Studies on the Reactivity and Structure of Phenyl 7-Fluoro-4-chromone-3-sulfonate

Werner Löwe* and Susan Bischoff

Institut für Pharmazie, Freie Universität Berlin, Königin-Luise-Str. 2+4, D-14195 Berlin, Germany

Manuela Weber, Genivaldo Perpetuo, and Peter Luger

Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, D-14195 Berlin, Germany

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Dedicated to Professor Fritz Eiden, München, on the occasion of his seventieth birthday

The new, fluorinated benzoxathiinopyrazole **4** and the hitherto unknown fluorinated benzoxathiinodihydropyridine **5** can be produced by reacting the title compound **1** with cyanoacetic hydrazide (**3**) in the presence of sodium acetate. The structures of the compounds **4** and **5** were confirmed with the help of spectroscopic techniques, and their respective paths of formation have been discussed. The structure of the ester **1** was extensively studied by single crystal X-ray analysis, then compared with that of the unfluorinated phenylsulfonate **2**.

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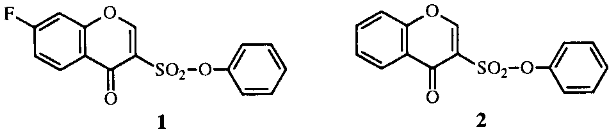
We recently reported on unusual ring transformations [1] in which two benzoxathiinopyridines, a dibenzopyrone derivative and a heterocyclic enaminone were produced by reacting the phenyl 7-fluoro-4-chromone-3-sulfonate (**1**) [2] with methyl 3-oxopentanoate in the presence of ammonium acetate. Primarily, we found that a) the C-2 atom of compound **1** can be highly electrophilic, and b) that it reacts in different ways with the enaminoester produced *in situ*. The clearly electrophilic nature of the C-2 atom of **1** can be attributed to the presence of the acyl-vinyl-sulfonyl structure. Furthermore, electrophilia may also be enhanced by fluorine substitution in the benzene ring.

Another notable finding that the ester **1** was orange in colour, as compared to the unfluorinated, colourless phenyl 4-chromone-3-sulfonate (**2**) [3] (Scheme 1).

Scheme 1

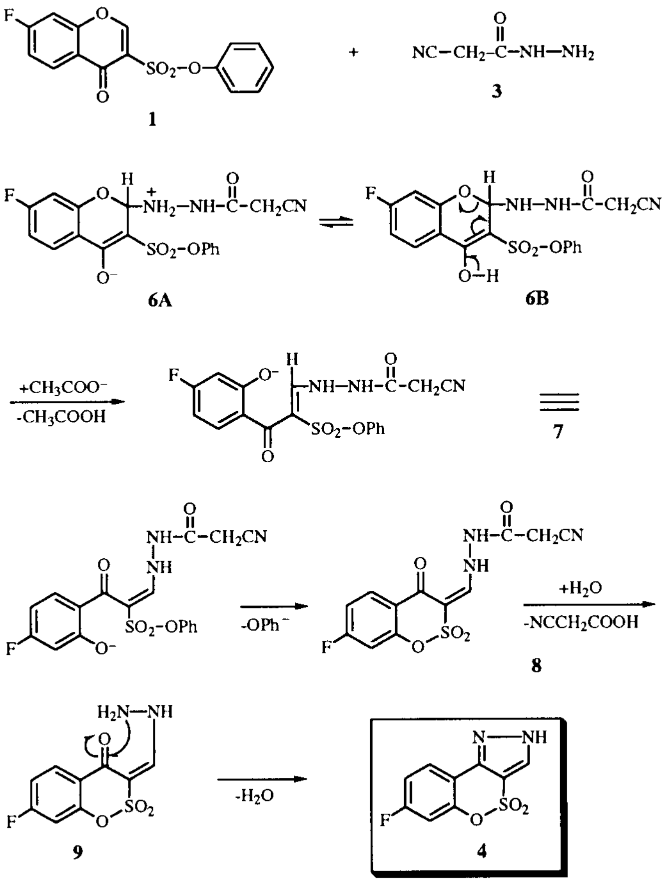


To further substantiate these findings, we performed additional studies on the reactivity of the C-2 atom of the phenyl 7-fluoro-4-chromone-3-sulfonate (**1**). Subsequently, the structures of the compounds **1** and **2** were compared utilizing crystallographic techniques.

First, compound **1** was reacted with cyanoacetic hydrazide (**3**) in the presence of sodium acetate. Cyanoacetic hydrazide thereby acts as an ambident nucleophile, that is, as both an *N*- and a *C*-nucleophile. Both benzoxathiinopyrazole **4** and benzoxathiinodihydropyridine **5** are produced in the course of the ring transformations. We seperated these ring transformation products by means of rotational chromatography.

