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# A Mesoionic Pyridazinium Sulfonate; an Unexpected Reaction Product

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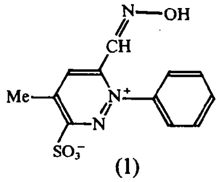
## Abstract

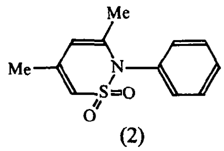
The title compound is an 'inner' salt: 6-(hydroxyiminomethyl)-4-methyl-1-phenylpyridazinium-3-sulfonate, $C_{12}H_{11}N_3O_4S$ (1). The pyridazinium ring is almost planar and twisted approximately 50° out of the benzene ring plane. The oxime —OH group forms an intermolecular hydrogen bond to one of the sulfonate O atoms. The identification of (1) has revealed an unusual rearrangement.

## Comment

The present structure determination was undertaken to characterize a new reaction product (1), obtained from reacting 3,5-dimethyl-1,1-dioxo-2-phenyl-1$\lambda^6$,2-thiazine (2) with aqueous $NaNO_2$ in acidic acetonitrile solution. Analysis of the nitrogen content left some doubt about the composition of (1) and the structure could not be solved unambiguously from spectroscopic data.



(1)



(2)

Crystals of (1) used in the X-ray investigation were recrystallized from water with a small amount of (aqueous) HCl, and separated as red–brown prisms. The red–brown colour may be caused by small amounts of impurities.

Because of uncertainty concerning the composition of (1), refinement was also carried out for a model (1′) with N1 replaced by an O atom. This refinement, however, gave an N—O distance in poor agreement with reported $N^+$—O bond distances: for (1′), N2—O = 1.349 (3) Å, compared with $N^+$—O = 1.41 (1) Å for $(C_2H_5)(C_6H_5)CH_3N^+$—OH (Muntz, Pirkle & Paul, 1972). Furthermore, the molecule (1′) ($C_{12}H_{12}N_2O_5S$, $M_r$ = 296.3) would require an additional H atom, which could neither be located from the data collected at 293 K nor from another set of data collected at 8 K. From a FAB-mass spectrum, the molecular weight of (1)/(1′) was determined as 293, corresponding to the calculated value for (1).

The pyridazinium ring is almost planar with a maximum deviation of 0.05 Å from the least-squares plane defined by the ring atoms. The benzene ring plane is twisted 50.12 (8)° out of the pyridazinium ring plane.

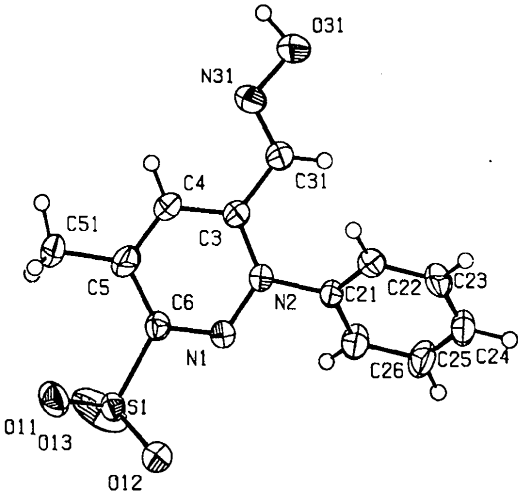


Fig. 1. Displacement ellipsoid plot of (1). Ellipsoids are drawn at the 50% probability level.

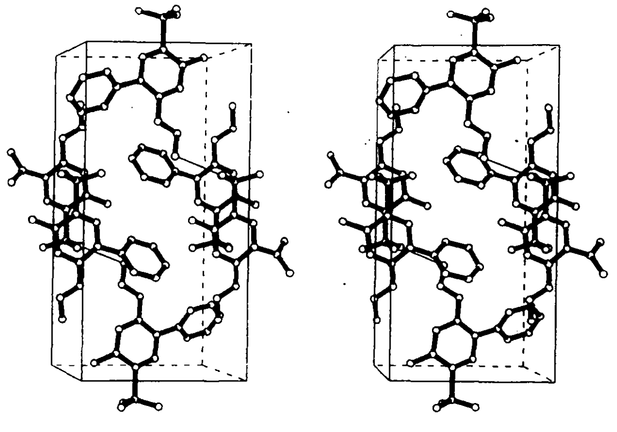


Fig. 2. Stereo drawing (*ATOMS*2.0; Dowty, 1991) of the unit cell of (1).

