Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.102$
$S = 1.071$
2570 reflections
245 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2 + 0.4791P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.181$ e Å^{-3}
$\Delta\rho_{\min} = -0.185$ e Å^{-3}
Extinction correction: *SHELXL93*
Extinction coefficient: 0.0178 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

The structure was solved by direct methods and refined anisotropically on non-H atoms by using full-matrix least-squares methods. All H atoms were placed in idealized positions geometrically and allowed to ride with the parent atom to which each was bonded for the final cycles of refinement. Three reflections $[\Delta(F^2)/\sigma > 5.0]$ were suppressed during the last cycles of refinement.

Data collection: Siemens *P*3 software. Cell refinement: Siemens *P*3 software. Data reduction: Siemens *P*3 software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965), *PLUTO* (Motherwell & Clegg, 1978) and *ALCHEMY-III* (Tripos Associates Inc., 1972). Software used to prepare material for publication: *CIFTAB SHELXL*93.

SS thanks the Department of Biotechnology (India) for his Research Assistantship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1041). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 136–138

5-Amino-1-phenylsulfonyl-4-pyrazolin-3-one

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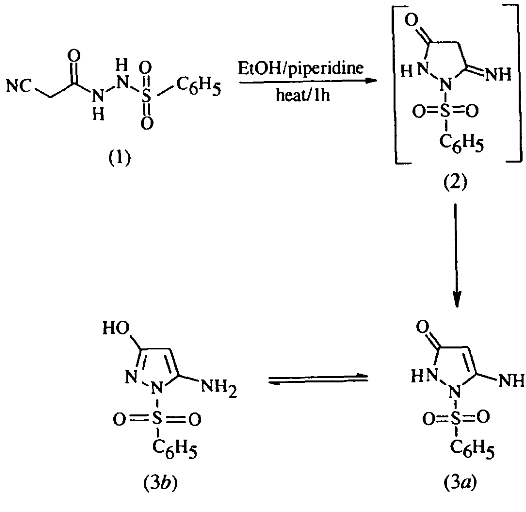
(Received 6 August 1997; accepted 22 September 1997)

Abstract

The title compound, $C_9H_9N_3O_3S$, crystallizes with two independent molecules in $P2_1$, although the symmetry is close to $P2_1/c$. The keto tautomer is the only solid-state form. The main difference between the two molecules is the orientation of the phenyl rings. The five-membered rings are planar. An extensive hydrogen-bonding system connects the molecules into layers parallel to the *xy* plane.

Comment

We are interested in the synthesis and properties of antimetabolites (Elgemeie, Attia *et al.*, 1994; Elgemeie & Hussain, 1994; Elgemeie, El-Ezbawy *et al.*, 1994) and have extensively investigated the synthesis of *N*-sulfonated heterocycles. We report here the synthesis and structure of the *N*-sulfonated pyrazole (3), obtained by intramolecular cyclization of cyanoaceto-*N*-phenylsulfonylhydrazide, (1).



Compound (3) can potentially exist in two tautomeric forms, 5-amino-1-phenylsulfonylpyrazolin-3-one, (3*a*) and 5-amino-3-hydroxy-1-phenylsulfonylpyrazole, (3*b*). The hydroxy form (3*b*) would be expected to be more stable, because of the weakened basicity of the ring N atoms at the 2-position, in turn arising from the adjacent heteroatom and the O atom at the 3-position. Spectral studies, however, indicated the presence of the NH tautomer in solution (*e.g.* the ^{13}C NMR signal at 170.81 p.p.m. indicates a carbonyl carbon rather than C—OH; Hawkes *et al.*, 1977; Steigel & Fey, 1980). No significant amounts of the alternative tautomer could be detected.

The X-ray analysis (Fig. 1) establishes the exclusive presence of the form (3*a*) in the solid state; all H atoms could be located unambiguously and bond lengths are also consistent with form (3*a*).

There are two independent molecules in the asymmetric unit. The main difference between them being the orientation of the phenyl groups. A least-squares fit with one molecule inverted, excluding H and phenyl C atoms, gave a mean deviation of 0.05 Å. The five-membered rings and the exocyclic N atoms are coplanar [mean deviations 0.039, 0.040 Å; deviation from plane 0.210 (4), 0.248 (4) Å for O1, −0.944 (4), −0.911 (4) Å for S1 and 0.50 (3), 0.49 (3) Å for H2].