In the ^{1}H-nmr studies of pyrazole **4**, the H-3 atom exhibited a singlet at 8.90 ppm, and the NH proton demonstrated a broad, with deuterium oxide exchangeable singlet at 14.47 ppm. In the ir-spectra, a stretching vibration of the NH proton was seen at 3268 cm^{-1}, and the

Scheme 2

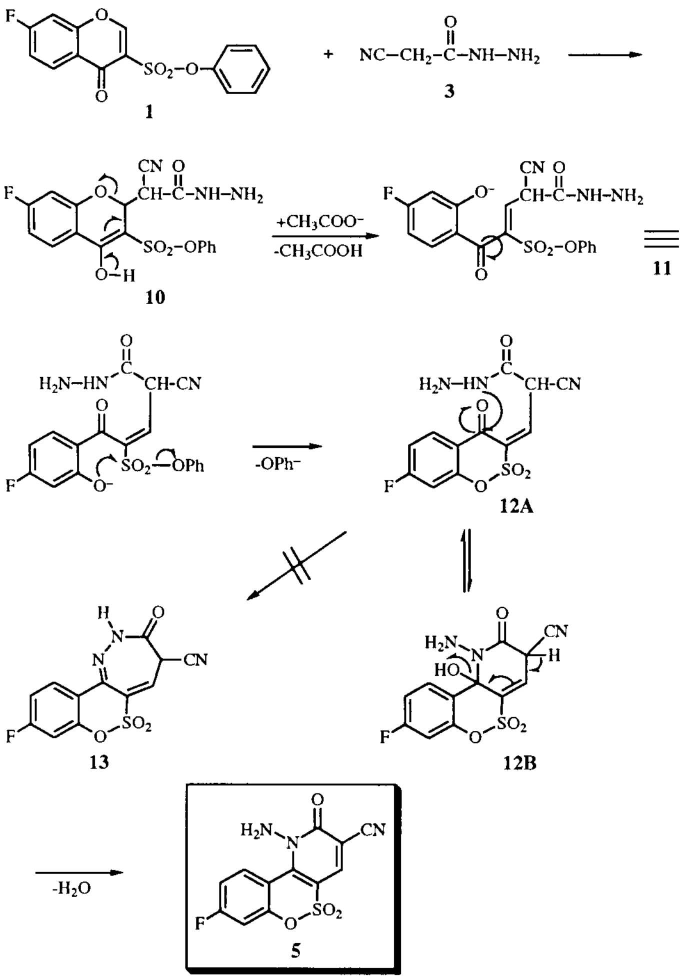


characteristic sultone bands appeared at 1370 and 1166 cm^{-1}.

In the ^{1}H-nmr-spectra of benzoxathiinodihydropyridine **5**, the amino group shows a singlet at 6.35 ppm, and H-4 appeared as a singlet at 8.83 ppm. Down-field shift of the H-10 signal occured after 9.05 ppm. In the ir-spectra, the amino protons appeared at 3429 and 3310 cm^{-1}, and an unusually sharp nitrile band was seen at 2235 cm^{-1}. Additionally, C=O stretching vibration was seen at 1673 cm^{-1}, sultone bands were detected at 1379 and 1192 cm^{-1}.

The mass spectrum of the compound **5** exhibited a mole peak at 307 (100%). In the first step, a fragment of the mass 15 is broken down. This is surprising, because one would normally assume that NH_2, as the M-16, is first broken down *via* α-fission, in view of the fact that α-bonds to heteroatoms normally are preferentially broken [4]. However, the high-resolution mass spectrum showed that NH fission occurs. This fragmentation does not occur in the primary amines, but does occur in the hydrazine series [5].

Scheme 3



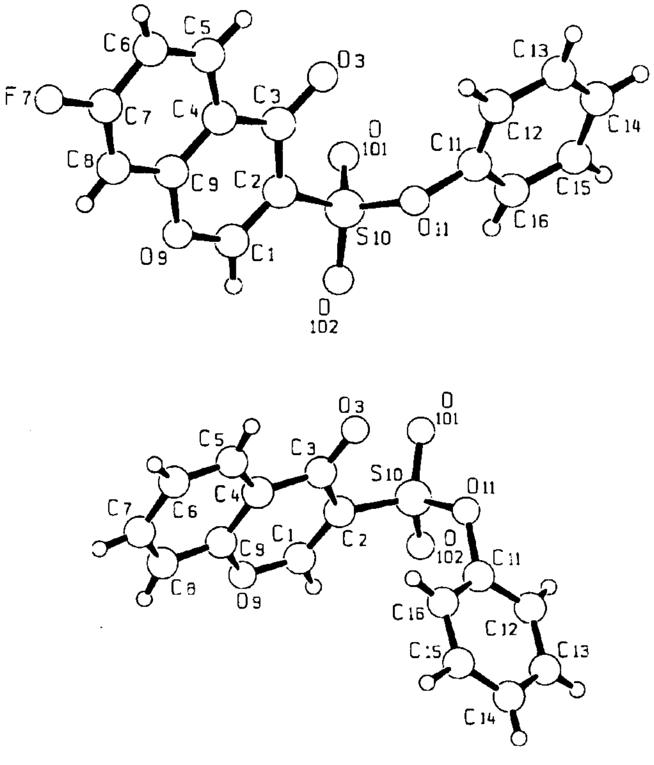


Figure 1. Molecular structure of compound **1**, above, and compound **2**, below, in the crystal, generated with SCHAKAL [7].

