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Pyridinium methylsulfonate: a pseudosymmetric structure

Michael Bolte,* Christian Griesinger and Peyman Sakhaii

Institut für Organische Chemie, J. W. Goethe-Universität Frankfurt, Marie-Curie-Straße 11, 60439 Frankfurt/Main, Germany

Correspondence e-mail: bolte@chemie.uni-frankfurt.de

Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.004 Å
R factor = 0.037
wR factor = 0.098
Data-to-parameter ratio = 16.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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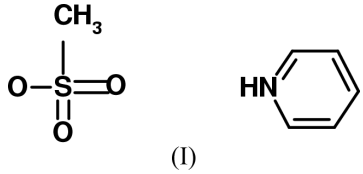
The title compound, $C_5H_6N^+\cdot CH_3SO_3^-$, shows pseudosymmetry. More than 80% of the structure is centrosymmetric, whereas the remaining atoms do not fulfil this symmetry, and the structure is actually non-centrosymmetric.

Comment

Under chemical conditions, numerous procedures are available for the conversion of thiols to the corresponding disulfides. Usual potent oxidizing agents, *e.g.* O_2 in the presence of basic alumina (Liu & Tong, 1979), superoxide anion O_2^- (Kim & Yon, 1981) nitro compounds (Riordan *et al.*, 1966) and halogens can oxidize thiols to disulfides. The possibility of synthesizing disulfides exclusively from thiols and sulfonyl chlorides has received more attention (Schiller & Otto, 1876; Otto, 1882). We have focused our interest on the reaction of thiols with corresponding sulfonyl chlorides and extended it to the preparation of thiosulfonates (*R*–S–SO_2–*R*) and disulfides (*R*–S–S–*R*). In the present work, we describe the reaction between methanethiosulfonyl chloride and 2-amino-5-mercapto-1,3,4-thiadiazole, which did not yield to the expected disulfides (*R*–S–S–*R*) or to the less stable thiosulfonates (*R*–S–SO_2–*R*).



(I)

Compound (I) (Fig. 1) crystallizes in the noncentrosymmetric space group $Pna2_1$. However, more than 80% of the atoms show perfect centrosymmetry, as suggested by the program *PLATON* (Spek, 1990). As a result, one might assume that the space group is *Pnma*. Our refinement, on the other hand, reveals that the higher symmetry is not real and the correct space group is $Pna2_1$. Apart from the N—H···O hydrogen bond, there are three short C—H···O contacts.

Experimental

2-Amino-5-mercapto-1,3,4-thiadiazole (3.0 g, 22.52 mmol) in dry CH_2Cl_2 (200 ml) was added slowly (for 2 h) under an argon atmosphere to methanethiosulfonyl chloride (2.6 g, 22.52 mmol) in dry CH_2Cl_2 (40 ml) and pyridine solution (1.8 g, 22.52 mmol), keeping the temperature at 277 K. The reaction mixture was vigorously stirred for 24 h. The pyridinium chloride was filtered off and the solution concentrated. The precipitate was isolated and washed with dry ethanol. The solid residue was purified by crystallization from dry ethanol to give a white solid (800 mg, 4.56 mmol; 20%). However, the

formation of an unexpected by-product could be observed. Single crystals suitable for X-ray diffraction were obtained by recrystallization (three times) of the solid residue from dry ethanol at 243 K.

Crystal data

$C_5H_6N^+\cdot CH_3SO_3^-$
M_r = 175.20
Orthorhombic, $Pna2_1$
a = 11.0853 (9) Å
b = 8.1425 (7) Å
c = 8.4530 (8) Å
V = 762.99 (12) Å^3
Z = 4
D_x = 1.525 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 512 reflections
θ = 2–20°
μ = 0.38 mm^{-1}
T = 173 (2) K
Block, colourless
0.62 × 0.58 × 0.56 mm

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.799, T_{max} = 0.816
7984 measured reflections
1658 independent reflections
1593 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 28.6°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 10$
$l = -11 \rightarrow 10$
239 standard reflections
frequency: 1200 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.098
S = 1.10
1658 reflections
100 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2 + 0.5001P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.21 (13)

Table 1
Selected geometric parameters (Å, °).

