$C_{16}H_{12}O_5$
M_r = 284.27
Monoclinic
$P2_1/c$
a = 9.784 (1) Å
b = 16.112 (2) Å
c = 8.397 (1) Å
β = 91.32 (3)°
V = 1323.3 (4) Å^3
Z = 4
D_x = 1.43 Mg m^{-3}
D_m = 1.3 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 16–28°
μ = 0.92 mm^{-1}
T = 293 K
Needle
0.30 × 0.20 × 0.20 mm
Clear
Crystal source: Indofine Chemical Company; grown from MeOH

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: none
2200 measured reflections
2108 independent reflections
1292 observed reflections $[|F_o| > 3\sigma(|F_o|)]$

$R_{\rm int}$ = 0.021
$\theta_{\max}$ = 60°
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 9$
3 standard reflections monitored every 200 reflections intensity variation: 0.1%

Refinement

Refinement on F
R = 0.036
wR = 0.046
S = 1.364
1292 reflections
239 parameters
All H-atom parameters refined
$w = 4F^2/[\sigma^2(I) + (0.04F^2)^2]$
$(\Delta/\sigma)_{\max}$ = 0.05

$\Delta\rho_{\max}$ = 0.24 e Å^{-3}
$\Delta\rho_{\min}$ = −0.31 e Å^{-3}
Extinction correction: Gaussian
Extinction coefficient: 7.2 × 10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{\rm eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$B_{\rm eq}$
O(1)	0.6440 (2)	0.13107 (9)	0.6789 (2)	3.86 (4)
O(2)	0.8117 (2)	−0.0285 (1)	0.3609 (2)	5.16 (4)
O(3)	0.6048 (2)	−0.0048 (1)	0.1713 (2)	4.70 (4)
O(4)	0.2730 (2)	0.1867 (1)	0.3173 (2)	6.01 (5)
O(5)	0.3645 (2)	0.0827 (1)	0.1117 (2)	5.28 (4)
C(1′)	0.8187 (2)	0.1179 (1)	0.8716 (3)	3.46 (5)
C(2)	0.7675 (2)	0.0939 (1)	0.7125 (3)	3.54 (5)
C(2′)	0.7364 (3)	0.1604 (2)	0.9760 (3)	4.54 (6)
C(3′)	0.7844 (3)	0.1813 (2)	1.1277 (4)	5.03 (7)
C(3)	0.8256 (2)	0.0420 (2)	0.6084 (3)	4.17 (6)
C(4)	0.7613 (2)	0.0215 (2)	0.4587 (3)	3.85 (6)
C(4′)	0.9162 (3)	0.1595 (2)	1.1752 (4)	5.06 (7)
C(5)	0.5588 (2)	0.0500 (1)	0.2810 (3)	3.62 (5)
C(5′)	0.9982 (3)	0.1177 (2)	1.0725 (3)	4.82 (6)
C(6)	0.4392 (2)	0.0922 (2)	0.2498 (3)	3.91 (6)
C(6′)	0.9519 (2)	0.0973 (2)	0.9207 (3)	4.15 (6)
C(7)	0.3907 (2)	0.1475 (2)	0.3627 (3)	4.20 (6)
C(8)	0.4589 (2)	0.1605 (1)	0.5064 (3)	4.08 (6)
C(9)	0.5790 (2)	0.1168 (1)	0.5337 (3)	3.52 (5)
C(10)	0.6323 (2)	0.0621 (1)	0.4250 (3)	3.31 (5)
C(11)	0.2135 (3)	0.2422 (2)	0.4295 (4)	8.54 (8)

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

O(1)—C(2)	1.372 (3)	C(3′)—C(4′)	1.385 (4)
O(1)—C(9)	1.381 (3)	C(3)—C(4)	1.432 (4)
O(2)—C(4)	1.258 (3)	C(4)—C(10)	1.444 (3)
O(3)—C(5)	1.360 (3)	C(4′)—C(5′)	1.368 (4)
O(4)—C(7)	1.361 (3)	C(5′)—C(6′)	1.383 (4)
O(4)—C(11)	1.431 (4)	C(5)—C(6)	1.373 (3)
O(5)—C(6)	1.365 (3)	C(5)—C(10)	1.406 (3)
C(1′)—C(2)	1.468 (3)	C(6)—C(7)	1.392 (4)
C(1′)—C(2′)	1.385 (4)	C(7)—C(8)	1.381 (4)
C(1′)—C(6′)	1.397 (3)	C(8)—C(9)	1.384 (3)
C(2)—C(3)	1.345 (4)	C(9)—C(10)	1.380 (3)
C(2′)—C(3′)	1.390 (4)		
C(2)—O(1)—C(9)	119.7 (2)	O(3)—C(5)—C(10)	120.1 (2)
C(7)—O(4)—C(11)	117.4 (2)	C(6)—C(5)—C(10)	120.8 (2)
C(2)—C(1′)—C(2′)	121.0 (2)	O(5)—C(6)—C(5)	122.9 (2)
C(2)—C(1′)—C(6′)	120.2 (2)	O(5)—C(6)—C(7)	117.8 (2)
C(2′)—C(1′)—C(6′)	118.9 (2)	C(5)—C(6)—C(7)	119.3 (2)

