

Flavone-3'-sulfonamide¹Engin Kendi,^{a*} Süheyla Özbey,^a Oya Bozdağ^b and
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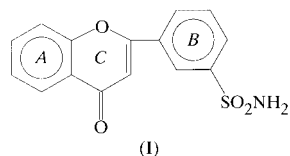
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In the title molecule, C₁₅H₁₁NO₄S, the phenyl and benzene rings are quite planar, with maximum deviations from planarity of 0.009 (2) and 0.004 (1) Å, respectively. The γ -pyrone ring deviates from planarity and makes a dihedral angle of 8.3 (3)° with the 2-phenyl substituent. The sulfonamide group is involved in N—H...O hydrogen bonding.

Comment

Besides the extensive biological activity of flavonoids, this class of compounds exhibits antidiabetic (Hii & Howell, 1985; Basnet *et al.*, 1993; Ragunathan & Sulochana, 1994) and aldose reductase inhibitory activity (Varma & Kinoshita, 1976; Okuda *et al.*, 1984; Aida *et al.*, 1990). Aryl sulfonamides are widely used as starting materials in the synthesis of anti-diabetic sulfonylureas (AFECT, 1995). The title compound, (I), is a flavonesulfonamide and was synthesized as a starting material for antidiabetic flavonesulfonylureas. The structure was elucidated by ¹H NMR, mass and IR spectroscopic techniques. The X-ray structure was determined in order to establish the conformation of the molecule.



All bond lengths and angles in (I) are normal. Rings A and B are quite planar: the maximum deviations are 0.009 (2) and 0.004 (1) Å from the ring planes A and B, respectively. The pyrone ring C is distorted ($\chi^2 = 210.2$). The angles between rings A and C and B and C are 1.8 (2) and 8.3 (3)°, respectively, showing that the rings A, B and C are coplanar.

In the generally preferred conformation of flavones, the dihedral angle between the phenyl and the γ -pyrone rings is expected to be small, as in the case of (I). This angle is 13.9 (4)° in 2-(2-ethoxycarbonyl-1,4-benzodioxan-7-yl)-4H-1-benzopyran-4-one (Özbey *et al.*, 1997). Another parameter of

interest in flavone structures is the bond length between the benzopyrone and phenyl rings. In flavones, the increase in dihedral angle has the effect of increasing the length of this bond to the expected value for an sp^2-sp^2 single bond. In compound (I), the corresponding C2—C11 bond length is 1.478 (3) Å. In 5-hydroxyflavone, the dihedral angle is 5.2 (9)° and the C2—C11 bond is 1.465 (4) Å (Shoja, 1990). In 2'-methyl-3'-nitroflavone, these values are 139.8 (2)° and 1.491 (8) Å, respectively (Kendi *et al.*, 1996). The widening of the O1—C9—C10 angle to 121.6 (2)° and the narrowing of the C3—C4—C10 angle to 115.2 (2)° in the γ -pyrone ring may be attributed to the ring strain caused by the neighbouring Csp^2-Csp^2 atoms.

Atoms S1 and O3 of the sulfonamide group lie close to the plane of ring B, with deviations of 0.032 (1) and 0.045 (1) Å from the plane, respectively. Atoms O4 and N1 are displaced from the least-squares plane of the atoms in ring B by 0.928 (2) and -1.474 (2) Å, respectively.

The sulfonamide group in (I) is involved in intermolecular as well as intramolecular hydrogen bonding. It has been proposed by Rossi *et al.* (1980) that the hydrogen bonds involving O2 would enhance the electron-withdrawing power of the pyrone ring on the phenyl ring, thus giving C2—C11 more double-bond character and forcing coplanarity between rings B and C. The crystal packing shows that the smaller the dihedral angle between the benzopyrone and phenyl rings, the stronger the stacking interactions that occur between adjacent molecules. Details of the hydrogen bonds and short contacts in (I) are given in Table 2.

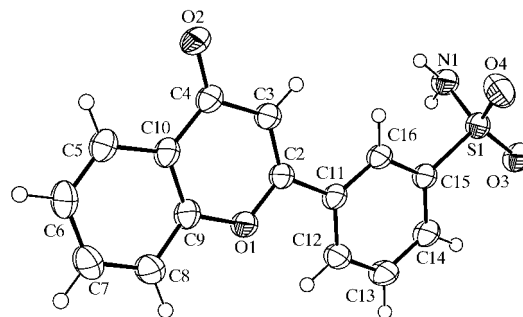


Figure 1

ORTEP II (Johnson, 1976) drawing of (I) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H-atoms are shown as small circles of arbitrary radii.

Experimental

Flavone (2.50 g, 0.0113 mol), obtained by the Baker–Venkataraman method, was added slowly with stirring to chlorosulfonic acid (25 ml, 0.376 mol), which had been cooled to 263 K in an ice–salt bath. The reaction mixture was stirred for 2 d at room temperature and was then poured into iced water. The crude sulfonylchloride (1.40 g, 4.37 mmol) was treated with aqueous ammonia (100 ml) and stirred for 3 h at 273 K, and flavone-3'-sulfonamide, (I), was obtained by removing the excess ammonia under reduced pressure. The crude product was crystallized from ethanol–dimethyl sulfoxide (10:1)

¹ Systematic name: 3-(4-oxo-4H-1-benzopyran-2-yl)benzenesulfonamide.

