

Fig. 3. Packing of the molecules in the unit cell projected down the *a* axis. Hydrogen bonds are shown as dotted lines.

3.192 (5) Å, C(12)—HC(12) = 0.91 (6) Å and C(12)—HC(12)···O(19) = 136 (4)° at the symmetry position  $-x, -y, -z$ . The hydrogen-bond geometry is shown in Fig. 3.

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## Structure of 2-(2,6-Dimethoxyphenyl)-4H-1-benzopyran-4-one (2',6'-Dimethoxyflavone)

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**Abstract.**  $C_{17}H_{14}O_4 \cdot C_2H_4O_2$ ,  $M_r = 342.34$ , triclinic,  $P\bar{1}$ ,  $a = 9.488$  (3),  $b = 12.957$  (4),  $c = 7.664$  (2) Å,  $\alpha = 102.9$  (1),  $\beta = 105.9$  (1),  $\gamma = 91.1$  (1)°,  $V = 880.0$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.35$ ,  $D_x = 1.29$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å,  $\mu = 0.9$  cm<sup>-1</sup>,  $F(000) = 360$ ,  $T = 293$  K,  $R = 0.046$  for 1327 reflections. The dimethoxyphenyl ring at C2 is rotated 70.7° with respect to the fused two-ring system because of steric interaction between the methoxy groups at C2' and C6' and the H atom at C(3). The effect of the hydrogen bond with a molecule of solvent is investigated by comparison with a similar structure reported earlier.

**Introduction.** Structures of bioflavonoids and their synthetic analogues have been investigated to try to explain their mechanism of action and their biological activity (Rossi, Rickles & Halpin, 1986; Cantrell, 1986). As part of our studies on hydroxy- and methoxyflavonoids (Wallet, Gaydou, Fadlane & Baldy, 1988) the structure of 2',6'-dimethoxyflavone (I) has been determined by single-crystal X-ray methods to provide conformational information.

Compound (I) was prepared by addition of excess thionyl chloride to 2,6-dimethoxybenzoic acid. The flask was mildly warmed until reaction ceased. After removal of unreacted thionyl chloride on a rotary evaporator, pyridine and *o*-hydroxyacetophenone were

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Table 1. Positional parameters and their e.s.d.'s

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:  $\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$ .

	x	y	z	$B_{eq}(\text{\AA}^2)$
O1	0.6831 (2)	0.0867 (2)	0.4878 (3)	4.10 (6)
C2	0.7040 (4)	0.1918 (3)	0.4904 (5)	3.61 (8)
C3	0.8319 (4)	0.2501 (3)	0.5815 (5)	4.09 (9)
C4	0.9582 (4)	0.2060 (3)	0.6833 (5)	4.02 (9)
C5	1.0458 (4)	0.0387 (3)	0.7768 (5)	4.5 (1)
C6	1.0191 (4)	-0.0669 (3)	0.7710 (6)	5.1 (1)
C7	0.8810 (5)	-0.1198 (3)	0.6724 (6)	5.4 (1)
C8	0.7702 (4)	-0.0678 (3)	0.5791 (6)	4.9 (1)
C9	0.7985 (4)	0.0385 (3)	0.5846 (5)	3.70 (9)
C10	0.9348 (4)	0.0939 (3)	0.6828 (5)	3.57 (8)
O4	1.0789 (3)	0.2584 (2)	0.7655 (4)	5.75 (7)
C1'	0.5713 (3)	0.2330 (3)	0.3850 (5)	3.64 (8)
C2'	0.4947 (4)	0.3056 (3)	0.4803 (5)	4.3 (1)
C3'	0.3739 (4)	0.3497 (3)	0.3810 (6)	5.1 (1)
C4'	0.3311 (4)	0.3189 (3)	0.1882 (6)	5.7 (1)
C5'	0.4019 (4)	0.2460 (3)	0.0893 (5)	5.1 (1)
C6'	0.5249 (4)	0.2037 (3)	0.1893 (5)	4.13 (9)
O3	0.5461 (3)	0.3274 (2)	0.6693 (4)	5.75 (7)
C12	0.4873 (6)	0.4096 (4)	0.7790 (7)	7.5 (1)
O2	0.6088 (3)	0.1335 (2)	0.1088 (4)	5.14 (7)
C11	0.5721 (6)	0.1031 (4)	-0.0920 (6)	6.8 (1)
C1S	1.0622 (5)	0.5334 (4)	0.7899 (7)	6.8 (1)
C2S	1.1234 (6)	0.6465 (4)	0.8554 (8)	8.5 (2)
O1S	1.1527 (3)	0.4641 (2)	0.8279 (5)	7.46 (9)
O2S	0.9321 (4)	0.5082 (3)	0.7143 (7)	12.1 (2)

