There exist two significantly different C—N bonds within the C(1)—N(1)—C(2) unit. While C(1)—N(1) [1·278 (9) Å] is a double bond, C(2)—N(1) [1·386 (9) Å] has a value halfway between a single and a double bond. In the *S*-methyl ester of guanidinodithioformic acid one can note the opposite effect. Here C(2)—N(1) [1·295 (5) Å] is a double bond whereas C(1)—N(1) [1·370 (5) Å] lies between a single and a double bond (Kiel, Gattow & Eul, 1984). The other C—N bonds C(1)—N(3) [1·334 (10)] and C(2)—N(2) [1·326 (9) Å] also have values between a single and a double bond. The C—N bond lengths involving C(1) are in good agreement with those found in acetamidine [C(1)—N(1) 1·298 (1), C(1)—N(3) 1·344 (1) Å] (Norrestam, Mertz & Crossland, 1983). The atoms of the phenyl ring C(7)—C(12) are coplanar within the experimental error. The least-squares plane defined by these atoms makes a dihedral angle of 23·3 (4)° with the plane defined by the atoms N(1), C(1), N(3).

The crystal structure is built up from isolated molecules. Surprisingly the molecule does not form an intermolecular hydrogen bridge. However, there are relatively short intramolecular S···H(2) (2·68 Å) and S—N(3) (3·26 Å) distances. The angle S—H(2)—N(3) has a value of 131°. In contrast to *N*-(pivaloyl)-pivalamidine a planar arrangement of the S—C(2)—N(1)—C(1)—N(3)—H(2) unit is not possible because of the greater van der Waals radius of S compared with O.

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Structure of 3-Methoxy-2-phenyl-4*H*-1-benzopyran-4-one (3-Methoxyflavone)

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Abstract. $C_{16}H_{12}O_3$, $M_r = 252·27$, monoclinic, $P2_1/c$, $a = 10·267$ (3), $b = 14·679$ (4), $c = 8·738$ (2) Å, $\beta = 111·9$ (1)°, $Z = 4$, $D_m = 1·3$, $D_x = 1·37$ g cm^{-3}, $V = 1222$ (1) Å^3, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·883$ cm^{-1}, $F(000) = 528$, $T = 293$ K, $R = 0·044$ for 1005 reflections. The torsion angle between the phenyl ring and the fused two-ring system is 37·2° due to the steric interaction between the methoxy C(3) and adjacent hydrogen atoms on the phenyl ring. A comparison is made with three other 3-substituted flavones reported earlier.

Introduction. Owing to the pharmacological interest of the flavonoids a certain number of crystal structures have been resolved. A recent review has been published by Cantrell (1986). The structure of 5-hydroxy-6′,8-dimethoxy-2′,5′,7-triethoxyflavone has been elucidated by X-ray methods (Kimura, Okuda, Taira, Shoji, Takemoto & Arichi, 1984) as has that of 5,3′-dihydroxy-6,7,8,2′,4′,5′-hexamethoxyflavone (Quijano, Calderon, Gomez, Escobar & Rios, 1985) but in the latter case no crystallographic data were available.

In order to collect conformational information about methoxyflavones and to find relationships between chemical structure, chromatographic behaviour and

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NMR spectroscopic properties we carried out some X-ray structure determinations. We now report the results for 3-methoxyflavone.

This compound was prepared by methylation of 3-hydroxyflavone according to a procedure previously described (Gaydou & Bianchini, 1978). 3-Hydroxyflavone was obtained from the reaction of 2-hydroxyacetophenone and benzaldehyde (Simpson, 1963).

Experimental. Crystal (0·4 × 0·4 × 0·2 mm) mounted on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator. Unit-cell parameters refined by least squares on $2(\sin\theta)/\lambda$ values of 25 reflections ($14 < \theta < 16°$). The density was measured by flotation. Intensities were measured using ω–2θ scan of 0·91–10·06° min^{-1} over a range of $(1{\cdot}0 + 0{\cdot}35\tan\theta)°$, $\theta_{\max} = 22°$. The intensities of three standard reflections measured every 5000 s throughout the data collection remained constant within 2%. 3196 reflections were measured, 1919 symmetry-related reflections averaged (agreement factor on $I = 0{\cdot}023$), and finally 1005 with $I > 3\sigma(I)$ kept for structure determination. $-10 \leq h \leq 10$, $0 \leq k \leq 15$, $0 \leq l \leq 9$. All computations were performed on a PDP 11/44 using the *SDP* software package (Frenz, 1978). The structure was solved by direct-methods *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 $w = 1$. Final refinements converged with $R = 0{\cdot}044$ ($wR = 0{\cdot}043$); $S = 1{\cdot}26$; $(\Delta/\sigma)_{\max} = 0{\cdot}04$. A final difference Fourier synthesis did not reveal any peak of density >0·25 e Å^{-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.* A view of the molecule and the numbering scheme used are given in Fig. 1. Bond distances and angles are within the expected range for aromatic compounds. The three benzo, pyrone and phenyl rings are planar, the greatest deviations from the least-squares planes being 0·005, 0·005 and 0·006 Å respectively. The angle between the phenyl and pyrone rings is 37·2°. The dihedral angle between the pyrone ring and the C3—O2—C11 plane is 62·6°.