S1—O3	1.453 (2)	N1—C2	1.336 (4)
S1—O2	1.454 (2)	C2—C3	1.376 (3)
S1—O1	1.467 (2)	C3—C4	1.377 (5)
S1—C1	1.762 (3)	C4—C5	1.382 (4)
N1—C6	1.336 (4)	C5—C6	1.369 (4)
O3—S1—O2	113.86 (11)	C6—N1—C2	122.2 (3)
O3—S1—O1	111.26 (13)	N1—C2—C3	119.7 (4)
O2—S1—O1	112.23 (12)	C2—C3—C4	119.4 (3)
O3—S1—C1	105.83 (14)	C3—C4—C5	119.5 (3)
O2—S1—C1	106.63 (15)	C6—C5—C4	119.2 (3)
O1—S1—C1	106.43 (12)	N1—C6—C5	120.0 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.88	1.87	2.730 (3)	165
C4—H4···O1^{i}	0.95	2.48	3.313 (4)	147
C2—H2···O2^{ii}	0.95	2.36	3.249 (4)	155
C3—H3···O3^{ii}	0.95	2.46	3.288 (4)	146

Symmetry codes: (i) $x, y, 1+z$; (ii) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}+z$.

All H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [U(H) = 1.5 U_{eq}(C$_{methyl}$), U(H) = 1.2 U_{eq}(C) or U(H) = 1.2 U_{eq}(N)] using a riding model with C—H$_{aromatic}$ = 0.95, C—H$_{methyl}$ = 0.98 and N—H = 0.88 Å. When the structure is refined in the centrosymmetric space group *Pnma*, both ions must individually possess some mirror symmetry.

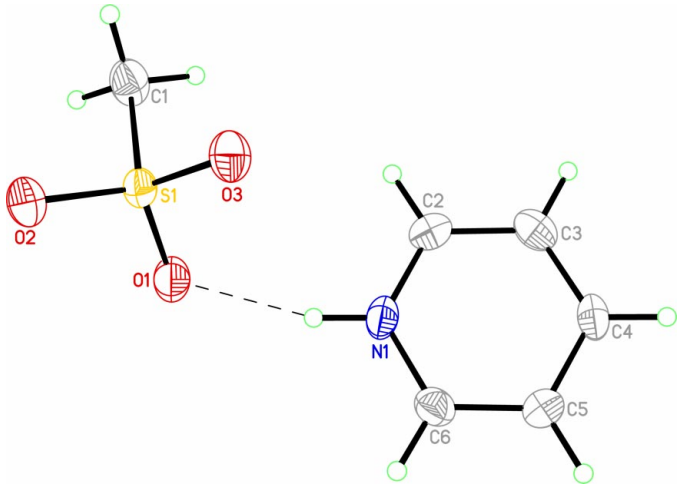


Figure 1
A perspective view of (I) with the atom-numbering scheme. Displacement ellipsoids are at the 50% probability level

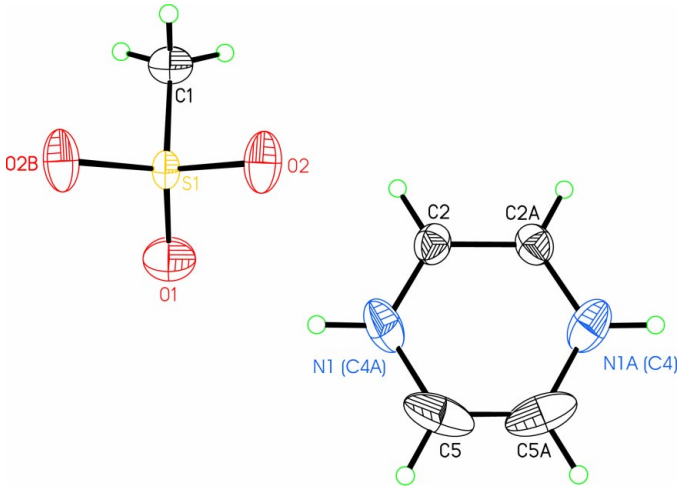


Figure 2
A perspective view of (I) refined in the centrosymmetric space group *Pnma*, with the atom-numbering scheme. Displacement ellipsoids are at the 50% probability level [symmetry codes: (*A*) $x, -\frac{1}{2}-y, z$; (*B*) $x, \frac{1}{2}-y, z$].

The methylsulfonate fulfils C_s symmetry with C1, S1 and O1 lying on the mirror plane. In the case of the pyridinium ring, the mirror plane bisects the C2—C3 and C5—C6 bonds, and atoms N1 and C4 are disordered over two positions across the mirror plane and occupy the same positions. Refinement in *Pnma* results in $wR2$ = 0.2492 and $R1$ = 0.095 for all data. The results of the refinement carried out in *Pnma* also reveal that two atoms (N1 and C5) show strange anisotropic displacement parameters (Fig. 2), which is an indication that the structure is actually noncentrosymmetric and the correct space group is $Pna2_1$. Furthermore, the geometric parameters of N1 and C4 indicate that the pyridinium ring is not disordered.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

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