The reaction path that leads to benzoxathiinopyrazole **4** is assumed to proceed as follows: First, cyanoacetic hydrazide **3**'s hydrazine-nitrogen group nucleophilically attacks the chromone **1**'s positive C-2 atom. This produces the zwitterion **6A**, which is in equilibrium with the neutral from **6B**. After sodium acetate-induced deprotonation, the ring opens, thereby producing the intermediate **7**. A phenolate group is eliminated forming sultone **8**. Subsequently, hydrolytic cleavage of cyanoacetic acid occurs to **9**. Finally, the ring closes, thereby producing the benzoxathiinopyrazole **4** (Scheme 2).

During the course of benzoxathiinodihydropyridine **5** synthesis, the nucleophilic methylene group of the cyanoacetic hydrazide **3** adds to the activated, electrophilic C-2 atom of the chromone **1**. This gives the intermediate **10**, from which the open-ringed form **11** develops after sodium acetate-induced deprotonation. After the elimination of phenolate, this subsequently gives the sultone **12A**, which is in equilibrium with the tricyclic compound **12B**. Subsequent dehydration leads to the production of the benzoxathiinodihydropyridine **5** [6]. The formation of the anellated system **13**, with its seven-membered ring, was not observed (Scheme 3).

Crystal Structure of Compound 1.

The molecular and crystal structure of **1** was determined by single crystal X-ray analysis.

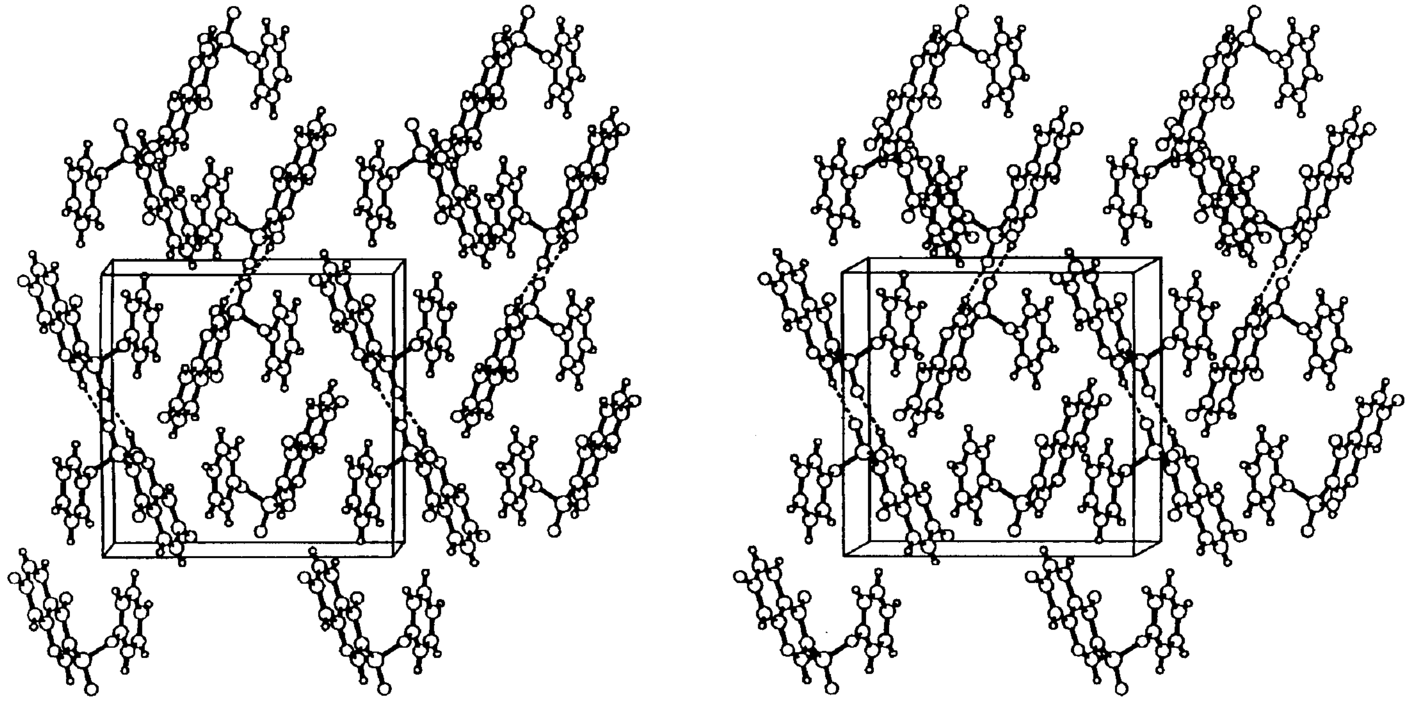


Figure 2. Stereo representation [7] of the crystal lattice of **1**, projected down the crystallographic c-axis. The shortest intermolecular contact H1 ... O102 *via* the inversion center at (1/2,1,1) is shown by dashed lines.