The out-of-plane conformation of the methoxy group agrees with the fact that this group is flanked by two

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

	x	y	z	B_{eq}(Å^2)
O1	0·7790 (3)	0·4907 (2)	0·0981 (4)	3·18 (8)
C2	0·8340 (5)	0·5645 (3)	0·0471 (6)	2·9 (1)
C3	0·7668 (5)	0·6018 (3)	−0·1040 (6)	3·0 (1)
C4	0·6334 (5)	0·5675 (4)	−0·2192 (6)	3·6 (1)
C5	0·4661 (5)	0·4369 (4)	−0·2682 (7)	3·9 (1)
C6	0·4264 (5)	0·3562 (4)	−0·2130 (7)	4·2 (1)
C7	0·5023 (6)	0·3232 (4)	−0·0533 (7)	4·2 (1)
C8	0·6203 (5)	0·3699 (4)	0·0513 (6)	3·5 (1)
C9	0·6593 (5)	0·4493 (3)	−0·0092 (6)	3·0 (1)
C10	0·5863 (5)	0·4838 (3)	−0·1627 (6)	3·1 (1)
O3	0·5674 (4)	0·6059 (3)	−0·3487 (4)	4·8 (1)
O2	0·8216 (4)	0·6788 (2)	−0·1458 (4)	3·89 (9)
C11	0·8611 (6)	0·6687 (4)	−0·2882 (7)	5·2 (2)
C1′	0·9637 (5)	0·5951 (3)	0·1774 (6)	3·0 (1)
C2′	1·0757 (5)	0·6307 (4)	0·1396 (6)	3·7 (1)
C3′	1·1992 (6)	0·6568 (4)	0·2667 (7)	4·3 (1)
C4′	1·2124 (6)	0·6481 (4)	0·4319 (7)	4·9 (2)
C5′	1·0986 (6)	0·6146 (4)	0·4684 (7)	5·3 (2)
C6′	0·9754 (6)	0·5870 (4)	0·3419 (7)	4·3 (1)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

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

O1—C2	1·368 (7)	C7—C8	1·395 (10)
O1—C9	1·378 (8)	C8—C9	1·399 (9)
C2—C3	1·359 (9)	C9—C10	1·367 (9)
C2—C1′	1·462 (9)	O2—C11	1·452 (9)
C3—C4′	1·454 (10)	C1′—C2′	1·409 (9)
C3—O2	1·372 (8)	C1′—C6′	1·403 (10)
C4—C10	1·471 (10)	C2′—C3′	1·392 (10)
C4—O3	1·220 (8)	C3′—C4′	1·404 (11)
C5—C6	1·396 (11)	C4′—C5′	1·409 (11)
C5—C10	1·414 (10)	C5′—C6′	1·394 (10)
C6—C7	1·406 (11)		
C2—O1—C9	120·0 (6)	O1—C2—C3	120·9 (6)
O1—C2—C1′	111·0 (6)	C3—C2—C1′	128·1 (7)
C2—C3—C4	122·7 (7)	C2—C3—O2	118·8 (6)
C4—C3—O2	118·4 (6)	C3—C4—C10	113·5 (7)
C3—C4—O3	122·4 (7)	C10—C4—O3	124·0 (7)
C6—C5—C10	118·9 (7)	C5—C6—C7	120·6 (7)
C6—C7—C8	120·4 (7)	C7—C8—C9	117·6 (7)
O1—C9—C8	114·8 (6)	O1—C9—C10	121·8 (6)
C8—C9—C10	123·4 (7)	C4—C10—C5	120·2 (7)
C4—C10—C9	120·7 (7)	C5—C10—C9	119·1 (7)
C3—O2—C11	114·7 (6)	C2—C1′—C2′	121·2 (7)
C2—C1′—C6′	118·3 (7)	C2′—C1′—C6′	120·4 (7)
C1′—C2′—C3′	119·6 (7)	C2′—C3′—C4′	120·4 (8)
C3′—C4′—C5′	119·6 (8)	C4′—C5′—C6′	120·4 (8)
C1′—C6′—C5′	119·5 (8)		