added according to a procedure used in our laboratory (Gaydou & Bianchini, 1978).

Single crystals suitable for X-ray data collection were difficult to obtain. Recrystallization in ethanol, acetonitrile and chloroform gave well formed colourless needles but diffraction photographs showed a twinned structure unsuitable for crystal data measurements. We finally obtained suitable crystals by evaporation from an ethanol-acetic anhydride mixture (20% ethanol).

**Experimental.** Crystal (0.3 × 0.3 × 0.4 mm) mounted on a CAD-4 Enraf-Nonius diffractometer equipped with a graphite monochromator. Unit-cell parameters refined by least squares on  $2(\sin\theta)/\lambda$  values for 25 reflections ( $14 < \theta < 16^\circ$ ). The density was measured by flotation. Intensities were measured using  $\omega$ - $2\theta$  scan of  $0.91$ - $10.06^\circ \text{ min}^{-1}$  over a range of  $(0.8 + 0.35\tan\theta)^\circ$ ,  $\theta_{\text{max}} = 23^\circ$ . The intensities of three standard reflections measured every 3600 s throughout the data collection remained constant within 2%. 2390 reflections were measured, 223 symmetry-related reflections averaged (agreement factor on  $I = 0.014$ ), and finally 1327 with  $I > 3\sigma(I)$  kept for structure determination.  $-9 \leq h \leq 9$ ,  $-12 \leq k \leq 12$ ,  $0 \leq l \leq 7$ . All computations were performed on a PDP 11/44 using the SDP software package (Frenz, 1978). The structure was solved by direct methods with MULTAN (Main, Woolfson & Germain, 1977) and H atoms introduced in the calculation before last refinement cycles. Full-matrix least-squares refinement included isotropic thermal parameters for all non-H atoms and minimized the function  $\sum w(|F_o| - |F_c|)^2$  where  $w = 1$ .

Table 2. Bond distances (Å), bond angles (°) and torsion angles (°) with e.s.d.'s in parentheses