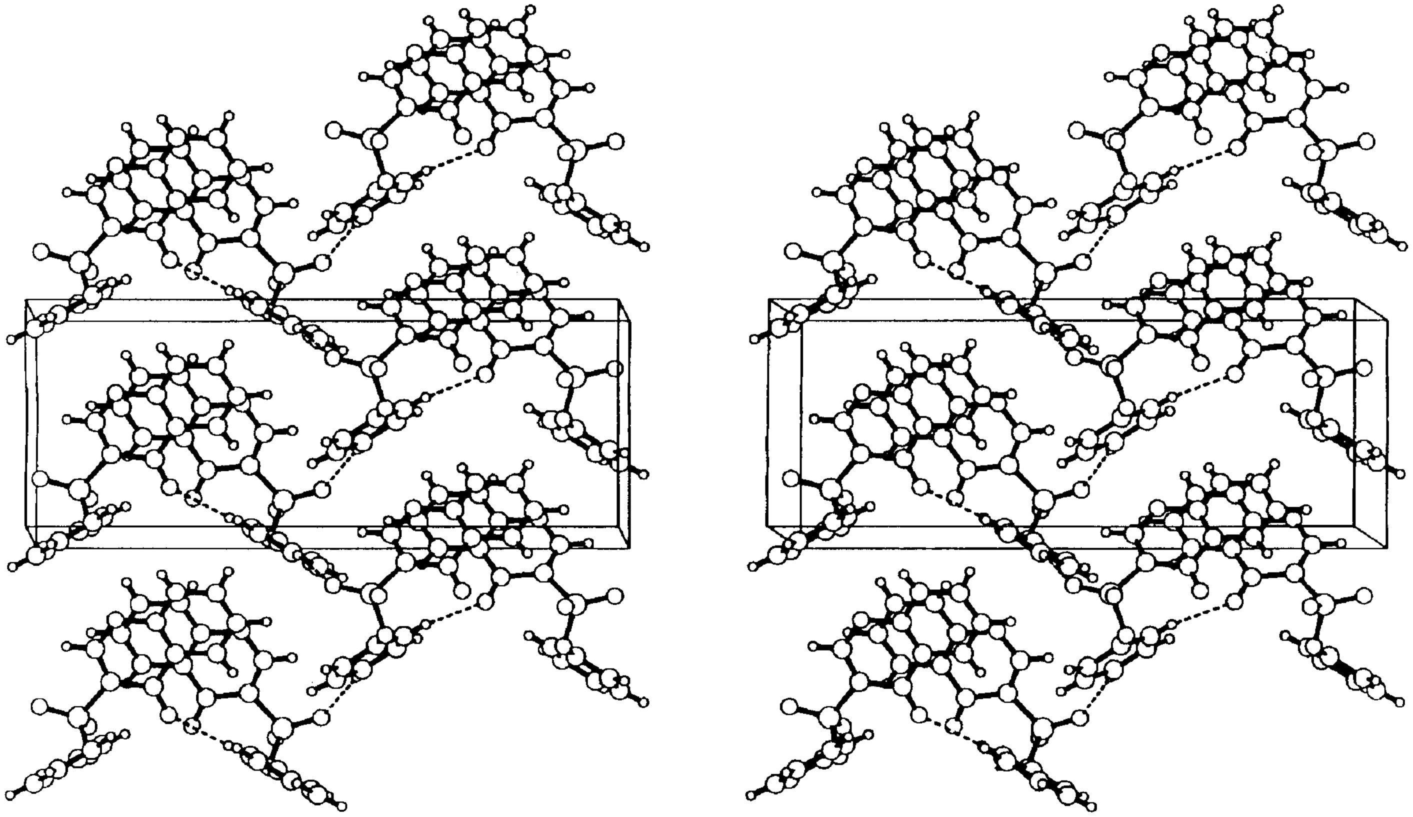


Figure 3. Stereo representation [7] of the crystal lattice of **2** projected down the crystallographic c-axis. Shortest intermolecular contacts are indicated by dashed lines.