O(1)—C(2)—C(1′)	110.7 (2)	C(1′)—C(6′)—C(5′)	119.9 (2)
O(1)—C(2)—C(3)	121.4 (2)	O(4)—C(7)—C(6)	114.0 (2)
C(1′)—C(2)—C(3)	127.9 (2)	O(4)—C(7)—C(8)	124.2 (2)
C(1′)—C(2′)—C(3′)	120.7 (2)	C(6)—C(7)—C(8)	121.8 (2)
C(2′)—C(3′)—C(4′)	119.7 (3)	C(7)—C(8)—C(9)	117.3 (2)
C(2)—C(3)—C(4)	122.0 (2)	O(1)—C(9)—C(8)	115.7 (2)
O(2)—C(4)—C(3)	123.4 (2)	O(1)—C(9)—C(10)	121.1 (2)
O(2)—C(4)—C(10)	121.1 (2)	C(8)—C(9)—C(10)	123.2 (2)
C(3)—C(4)—C(10)	115.6 (2)	C(4)—C(10)—C(5)	122.2 (2)
C(3′)—C(4′)—C(5′)	119.9 (3)	C(4)—C(10)—C(9)	120.2 (2)
C(4′)—C(5′)—C(6′)	120.9 (2)	C(5)—C(10)—C(9)	117.6 (2)
O(3)—C(5)—C(6)	119.1 (2)		

Lorentz and polarization corrections were applied. The structure was solved by direct methods (*MULTAN*11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). The H atoms were located by difference Fourier synthesis. Anisotropic full-matrix least-squares refinement was performed for non-H atoms, isotropic for H atoms, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. Calculations were performed using *SDP* (Frenz, 1984).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and least-squares-planes data including dihedral angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71699 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1070]

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3-Bromo-6-methylamino-2′-methoxybenzophenone

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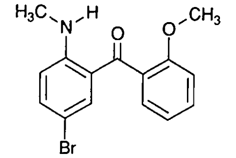
Abstract

The two molecules, *A* and *B*, of $C_{15}H_{14}BrNO_2$ in the asymmetric unit only differ significantly in the dihedral angle O(5)—C(5)—C(1′)—C(2′) [95.1 (3) and 107.9 (3)°, respectively]. The carbonyl O atom and the N atom are connected *via* an intramolecular hydrogen bond.

Comment

In an attempt to protonate 7-bromo-1-methyl-5-(*o*-methoxyphenyl)-1,3-dihydro-2*H*-1,4-benzodiazepin-2-one with dilute sulfuric acid we obtained the title compound (I), which was formed on hydrolysis. Thus the conclusion can be drawn that the protonation has to be carried out in the absence of water, for example, with dried hydrochloric acid (Berger, 1993).



(I)

The only significant difference between the two molecules in the asymmetric unit is the angle between the two nearly planar moieties [moiety (1) of molecule *A*: C(11), N(1), C(9*A*), C(9), C(8), C(7), Br(7), C(6), C(5*A*), C(5), O(5); moiety (2) of molecule *A*: C(1′), C(2′), C(3′), C(4′), C(5′), C(6′), O(21′), C(21′); moiety (1) of molecule *B*: C(11*B*), N(1*B*), C(9*AB*), C(9*B*), C(8*B*), C(7*B*), Br(7*B*), C(6*B*), C(5*AB*), C(5*B*), O(5*B*); moiety (2) of molecule *B*: C(1′*B*), C(2′*B*), C(3′*B*), C(4′*B*), C(5′*B*), C(6′*B*), O(21*B*), C(21*B*)]: 83.5 (molecule *A*), 77.3° (molecule *B*).

An intramolecular hydrogen bond is formed between the carbonyl O atom and the N atom: N(1)···O(5) 2.623 (6) Å, N(1)—H(1)···O(5) 133.3 (7)° and N(1*B*)···O(5*B*) 2.675 (6) Å, N(1*B*)—H(1*B*)···O(5*B*) 133.3 (7)°.

The title compound compares well with 2-aminobenzophenone (Antolini, Vezzosi, Battaglia & Corradi, 1985); however, a smaller torsion angle

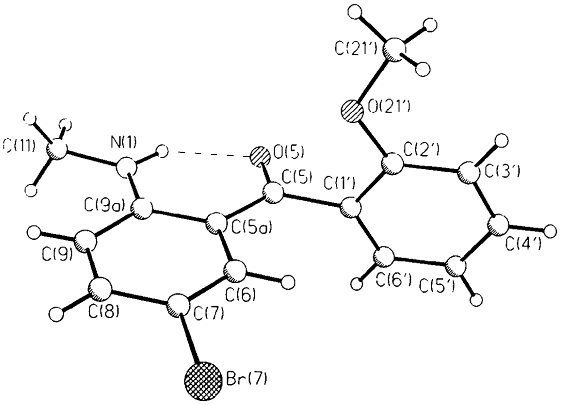


Fig. 1. Perspective view of molecule *A* with the atomic numbering.