O1-C2	1.368 (5)	C1'-C2'	1.399 (5)
O1-C9	1.389 (5)	C1'-C6'	1.402 (5)
C2-C3	1.340 (4)	C2'-C3'	1.401 (5)
C2-C1'	1.478 (5)	C2'-O3	1.357 (5)
C3-C4	1.444 (5)	C3'-C4'	1.382 (6)
C4-C10	1.465 (5)	C4'-C5'	1.379 (6)
C4-O4	1.247 (4)	C5'-C6'	1.405 (5)
C5-C6	1.376 (5)	C6'-O2	1.373 (5)
C5-C10	1.409 (5)	O3-C12	1.425 (6)
C6-C7	1.397 (5)	O2-C11	1.441 (5)
C7-C8	1.379 (6)	C1S-C2S	1.489 (6)
C8-C9	1.387 (5)	C1S-O1S	1.280 (5)
C9-C10	1.396 (4)	C1S-O2S	1.215 (5)
C2-O1-C9	118.8 (2)	C2-C1'-C2'	119.9 (4)
O1-C2-C3	122.6 (4)	C2-C1'-C6'	120.6 (3)
O1-C2-C1'	112.9 (3)	C2'-C1'-C6'	119.5 (4)
C3-C2-C1'	124.5 (3)	C1'-C2'-C3'	120.3 (3)
C2-C3-C4	122.3 (3)	C1'-C2'-O3	115.1 (4)
C3-C4-C10	115.0 (3)	C3'-C2'-O3	124.6 (3)
C3-C4-O4	123.2 (3)	C2'-C3'-C4'	118.7 (4)
C10-C4-O4	121.8 (3)	C3'-C4'-C5'	122.7 (4)
C6-C5-C10	120.4 (4)	C4'-C5'-C6'	118.4 (3)
C5-C6-C7	120.0 (4)	C1'-C6'-C5'	120.4 (3)
C6-C7-C8	121.0 (4)	C1'-C6'-O2	115.0 (3)
C7-C8-C9	118.7 (3)	C5'-C6'-O2	124.6 (3)
O1-C9-C8	116.3 (3)	C2'-O3-C12	119.4 (3)
O1-C9-C10	121.9 (4)	C6'-O2-C11	118.3 (3)
C8-C9-C10	121.8 (3)	C2S-C1S-O1S	116.3 (4)
C4-C10-C5	122.4 (3)	C2S-C1S-O2S	122.1 (4)
C4-C10-C9	119.4 (4)	O1S-C1S-O2S	121.4 (5)
C5-C10-C9	118.2 (3)		
C9-O1-C2-C3	0.49 (49)	O1-C9-C10-C4	-0.53 (50)
C9-O1-C2-C1'	-178.86 (28)	O1-C9-C10-C5	-179.91 (35)
C2-O1-C9-C8	179.14 (32)	C8-C9-C10-C4	179.94 (30)
C2-O1-C9-C10	-0.42 (47)	C8-C9-C10-C5	0.56 (53)
O1-C2-C3-C4	0.42 (56)	C2-C1'-C2'-C3'	176.25 (34)
C1'-C2-C3-C4	179.69 (34)	C2-C1'-C2'-O3	-4.06 (49)
O1-C2-C1'-C2'	110.40 (37)	C6'-C1'-C2'-C3'	-0.91 (54)
O1-C2-C1'-C6'	-72.47 (42)	C6'-C1'-C2'-O3	178.77 (32)
C3-C2-C1'-C2'	-68.93 (50)	C2-C1'-C6'-C5'	-177.63 (34)
C3-C2-C1'-C6'	108.20 (43)	C2-C1'-C6'-O2	1.78 (49)
C2-C3-C4-C10	-1.30 (52)	C2'-C1'-C6'-C5'	-0.48 (54)
C2-C3-C4-O4	178.47 (36)	C2'-C1'-C6'-O2	178.92 (32)
C3-C4-C10-C5	-179.32 (34)	C1'-C2'-C3'-C4'	0.98 (57)
C3-C4-C10-C9	1.32 (48)	O3-C2'-C3'-C4'	-178.67 (36)
O4-C4-C10-C5	0.91 (55)	C1'-C2'-O3-C12	172.50 (36)
O4-C4-C10-C9	-178.45 (34)	C3'-C2'-O3-C12	-7.83 (56)
C10-C5-C6-C7	-0.43 (59)	C2'-C3'-C4'-C5'	0.37 (61)
C6-C5-C10-C9	-179.41 (35)	C3'-C4'-C5'-C6'	-1.73 (62)
C6-C5-C10-C4	-0.04 (63)	C4'-C5'-C6'-C1'	1.77 (57)
C5-C6-C7-C8	0.41 (64)	C4'-C5'-C6'-O2	-177.57 (36)
C6-C7-C8-C9	0.09 (63)	C1'-C6'-O2-C11	-177.29 (35)
C7-C8-C9-O1	179.86 (35)	C5'-C6'-O2-C11	2.08 (55)
C7-C8-C9-C10	-0.58 (58)		