Table 1

Intermolecular Contacts < 3 Å of **1**

X ... Y	Distance X ... Y (Å)	Sym. op. for Y
O102 ... H1	2.44 (3)	1-x, -y, -z
O101 ... H8	2.56 (3)	x, y, 1+z
F7 ... H1	2.60 (3)	3/2-x, 1/2+y, -1/2-z
O3 ... H13	2.65 (4)	1-x, 1-y, 1-z
F7 ... H15	2.80 (4)	-1/2+x, 1/2-y, -3/2+z
F7 ... H13	2.96 (4)	1-x, 1-y, -z

Table 2

Bond Lengths [Å] and Angles [deg] of compound **1**

C (1) - C (2)	1.337 (4)
C (1) - O (9)	1.337 (3)
C (2) - C (3)	1.464 (3)
C (2) - S (10)	1.740 (3)
C (3) - O (3)	1.225 (3)
C (3) - C (4)	1.465 (4)
C (4) - C (5)	1.399 (4)
C (4) - C (9)	1.386 (4)
C (5) - C (6)	1.366 (5)
C (6) - C (7)	1.377 (5)
C (7) - F (7)	1.353 (4)
C (7) - C (8)	1.357 (4)
C (8) - C (9)	1.385 (4)
C (9) - O (9)	1.381 (3)
S (10) - O (101)	1.419 (2)
S (10) - O (102)	1.421 (2)
S (10) - O (11)	1.577 (2)
O (11) - C (11)	1.419 (3)
C (11) - C (12)	1.366 (4)
C (11) - C (16)	1.372 (4)
C (12) - C (13)	1.384 (6)
C (13) - C (14)	1.375 (6)
C (14) - C (15)	1.367 (6)
C (15) - C (16)	1.384 (5)
C (2) - C (1) - O (9)	124.3 (2)
C (1) - C (2) - C (3)	121.7 (2)
C (1) - C (2) - S (10)	117.6 (2)
C (3) - C (2) - S (10)	120.6 (2)
C (2) - C (3) - O (3)	123.4 (2)
C (2) - C (3) - C (4)	113.0 (2)
O (3) - C (3) - C (4)	123.6 (2)
C (3) - C (4) - C (5)	121.6 (2)
C (3) - C (4) - C (9)	120.8 (2)
C (5) - C (4) - C (9)	117.6 (3)
C (4) - C (5)- C (6)	120.7 (3)
C (5) - C (6) - C (7)	118.9 (3)
C (6) - C (7) - F (7)	118.2 (3)
C (6) - C (7)- C (8)	123.3 (3)
F (7) - C (7) - C (8)	118.5 (3)
C (7) - C (8) - C (9)	116.9 (3)
C (4) - C (9) - O (9)	121.8 (2)
C (8) - C (9)- O (9)	115.6 (2)
C (1) - O (9) - C (9)	118.4 (2)
C (2) - S (10) - O (110)	110.8 (1)
C (2) - S (10) - O (102)	108.1 (1)
C (2) - S (10) - O (11)	99.5 (1)
O (101) - S (10) - O (102)	119.1 (1)
O (101) - S (10) - O (11)	109.7 (1)
O (102) - S (10) - O (11)	107.8 (1)
S (10) - O (11) - C (11)	121.3 (2)
O (11) - C (11) - C (12)	117.7 (3)
O (11) - C (11) - C (16)	119.9 (3)
C (12) - C (11) - C (16)	122.3 (3)
C (11) - C (12) - C (13)	118.4 (3)
C (12) - C (13) - C (14)	120.5 (4)
C (13) - C (14) - C (15)	119.9 (4)
C (14) - C (15) - C (16)	120.7 (4)
C (11) - C (16) - C (15)	118.2 (3)

Table 3

Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 x 10^3) of Compound **1**. U (eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U (eq)
C (1)	5961 (2)	1635 (2)	-480 (3)	47 (1)
H (1)	5750 (2)	930 (2)	-600 (4)	62 (8)
C (2)	5900 (2)	2134 (2)	975 (3)	41 (1)
C (3)	6190 (2)	3202 (2)	1174 (3)	46 (1)
O (3)	6133 (2)	3684 (1)	2480 (2)	68 (1)
C (4)	6551 (2)	3633 (2)	-353 (3)	46 (1)
C (5)	6890 (3)	4636 (2)	-399 (4)	63 (2)
H (5)	6760 (2)	5040 (2)	550 (4)	73 (9)
C (6)	7261 (3)	5013 (3)	-1812 (4)	70 (2)
H (6)	7480 (3)	5580 (3)	-1890 (4)	80 (1)
C (7)	7289 (2)	4390 (2)	-3202 (4)	58 (2)
F (7)	7665 (2)	4772 (2)	-4588 (2)	81 (1)
C (8)	6969 (2)	3413 (2)	-3241 (3)	52 (2)
H (8)	6940 (2)	3050 (2)	-4190 (4)	62 (9)
C (9)	6605 (2)	3044 (2)	-1789 (3)	43 (1)
O (9)	6307 (1)	2040 (1)	-1852 (2)	50 (1)
S (10)	5491 (1)	1459 (1)	2659 (1)	47 (1)
O (101)	6211 (1)	1515 (2)	4112 (2)	58 (1)
O (102)	5151 (2)	493 (1)	2045 (3)	75 (1)
O (11)	4533 (1)	2109 (2)	2961 (2)	57 (1)
C (11)	4318 (2)	2369 (2)	4622 (3)	51 (2)
C (12)	4300 (3)	3375 (3)	5031 (4)	67 (2)
H (12)	4550 (2)	3860 (3)	4290 (4)	80 (1)
C (13)	4008 (3)	3645 (3)	6593 (5)	82 (2)
H (13)	4030 (3)	4360 (3)	6840 (5)	120 (1)
C (14)	3759 (3)	2913 (3)	7712 (5)	77 (2)
H (14)	3590 (3)	3150 (3)	8810 (5)	100 (1)
C (15)	3795 (3)	1911 (3)	7277 (4)	71 (2)
H (15)	3630 (3)	1390 (3)	8120 (5)	100 (1)
C (16)	4086 (2)	1623 (3)	5723 (4)	61 (2)
H (16)	4180 (2)	960 (3)	5380 (4)	70 (1)