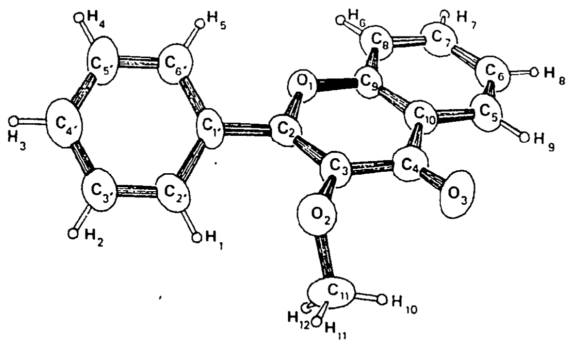

Fig. 1. View of the title compound showing atom-numbering scheme.

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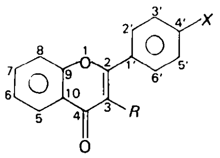
* Lists of structure factors, anisotropic thermal parameters and distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44494 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Comparative bond lengths and torsion angles in various* 3,4′-*substituted flavones*



Substituent			Bond lengths (Å)			Torsion angle
	R	*X*	C4=O	C2–C1′	C2–C3	C2–phenyl
(1)	OH	H	1·232 (3)	1·474 (4)	1·363 (4)	5·5°
(2)	OH	Br	1·232 (6)	1·462 (6)	1·351 (6)	18·8°
	OCH_3	H	1·220 (8)	1·462 (9)	1·359 (9)	37·2°
(3)	Br	H	1·228 (9)	1·492 (9)	1·356 (9)	47·1°

(1) Etter, Urbanczyk-Lipkowska, Baer & Barbara (1986).
(2) Hayashi, Kawai, Ohno, Iitaka & Akimoto (1974).
(3) Cantrell & Stalzer (1982).

ortho substituents. The ^{13}C NMR spectrum shows a chemical shift for methoxy at 60·02 p.p.m. (in deuteriochloroform). So it seems possible to correlate the conformation of the methoxy group in the crystalline state with the ^{13}C NMR spectroscopic properties in solution.

This type of conformation has already been suggested in aromatic systems by studies using ^{13}C chemical shifts and spin-lattice relaxation times (Makriyannis & Knittel, 1979; Makriyannis & Fesik, 1982).

Bulky groups at C3 induce a greater torsion angle in the case of 3-methoxyflavone (Cantrell & Stalzer, 1982) than in 3-hydroxyflavone (Hayashi, Kawai, Ohno, Iitaka & Akimoto, 1974). For 3-methoxyflavone the value is only 37·2°, owing to the possibility of the methoxy group rotating around the C3–O2 bond. Some comparisons are given in Table 3.

There is no relationship between torsion angle and bond lengths. Compounds which have a smaller torsion angle, and therefore should be more conjugated, should have shorter C2–C1′ or C2–C3 bonds, but this is not the case. Other factors than steric ones must be considered.

The view of the unit cell and packing (Fig. 2) shows that molecules are packed in such a way that the fused ring systems of pairs of molecules overlap in an antiparallel fashion suggesting possible π–π stabilizing interactions, carbonyl groups, methoxy groups and phenyl rings being centrosymmetric.

We thank Dr Pierrot of the Crystallographic Department for his help and advice.

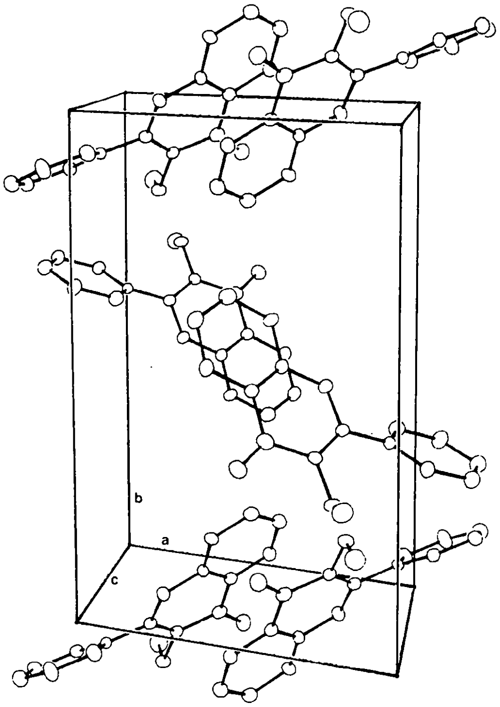


Fig. 2. View of the packing arrangement along **c**.

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