A comparison of the bond distance C21—N2 = 1.452 (2) Å with the corresponding bonds in *p*-nitroaniline and *p*-nitroaniline hydrochloride supports a pyridazinium structure with a positive charge located on N2: for $p$-$O_2N$—$C_6H_4$—$N^+H_3\,Cl^-$, C—$N^+H_3$ = 1.472 (5) Å (Ploug-Sørensen & Krogh Andersen, 1982), and for $p$-$O_2N$—$C_6H_4$—$NH_2$, C—$NH_2$ = 1.371 (7) Å (Trueblood, Goldish & Donohue, 1961).

The oxime —OH group forms an intermolecular hydrogen bond to the sulfonate atom O11 [O31···O11$^{i}$ = 2.797 (3) Å; symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$]. The hydrogen-bonded O11 atom has a significantly longer O—S bond distance than the other O atoms in the sulfonate group.

The identification of (1) has revealed an unusual rearrangement by the nitrosation of (2), resulting in a regioselective transformation of the 3-methyl group in (2) into a hydroxyiminomethyl group, followed by nitrosation and ring transformation to the mesionic pyridazinium salt (1) (Fanghänel & Hucke, 1994).

## Experimental

*Crystal data* (at 8.3 K in square brackets)

$C_{12}H_{11}N_3O_4S$
$M_r$ = 293.30
Monoclinic
$P2_1/n$
$a$ = 8.179 (3) [8.054 (3)] Å
$b$ = 18.217 (2) [17.856 (6)] Å
$c$ = 8.712 (1) [8.618 (2)] Å
$\beta$ = 101.98 (2) [100.62 (2)]°
$V$ = 1270 (1) [1218 (2)] Å$^3$
$Z$ = 4

$D_x$ = 1.534 Mg m$^{-3}$
$D_m$ = 1.53 (1) Mg m$^{-3}$
$D_m$ measured by flotation in $CCl_4$ and $CHCl_3$
Mo $K\alpha$ radiation
$\lambda$ = 0.71069 Å
$\theta$ = 11.36-13.70°
$\mu$ = 0.26 mm$^{-1}$
$T$ = 293 [8.3] K
Prism
0.52 × 0.39 × 0.18 mm
Red-brown

*Data collection*

Enraf-Nonius CAD-4F diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3700 measured reflections
3700 independent reflections
2968 observed reflections [$I > 2.5\sigma(I)$]
$\theta_{\max}$ = 30.0°

$h = 0 \rightarrow 11$
$k = 0 \rightarrow 25$
$l = -12 \rightarrow 11$
3 standard reflections monitored every 100 reflections (orientation) and every 180 min (intensity)
intensity variation: 5.7%