Table 4

Intermolecular Contact Distances (<3 Å) of **2**

X ... Y	Distance X-Y (Å)	Sym. op. for Y
0102 ... H14	2.63 (4)	-x, 1/2+y, 2-z
03 ... H16	2.61 (6)	1/2-x, y, -1/2+z
0101 ... H15	2.61 (5)	x, y, -1+z

In the molecular structure (Figure 1) the bicyclic ring system C1, ..., O9 is planar with a mean deviation of the contributing atoms from a least-squares plane of σ = 0.012 Å. One of the SO$_2$-oxygens, O102, is almost coplanar with this ring system (torsion angle C1-C2-S10-O102 = -8.3 (3)°). Moreover, since the phenyl ring plane

Table 5

Bond Lengths [Å] and Angles [deg.] of **2**

C (1) - C (2)	1.341 (8)
C (1) - O (9)	1.327 (7)
C (2) - C (3)	1.477 (5)
C (2) - S (10)	1.743 (6)
C (3) - O (3)	1.212 (7)
C (3) - C (4)	1.459 (7)
C (4) - C (5)	1.404 (5)
C (4) - C (9)	1.384 (7)
C (5) - C (6)	1.364 (8)
C (6) - C (7)	1.372 (8)
C (7) - C (8)	1.371 (7)
C (8) - C (9)	1.383 (8)
C (9) - O (9)	1.391 (4)
S (10) - O (101)	1.422 (2)
S (10) - O (102)	1.423 (3)
S (10) - O (11)	1.593 (7)
C (11) - O (11)	1.421 (4)
C (11) - C (12)	1.366 (6)
C (11) - C (16)	1.369 (5)
C (12) - C (13)	1.403 (6)
C (13) - C (14)	1.362 (6)
C (14) - C (15)	1.370 (6)
C (15) - C (16)	1.376 (5)
C (2) - C (1) - O (9)	125.0 (3)
C (1) - C (2) - C (3)	120.8 (4)
C (1) - C (2) - S (10)	118.1 (3)
C (3) - C (2) - S (10)	121.0 (4)
C (2) - C (3) - O (3)	122.6 (4)
C (2) - C (3) - C (4)	112.8 (4)
O (3) - C (3) - C (4)	124.6 (3)
C (3) - C (4) - C (5)	121.7 (5)
C (3) - C (4) - C (9)	121.7 (3)
C (5) - C (4) - C (9)	116.6 (5)
C (4) - C (5) - C (6)	120.9 (5)
C (5) - C(6) - C (7)	120.6 (4)
C (6) - C (7) - C (8)	120.6 (5)
C (7) - C (8) - C (9)	118.3 (5)
C (4) - C (9) - C (8)	122.9 (4)
C (4) -C (9) - O (9)	120.9 (4)
C (8) - C (9) - O (9)	116.2 (5)
C (1) - O (9) - C (9)	118.6 (4)
C (2) - S (10) - O (101)	110.6 (4)
C (2) - S (10) - O (102)	108.9 (3)
C (2) - S (10) - O (11)	102.9 (2)
O (101) - S (10) - O (102)	119.7 (2)
O (101) - S (10) - O (11)	103.8 (4)
O (102) - S (10) - O (11)	109.5 (3)
O (11) - C (11) - C (12)	118.6 (3)
O (11) - C (11) - C (16)	118.6 (3)
C (12) - C (11) - C (16)	122.7 (3)
S (10) - O (11) - C (11)	118.2 (4)
C (11) - C (12) - C (13)	117.6 (4)
C (12) - C (13) - C (14)	120.3 (4)
C (13) - C (14) - C (15)	120.5 (4)
C (14) - C (15) - C (16)	120.4 (4)
C (11) - C (16) - C (15)	118.6 (4)

C11-C16 (σ = 0.005 Å) has only an angle of 14.4 (1)° with the bicyclic ring plane the molecule in total does not deviate too much from planarity.