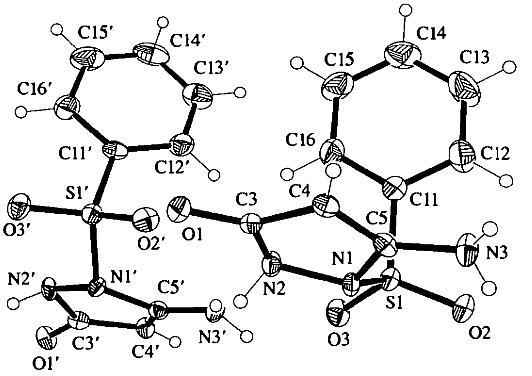


Fig. 1. The two independent molecules of the title compound in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary.

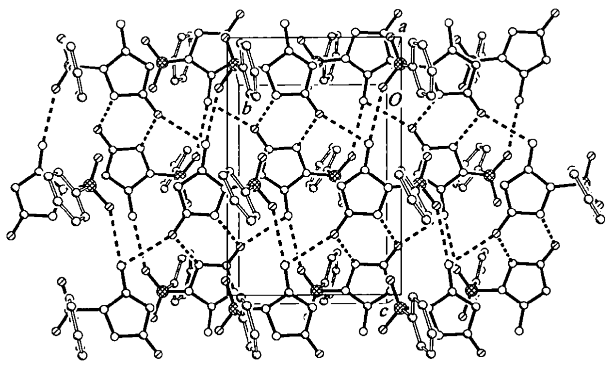


Fig. 2. Packing diagram viewed perpendicular to the *xy* plane (H atoms have been omitted). Hydrogen bonds are indicated by dashed lines.

The molecules are connected into layers parallel to the *yz* plane by a system of hydrogen bonds (Fig. 2 and Table 2); the interior of each layer is hydrophilic, with the phenyl groups projecting into hydrophobic regions. We assume that hydrogen bonding plays an important role in stabilizing the form (3*a*) both in the solid state and in solution.

Experimental

The title compound (3*a*) was obtained by refluxing an ethanolic solution of (1) containing a few drops of piperidine for 1 h. After cooling, the precipitate was filtered off and recrystallized from ethanol in 85% yield; m.p. 481–483 K.

Crystal data

$C_9H_9N_3O_3S$
$M_r = 239.25$
Monoclinic
$P2_1$
$a = 10.7794\,(10)$ Å
$b = 7.8301\,(8)$ Å
$c = 11.8317\,(12)$ Å
$\beta = 97.505\,(8)°$
$V = 990.09\,(17)$ Å^3
$Z = 4$
$D_x = 1.605$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 57 reflections
$\theta = 4.5–12.5°$
$\mu = 0.322$ mm^{-1}
$T = 173\,(2)$ K
Tablet
0.60 × 0.30 × 0.15 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
4442 measured reflections
4235 independent reflections
3531 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$

$\theta_{\rm max} = 27.50°$
$h = -14 \rightarrow 0$
$k = -10 \rightarrow 7$
$l = -15 \rightarrow 15$
3 standard reflections every 297 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F)[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.084$
$S = 1.040$
4235 reflections
314 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.027$

$\Delta\rho_{\rm max} = 0.358$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.381$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.55 (9)

Table 1. *Selected geometric parameters (Å, °)*

S1—N1	1.691 (3)	S1′—N1′	1.686 (3)
N1—C5	1.412 (4)	N1′—N2′	1.423 (3)
N1—N2	1.424 (3)	N1′—C5′	1.424 (4)
N2—C3	1.389 (4)	N2′—C3′	1.382 (4)
N3—C5	1.352 (4)	N3′—C5′	1.334 (4)
O1—C3	1.242 (4)	O1′—C3′	1.262 (4)
C3—C4	1.436 (4)	C5′—C4′	1.375 (5)
C4—C5	1.353 (5)	C4′—C3′	1.411 (4)