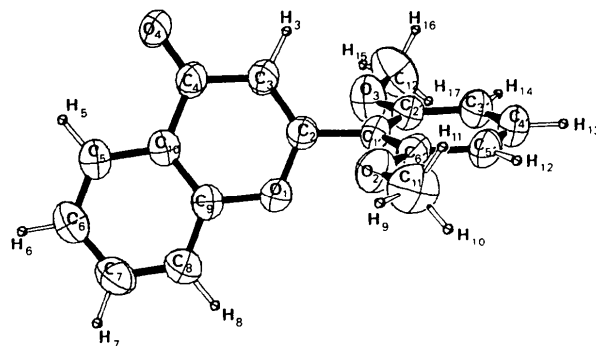


Fig. 1. View of the title compound showing atom-numbering scheme.

Final refinements converged with  $R = 0.046$  ( $wR = 0.062$ );  $S = 2.2$ ;  $(\Delta/\sigma)_{\max} = 0.05$ . A final difference Fourier synthesis did not reveal any peak of density  $> 0.4 \text{ e } \text{\AA}^{-3}$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). No corrections for absorption or secondary extinction.

**Discussion.** Final positional and thermal parameters are presented in Table 1, bond distances and angles in Table 2.\* These values are comparable with those found for similar compounds. A view of the molecule and the numbering scheme used in the text are given in Fig. 1. The three benzo, pyrone and phenyl rings are planar, the greatest deviation from the least-squares plane being  $0.004 \text{ \AA}$  for each ring. The angle between the phenyl ring and the pyrone ring is  $70.7^\circ$ . The conformation of the methoxy groups is, as expected, such that they are located in the plane of the exocyclic phenyl ring. Earlier  $^{13}\text{C}$  NMR investigations of this compound agree with this geometry (Iinuma, Matsuura & Kusuda, 1980).

The view of the unit cell (Fig. 2) shows that the molecules crystallize in a centrosymmetric space group, the hydroxyl of acetic acid forming a hydrogen bond with the carbonyl O atom of the flavone, the acid carbonyl O2S interacting with a C3 of the same flavone ( $3.309 \text{ \AA}$ ) and C4' of another flavone molecule

\* Lists of structure factors, anisotropic thermal parameters, least-squares planes, H-atom parameters, and distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51367 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

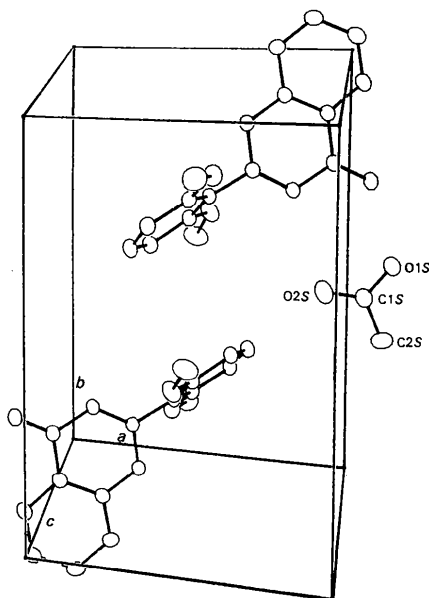
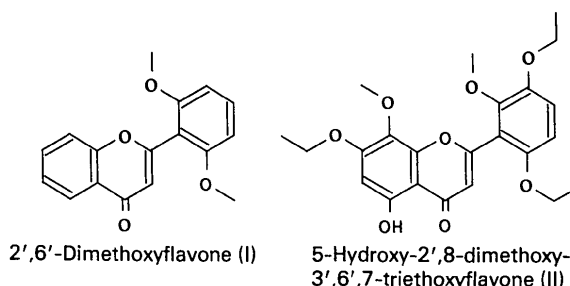


Fig. 2. View of the packing arrangement along  $c$ .

( $3.507 \text{ \AA}$ ). Distances and angles are comparable with those reported for acetic acid (Jones & Templeton, 1958).

To understand the effects of substituents on the torsion angle, we compared (I) with 5-hydroxy-2',8-dimethoxy-3',6',7-triethoxyflavone (II) (Kimura, Okuda, Taira, Shoji, Takemoto & Arichi, 1984),\* in which steric hindrance around the C2C1' bond is similar.