Table 6

Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameter (Å^2 x 10^3) of Compound **2**. U (eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	X	Y	Z	U (eq)
C (1)	1124 (2)	4866 (9)	7048 (5)	64 (2)
C (2)	1377 (2)	3540 (8)	6255 (4)	52 (2)
C (3)	2103 (2)	3350 (8)	6057 (4)	56 (2)
O (3)	2348 (1)	2183 (8)	5329 (3)	81 (2)
C (4)	2480 (2)	4686 (8)	6849 (4)	55 (2)
C (5)	3178 (2)	4713 (8)	6829 (5)	68 (2)
C (6)	3522 (2)	5952 (8)	7600 (6)	79 (3)
C (7)	3195 (2)	7211 (8)	8405 (6)	79 (3)
C (8)	2514 (2)	7240 (8)	8459 (5)	75 (3)
C (9)	2169 (2)	5979 (8)	7673 (5)	60 (2)
O (9)	1479 (1)	6068 (7)	7754 (3)	73 (2)
S (10)	827 (1)	2064 (6)	5447 (1)	58 (1)
O (101)	969 (1)	1810 (8)	3852 (2)	84 (2)
O (102)	169 (1)	2488 (7)	5916 (3)	66 (2)
C (11)	866 (1)	19 (8)	7803 (3)	45 (2)
O (11)	1044 (1)	302 (7)	6233 (2)	55 (1)
C (12)	296 (2)	-871 (8)	8113 (5)	60 (2)
C (13)	156 (2)	-1252 (8)	9665 (6)	70 (3)
C (14)	579 (2)	-734 (9)	10805 (5)	63 (2)
C (15)	1148 (2)	145 (8)	10449 (4)	54 (2)
C (16)	1298 (2)	527 (8)	8935 (4)	45 (2)
H (1)	640 (2)	4960 (5)	7250 (4)	60 (1)
H (5)	3440 (2)	3940 (6)	6270 (5)	70 (1)
H (6)	4030 (2)	5990 (6)	7700 (5)	90 (1)
H (7)	3410 (2)	8110 (7)	8990 (5)	90 (2)
H (8)	2280 (2)	7960 (5)	9070 (4)	70 (1)
H (12)	30 (2)	-1080 (5)	7270 (4)	53 (9)
H (13)	-250 (2)	-1770 (6)	9810 (5)	90 (1)
H (14)	460 (2)	-960 (6)	11830 (5)	90 (1)
H (15)	1480 (2)	640 (6)	11290 (5)	90 (1)
H (16)	1670 (2)	1000 (2)	8660 (4)	60 (1)

The intermolecular arrangement in the crystal structure is shown in Figure 2. There are a few intermolecular contacts below or in the range of van der Waals distances which are summarized in Table 1. With respect to the shortest intermolecular contact H1 ... O102 via the crystallographic inversion center at (1/2,0,0) a kind of dimer is formed where the contributing molecular fragments of both molecules consisting of C1 ... O9, S10, O102 are almost coplanar, since the angle between these two centrosymmetrically related planes is only 1.0°. This way a large planar system is generated in the crystal structure which may be the reason for the compound's colour.

Crystal Structure of Compound **2** (Comparison with **1**).

The crystal structure of **2** was determined by single crystal analysis, too. The molecular structure is mainly determined by two planar fragments. One is the bicyclic ring system (C1 ... O9), where the mean deviation of contributing atoms from a least squares plane is σ = 0.008 Å. The second plane is the phenyl ring C11 ... C16 (σ = 0.003 Å). Although the molecule of **2** differs from that of **1** only by the absence of the fluor substituent, both molecular structures are totally different in the relative orientation of these two planes. For **2** the dihedral angle is 64.9 (2)°, while it was 14.4 (1)° for **1**. Hence the nonplanarity of the **2** molecules is obvious and this holds also for the crystal structure, see Figure 3, showing the crystal packing in the xy-plane. While the bicyclic fragments of **2** pile up in stacks close to (x,y) = (1/4,1/2) and (x,y) = (3/4,1), the phenyl rings form a zig-zag arrangement in y-direction close x = 0,1/2,..., so that intermolecular larger planar arrangements no longer exist as were found for **1**.

EXPERIMENTAL

General Methods.

Melting points were determined on a Linström apparatus and are uncorrected. The ir spectra were recorded on a Perkin-Elmer 297 spectrometer. The ^{1}H-nmr spectra were recorded on a Bruker AC 300 spectrometer. Mass spectra were obtained on a Finnigan MAT Bremen CH-7A spectrometer and Finnigan MAT Bremen CH-5DF. Elemental analyses were performed by the Institut für Pharmazie Analytical Service Laboratory.

General Procedure for the Preparation of the Compounds **4** and **5**.

Compound **1** (300 mg, 0.94 mmole) [2] was triturated with 300 mg (3.0 mmoles) of cyanoacetic hydrazide **3** and 400 mg of sodium acetate. The mixture was then heated at 100° for 1 hour. After cooling to room temperature 5 ml of ethanol and subsequently 5 ml of water were added. After standing overnight 60 mg of a red colored, light syrupy solid separated out. From the mixture (200 mg) compounds **4** and **5** were isolated using a chromatotron with chloroform/methanol (24:1), silica gel 60 PF 254 (Merck); tlc (chloroform/methanol 24:1) 4: rf, 0.44; 5: rf, 0.54.