C5—N1—N2	106.0 (2)	N2′—N1′—C5′	106.8 (2)
C5—N1—S1	121.67 (19)	N2′—N1′—S1′	112.49 (19)
N2—N1—S1	112.2 (2)	C5′—N1′—S1′	122.5 (2)
C3—N2—N1	108.1 (3)	C3′—N2′—N1′	106.9 (3)
O1—C3—N2	121.5 (3)	N3′—C5′—C4′	132.1 (3)
O1—C3—C4	131.5 (3)	N3′—C5′—N1′	119.4 (3)
N2—C3—C4	107.0 (3)	C4′—C5′—N1′	108.6 (3)
C5—C4—C3	107.9 (3)	C5′—C4′—C3′	107.5 (3)
N3—C5—C4	130.9 (3)	O1′—C3′—N2′	120.3 (3)
N3—C5—N1	119.1 (3)	O1′—C3′—C4′	130.5 (3)
C4—C5—N1	110.0 (3)	N2′—C3′—C4′	109.2 (3)
C5—N1—N2—C3	−9.6 (3)	C5′—N1′—N2′—C3′	9.2 (3)
N1—N2—C3—C4	10.5 (3)	N2′—N1′—C5′—C4′	−3.9 (3)
N2—C3—C4—C5	−7.5 (4)	N1′—C5′—C4′—C3′	−2.9 (3)
C3—C4—C5—N1	1.4 (3)	N1′—N2′—C3′—C4′	−11.1 (4)
N2—N1—C5—C4	5.0 (3)	C5′—C4′—C3′—N2′	8.8 (4)
N1—S1—C11—C12	109.5 (3)	N1′—S1′—C11′—C12′	−73.0 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$\cdots$O1′^{i}	0.87 (2)	1.98 (2)	2.852 (3)	174 (4)
N3—H31$\cdots$O1′^{ii}	0.86 (2)	2.11 (2)	2.897 (4)	152 (3)
N2′—H2′$\cdots$O1^{iii}	0.84 (2)	2.02 (2)	2.852 (3)	171 (3)
N3′—H31′$\cdots$O1^{iv}	0.87 (2)	2.04 (2)	2.900 (4)	173 (3)
N3—H32$\cdots$O2	0.84 (2)	2.37 (3)	2.908 (4)	122 (2)
N3′—H32′$\cdots$O2′	0.86 (2)	2.31 (4)	2.836 (4)	119 (4)

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

The true space group is $P2_1$, but automatic space-group determination suggested $P2_1/c$, in which the structure can indeed be solved and refined with a disordered phenyl group to wR_2 20% and R_1 8%. However, the correctness of the lower symmetry is indicated by (i) the better refinement, and (ii) the presence of several reflections $h0l$, l odd, with significant intensity. The structure was refined as a racemic twin with components 0.55, 0.45 (9). A total of 1799 Friedel pairs were used. The origin was fixed by the method of Flack & Schwarzenbach (1988). H atoms bonded to N atoms were refined freely but with restrained N—H bond distances; other H atoms were refined using a riding model.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

We thank Professor L. Ernst, Dr H.-M. Schiebel and assistants for recording NMR and mass spectra, the Deutsche Forschungsgemeinschaft for supporting our collaboration, the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauf for technical assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1382). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 138–140

4-[2-(3,4-Dimethoxyphenyl)ethenyl]-1-methylpyridinium Tetrafluoroborate†

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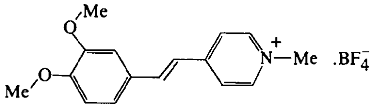
(*Received 30 June 1997; accepted 23 September 1997*)

Abstract

In the cation of the title compound, $C_{16}H_{18}NO_2^+.BF_4^-$, the pyridyl ring makes a dihedral angle of 12.4 (6)° with the phenyl ring. The cations are packed in an anti-parallel fashion along the *a* axis through $p\pi$–$p\pi$ and dipole–dipole interactions, and form layers through C—H$\cdots$O hydrogen bonds. The anions are located between the layers.

Comment

During our systematic study of organic salts with non-linear optical properties (Marder, Perry & Tiemann, 1990; Zhang *et al.*, 1997), we isolated the title compound, (I).



(I)

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† Alternative name: *N*-methyl-3′,4′-dimethoxy-4-stilbazolium tetrafluoroborate.

Acta Crystallographica Section C
ISSN 0108-2701 © 1998