	(I)	(II)
Torsion angle ( $^\circ$ )	70.7	59.2
C=O ( $\text{\AA}$ )	1.247	1.242
O—H...O ( $\text{\AA}$ )	2.646	2.584

The two compounds have hydrogen bonds through the carbonyl: an intramolecular bond in (II), an intermolecular bond with the solvent in (I). The more planar configuration in compound (II) can be explained by a greater resonance in the molecule, that is, owing to the presence of the hydroxyl at C5, the stabilization of the negative charge on the carbonyl O atom is more effective (Rossi, Rickles & Halpin, 1986). We can find another explanation in the fact that the methoxy at C2' in (II) has an out-of-plane configuration; but in that case two factors which have opposite results have to be considered:

(1) The repulsive steric hindrance at the lone-pair electron orbitals of the methoxy O atom and cyclic O1 atom is weaker.

(2) The negative charge on the methoxy O atom is increased (Wysocki, Jardon, Mains, Eisenbraun & Boykin, 1987) and ought to contribute to the enlargement of the torsion angle. The first consideration must override the second.

In summary, the electronic effects of substituents, steric interactions and hydrogen bonding have competing effects and care must be taken to avoid over-interpretation of the results. The increasing number of X-ray structures of flavonoids (Parmar, Jain, Simonsen & Boll, 1987; Iinuma, Tanaka, Ito & Mizuno, 1987) should clarify these effects.

Specific spectral properties of 2'- and/or 6'-oxygenated flavones are reported to be related to the

\* In this reference, this compound is called 5-hydroxy-6',8-dimethoxy-3',6',7-triethoxyflavone but the drawing of the molecule does not agree with the stereoscopic view and torsion angle.

torsion angle (Tanaka, Inuma & Mizuno, 1986). More detailed work on this subject is in progress.

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## Structure and Absolute Configuration of (*E*)-(–)-2-Cyclododecenyl Camphanate

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**Abstract.** C<sub>22</sub>H<sub>34</sub>O<sub>4</sub>,  $M_r = 362.51$ , monoclinic,  $P2_1$ ,  $a = 7.371$  (1),  $b = 10.571$  (1),  $c = 13.538$  (2) Å,  $\beta = 90.36$  (1)°,  $V = 1054.84$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.141$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 0.577$  mm<sup>-1</sup>,  $F(000) = 396$ ,  $T = 296$  K,  $R = 0.057$  for 1550 unique reflections with  $I \geq \sigma(I)$ . The crystal conformation of the 12-membered ring in the title compound and its absolute configuration (1*R*) have been determined. The ring adopts a conformation with a necessarily approximate twofold axis in the crystal but it appears to be highly flexible.

**Introduction.** As part of an ongoing study of the relation of the configuration and conformation of medium-ring 2-cycloalkenyl *p*-bromobenzoates with their chiroptical properties, we prepared a sample of (*E*)-2-cyclododecanol. Earlier studies by Ito, Kasai,

Ziffer & Silverton (1987) had shown that although the sign of the CD curve predicted for five-, six- and seven-membered 2-cycloalkenyl *p*-substituted benzoates is independent of the conformation of the cycloalkene ring, information on the conformations of eight- and nine-membered rings is required to reconcile the observed and predicted signs of the CD curves. The predictions are based on a theoretically based exciton model developed by Harada, Iwabuchi, Yokota, Uda & Nakanishi (1981). As (*E*)-2-cyclododecanol was resolved *via* its camphanate ester, a crystal-structure determination of the ester was carried out to establish its conformation and configuration. To our knowledge there has been no previous determination of the conformation of a 2-cyclododecene by crystallography although theoretical calculations were reported for (*Z*)-cyclododecene by Anet & Rawdah (1979). References to previous uses of camphanate derivatives for determining absolute configuration are given in our paper on the structure of a cycloundecene (Ito, Ziffer & Silverton, 1988).

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