7-Fluoro-2*H*-[1,2]benzoxathiino[4,3-*c*]pyrazole 4,4 Dioxide Monohydrate (**4**).

Colorless crystals were obtained (ethanol), mp 230°; ir (potassium bromide): 3268 (NH), 3144 (-CH=), 1370, 1166 (SO_2) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ = 7.38-8.13 (m, 3H, aromat.), 8.90 (s, 1H, H-3), 14.47 (br, s, 1H, NH, exchangeable); ms: m/z 240 (100%, $M^{+\bullet}$).

Anal. Calcd. for $C_9H_7FN_2O_4S$: C, 41.86; H, 2.73; N, 10.85. Found: C, 41.79; H, 2.52; N, 10.79.

1-Amino-3-cyano-8-fluoro-1,2-dihydro-2-oxo[1,2]benzoxathiino[4,3-*b*]pyridine 5,5 Dioxide (**5**).

Colorless crystals were obtained (ethanol), mp 252°; ir (potassium bromide): 3429, 3310 (NH_2), 3068 (-CH=), 2235 (CN), 1673 (CO), 1609 (-C=C-), 1379, 1192 (SO_2) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ = 6.35 (s, 2H, NH_2), 7.55 (m, 1H, H-9), 7.77 (m, 1H, H-7), 8.83 (s, 1H, H-4), 9.05 (m, 1H, H-10); ms: m/z 307 (100%, $M^{+\bullet}$), $[M-NH]^{+\bullet}$ hrms 291.995; Found: 291.993.

Anal. Calcd. for $C_{12}H_6FN_3O_4S$: C, 46.91; H, 1.97; N, 13.68. Found: C, 47.04; H, 2.06; N, 13.18.

Single Crystal X-ray Analysis of **1**.

Crystals of $C_{15}H_9O_5SF$ were grown from ethanol. Precise lattice parameters (from 133 high-order reflections with $60° \le 2\theta \le 90°$) and three-dimensional intensity data were measured on a STOE diffractometer using Ni-filtered CuKα-radiation (λ = 1.5418 Å). A single crystal with approximate dimensions 0.71 x 0.65 x 0.55 mm was used to collect the intensity data of 4325 reflections of one hemisphere ($2\theta \le 128°$, ± h, k, ± l) by using the ω–2θ scan technique. An intensity decrease of 8% monitored *via* three check reflections, was rescaled. Merging gave 2298 unique reflections (R_{int} = 1.0%, R_σ = 1.0%) of which 62 reflections with $F_o < 2\sigma\ (F_o)$ were considered unobserved.

Crystal Data of **1**.

Molecular formula $C_{15}H_9O_5SF$ (M_r = 320.29), space group, monoclinic $P2_1/n$; unit cell, a = 13.330(1), b = 13.184(1), c = 7.925(1) Å, β = 96.22(1), V = 1384.6(2) Å^3, Z = 4, ρ_x = 1.536 g·cm^{-3}, μ (CuKα) = 23.72 cm^{-1}. Phase determination was made with direct methods (program SHELXS 86 [8]); refinement was done with the corresponding least squares programs of the XTAL program system (version 3.2, 1992 [9]). All hydrogens were located from difference syntheses. No significant peaks or holes were seen in a final difference Fourier map. After convergence R-values of R = 3.9% and R_w = 4.1% were obtained.

Single Crystal X-ray Analysis of **2**.

Crystals of $C_{15}H_{10}O_5S$ were grown from ethanol. Precise lattice parameters (from 196 high-order reflections with $45° < 2\theta < 84°$) and intensity data were measured on a STOE diffractrometer (AED) using Ni-filtered CuKα-radiation (λ = 1.5418 Å). A single crystal with approximate dimensions 0.32 x 0.30 x 0.41 mm^3 was used to collect the intensity data of 1281 reflections of one octand ($8° < 2\theta < 128°$ and $0 \le h \le 23$, $0 \le k \le 9, 0 \le l \le 10$) by using the ω-2θ scan technique. No significant intensity variations monitored *via* three check-reflections were observed. Data reduction gave 1216 unique reflections of which 25 reflections with $F_o < 2\sigma\ (F_o)$ were considered unobserved.

Crystal Data of **2**.

Molecular formula $C_{15}H_{10}O_5S$, M_r = 302.29 gmol^{-1}, space group: orthorhombic $Pc2_1n$, unit cell parameters: a = 20.124(3) Å, b = 7.793(3) Å, c = 8.648(3) Å, Z = 4, V = 1356.2(7), Å^3, ρ_x = 1.479 gcm^{-3}, μ(CuKα) = 2.31 mm^{-1}. Phase determination was made with direct methods (program SIR92 [10]); refinement was done with the corresponding least squares programs of the XTAL program system [9]. All hydrogens were located from difference syntheses. After convergence R-values of R = 3.0% an R_w = 3.4% were obtained.

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