*Refinement*

Refinement on $F$
$R$ = 0.052
$wR$ = 0.046
$S$ = 5.8
3471 reflections
214 parameters
Only coordinates of H atoms refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max}$ = 0.074
$\Delta\rho_{\max}$ = 0.7 e Å$^{-3}$
$\Delta\rho_{\min}$ = −0.6 e Å$^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| S1 | 0.29278 (7) | −0.09279 (3) | 0.52657 (6) | 0.0304 (2) |
| O11 | 0.4380 (2) | −0.11034 (8) | 0.6457 (2) | 0.0528 (6) |
| O12 | 0.3106 (3) | −0.11466 (9) | 0.3734 (2) | 0.0632 (8) |
| O13 | 0.1404 (2) | −0.1126 (1) | 0.5682 (3) | 0.081 (1) |
| O31 | 0.0998 (3) | 0.33347 (9) | 0.5649 (2) | 0.0570 (7) |
| N1 | 0.2241 (2) | 0.03265 (9) | 0.3811 (2) | 0.0281 (5) |
| N2 | 0.1956 (2) | 0.10528 (9) | 0.3646 (2) | 0.0268 (5) |
| N31 | 0.1701 (3) | 0.2650 (1) | 0.5916 (2) | 0.0454 (7) |
| C3 | 0.2161 (3) | 0.1521 (1) | 0.4866 (2) | 0.0298 (6) |
| C4 | 0.2880 (3) | 0.1245 (1) | 0.6341 (2) | 0.0350 (7) |
| C5 | 0.3244 (3) | 0.0516 (1) | 0.6583 (2) | 0.0332 (7) |
| C6 | 0.2819 (2) | 0.0069 (1) | 0.5227 (2) | 0.0281 (6) |
| C21 | 0.1375 (3) | 0.1271 (1) | 0.2021 (2) | 0.0288 (6) |
| C22 | 0.2162 (3) | 0.1836 (1) | 0.1416 (3) | 0.0385 (8) |
| C23 | 0.1591 (4) | 0.2020 (1) | −0.0152 (3) | 0.0479 (9) |
| C24 | 0.0297 (3) | 0.1641 (1) | −0.1060 (3) | 0.0466 (9) |
| C25 | −0.0460 (3) | 0.1075 (1) | −0.0439 (3) | 0.0482 (9) |
| C26 | 0.0080 (3) | 0.0883 (1) | 0.1123 (3) | 0.0412 (8) |
| C31 | 0.1550 (3) | 0.2276 (1) | 0.4665 (2) | 0.0372 (7) |
| C51 | 0.4029 (4) | 0.0251 (1) | 0.8181 (3) | 0.053 (1) |

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| S1—O11 | 1.442 (2) | C3—C31 | 1.461 (3) |
| S1—O12 | 1.429 (2) | C4—C5 | 1.369 (3) |
| S1—O13 | 1.416 (2) | C5—C6 | 1.418 (3) |
| S1—C6 | 1.817 (2) | C5—C51 | 1.488 (3) |
| O31—N31 | 1.373 (3) | C21—C22 | 1.376 (3) |
| N1—N2 | 1.346 (2) | C21—C26 | 1.375 (3) |
| N1—C6 | 1.313 (2) | C22—C23 | 1.390 (3) |
| N2—C3 | 1.346 (3) | C23—C24 | 1.369 (4) |
| N2—C21 | 1.452 (2) | C24—C25 | 1.371 (4) |
| N31—C31 | 1.270 (3) | C25—C26 | 1.385 (3) |
| C3—C4 | 1.391 (3) | | |
| O11—S1—O12 | 112.5 (1) | C4—C5—C6 | 114.9 (2) |
| O11—S1—O13 | 113.4 (1) | C4—C5—C51 | 119.8 (2) |
| O12—S1—O13 | 115.7 (1) | C6—C5—C51 | 125.3 (2) |
| O11—S1—C6 | 105.4 (1) | S1—C6—N1 | 112.4 (1) |
| O12—S1—C6 | 106.0 (1) | S1—C6—C5 | 123.8 (2) |
| O13—S1—C6 | 102.6 (1) | N1—C6—C5 | 123.8 (2) |
| N2—N1—C6 | 118.2 (2) | N2—C21—C22 | 119.6 (2) |
| N1—N2—C3 | 123.3 (2) | N2—C21—C26 | 118.2 (2) |
| N1—N2—C21 | 112.8 (2) | C22—C21—C26 | 122.2 (2) |
| C3—N2—C21 | 123.9 (2) | C21—C22—C23 | 117.9 (2) |
| O31—N31—C31 | 112.3 (2) | C22—C23—C24 | 120.6 (2) |
| N2—C3—C4 | 117.3 (2) | C23—C24—C25 | 120.6 (2) |
| N2—C3—C31 | 121.2 (2) | C24—C25—C26 | 120.0 (2) |
| C4—C3—C31 | 121.3 (2) | C25—C26—C21 | 118.8 (2) |
| C3—C4—C5 | 122.0 (2) | N31—C31—C3 | 115.6 (2) |

The crystal was damaged when cooled to 8.3 K with a type 202 Displex refrigerator mounted on a type 512 Huber four-circle diffractometer (Henriksen, Larsen & Rasmussen, 1986), as judged from the broadening of the reflection profiles. The space group appeared to remain $P2_1/n$. A data set collected at 8.3 K was of inferior quality relative to the room-temperature data set. It did result in the same molecular structure but with higher standard deviations for parameters, so only room-temperature data have been refined.