(yield: 1.10 g, 83.66%; m.p. 481–483 K). Spectroscopic analysis: ^1H NMR (DMSO- d_6 , 400 MHz, δ , p.p.m.): 7.10 (s, 1H, 3-H), 7.52 (ddd, 1H, 6-H), 7.76–7.85 (m, 3H, 7-H, 4'-H, 6'-H), 7.98 (d, 1H, 8-H), 8.05 (dd, 1H, 5'-H), 8.28 (d, 1H, 5-H), 8.48 (s, 1H, 2'-H); mass spectroscopy (70 eV), m/e : 301 (M^+), 302 ($M+1$), 303 ($M+2$), 221, 193, 121, 120, 101, 92 (%100), 64, 63; IR (cm^{-1}): 1614 (γ -pyrone $\text{C}=\text{O}$).

Crystal data

$\text{C}_{15}\text{H}_{11}\text{NO}_4\text{S}$ $Z = 2$
 $M_r = 301.32$ $D_x = 1.531 \text{ Mg m}^{-3}$
 Triclinic, $P\bar{1}$ Mo $K\alpha$ radiation
 $a = 8.6654$ (5) Å Cell parameters from 25 reflections
 $b = 8.7898$ (6) Å $\theta = 9.4\text{--}18.2^\circ$
 $c = 10.0105$ (6) Å $\mu = 0.263 \text{ mm}^{-1}$
 $\alpha = 98.183$ (7)° $T = 295 \text{ K}$
 $\beta = 112.991$ (6)° Prismatic, colourless
 $\gamma = 104.673$ (6)° $0.56 \times 0.40 \times 0.20 \text{ mm}$
 $V = 653.6$ (2) Å 3

Data collection

Enraf–Nonius CAD-4 diffractometer $R_{\text{int}} = 0.010$
 $\omega/2\theta$ scans $\theta_{\text{max}} = 26.3^\circ$
 Absorption correction: empirical $h = -10 \rightarrow 0$
 via ψ scans (North *et al.*, 1968) $k = -10 \rightarrow 10$
 $T_{\text{min}} = 0.869$, $T_{\text{max}} = 0.951$ $l = -11 \rightarrow 12$
 2834 measured reflections 3 standard reflections
 2649 independent reflections frequency: 120 min
 2057 reflections with $I > 2\sigma(I)$ intensity decay: 1.5%

Refinement

Refinement on F H atoms constrained
 $R = 0.037$ $w = 1/(\sigma F^2)$
 $wR = 0.044$ $(\Delta/\sigma)_{\text{max}} < 0.001$
 $S = 0.90$ $\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$
 2057 reflections $\Delta\rho_{\text{min}} = -0.09 \text{ e \AA}^{-3}$
 192 parameters

Table 1

Selected geometric parameters (Å, °).

S1—O3	1.431 (2)	O1—C9	1.373 (3)
S1—O4	1.423 (2)	O2—C4	1.247 (3)
S1—N1	1.613 (2)	C2—C3	1.346 (3)
S1—C15	1.776 (2)	C2—C11	1.478 (3)
O1—C2	1.348 (3)		
O3—S1—O4	120.1 (1)	C3—C4—C10	115.2 (2)
O3—S1—N1	107.3 (9)	O1—C9—C10	121.6 (2)
O3—S1—C15	107.2 (1)		
O3—S1—C15—C16	176.82 (15)	O1—C2—C11—C16	−173.58 (16)
O4—S1—C15—C14	−135.03 (16)	C13—C14—C15—S1	−179.03 (15)
N1—S1—C15—C14	110.72 (16)		

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *MolEN* and *PARST* (Nardelli,

Table 2

Hydrogen-bond and short-contact geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
C7—H7 \cdots O3 ⁱ	0.95	2.67	3.442 (3)	139
C6—H6 \cdots N1 ⁱ	0.95	2.78	3.526 (4)	137
C8—H8 \cdots O4 ⁱⁱ	0.95	2.61	3.417 (3)	144
C12—H12 \cdots O4 ⁱⁱ	0.95	2.71	3.643 (3)	168
C12—H12 \cdots O4 ⁱⁱⁱ	0.95	2.89	3.391 (2)	115
N1—H1N \cdots O2 ^{iv}	0.95	1.99	2.928 (3)	172
N1—H2N \cdots O2 ^v	0.94	2.05	2.976 (3)	169

Symmetry codes: (i) $x-1, 1+y, z$; (ii) $x, 1+y, z$; (iii) $1-x, 1-y, 1-z$; (iv) $1+x, y, z$; (v) $1-x, 1-y, 2-z$.

1995); program(s) used to refine structure: *MolEN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1229). Services for accessing these data are described at the back of the journal.

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