The $\theta$ scan width was (1.20 + 0.35tan$\theta$)°. A prescan determined the speed of the final scan so that $\sigma(I)/I < 0.035$. At the beginning and the end of a scan, one sixth of the scan time was used for background measurements. 2968 reflections with $I > 2.5\sigma(I)$ were used in the refinement process together with 'less-than' reflections [$I < 2.5\sigma(I)$] with calculated values greater than the observed (3471 contributing reflections). The H-atom positional parameters were determined from $\Delta\rho$ maps. Data reduction: *Xtal*3.0 *ADDREF* and *SORTRF* (Hall & Stewart, 1990; Norrestam & Nielson, 1982). Program(s) used to solve structure: *XRAY76* (Stewart *et al.*, 1976). Program(s) used to refine structure: *Xtal*3.0 *CRYLSQ*. Software used to prepare material for publication: *Xtal*3.0 *BONDLA* and *ATABLE*.

The authors are grateful to Dr Gustav Bojesen, Odense University, who recorded the FAB-mass spectrum.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71845 (34 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1104]

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# 3,5-Difluorophenol

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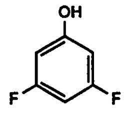
## Abstract

The X-ray crystallographic study of 3,5-difluorophenol, $C_6H_4F_2O$ (35-DFP), shows that the crystal structure has an amphiphilic layer-like arrangement. The hydrophilic contacts involve OH groups and H atoms; the hydrophobic contacts involve F atoms. This unique arrangement is not observed in the crystal structure of phenol.

## Comment

During the past few years special attention has been drawn to molecular assembly, with one of the major problems being the generation of an assembly with the desired architectural features. In crystal engineering one useful method of controlling the molecular arrangement is to add polar substituents to the starting component. 'Chlorosubstitution' has been established as an efficient method of controlling the arrangement (Sarma & Desiraju, 1986); in contrast, no systematic studies have been tried for fluorine although fluorine is also in Group 7. We have reported previously the crystal structure of phenyl 3-fluorobenzoate, indicating the effectiveness of 'fluorosubstitution' (Shibakami, Tamura, Arimura, Kurosawa & Sekiya, 1994). Here we report the crystal structure of 3,5-difluorophenol (35-DFP), demonstrating the unique layer-like arrangement which is not observed in the crystal structure of phenol.



35-DFP

Colourless prismatic crystals of 35-DFP were purchased from Aldrich Co. and a well shaped crystal was mounted on an automated four-circle diffractometer. The crystal structure as drawn by *ORTEP*II (Johnson, 1976) is depicted in Fig. 1. As Table 2 shows, bond distances and angles are in the range of the normal values, within experimental error. The most striking feature is that molecules of 35-DFP form hydrophilic and hydrophobic contacts parallel to the crystallographic *ac* plane. The hydrophilic contacts involve the OH groups and the H(6) atoms; the hydrophobic contacts are formed by the F(1) atoms. Within the hydrophilic contacts, hydrogen bonds are formed between the OH groups with an O···O distance of 2.794 (3) Å. The O(1)—H(1) distance is 1.06 Å and the C(1)—O(1)—H(1) angle is 98.7°. Since the van der Waals radius of F is 1.47 Å and the shortest distance between the F atoms is 2.980 (2) Å in the hydrophobic contacts, it may indicate that a van der Waals contact occurs between two F atoms.

The crystal structure of phenol, which belongs to space group $P2_1$ with $a = 6.05$, $b = 9.24$, $c = 15.29$ Å, $\gamma = 90°$ (Scheringer, Wehrhahn & Stackelberg, 1960), shows that the molecules are linked by hydrogen bonds which result in the formation of a hydrogen-bond network. Contrary to the 35-DFP structure, the layer-like structure is not observed in

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