

***p*-Tolylsulfonyl cyanide**

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**Key indicators**

Single-crystal X-ray study

$T = 120$  K

Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å

$R$  factor = 0.045

$wR$  factor = 0.130

Data-to-parameter ratio = 18.6

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

The first crystal structure of a sulfonyl cyanide,  $\text{C}_8\text{H}_7\text{NO}_2\text{S}$ , has been determined. The molecule has an unusual bond-length distribution, with a very long  $\text{S}-\text{C}_{\text{sp}}$  bond [1.772 (2) Å] and a short  $\text{S}-\text{C}_{\text{sp}^2}$  bond [1.7368 (17) Å].

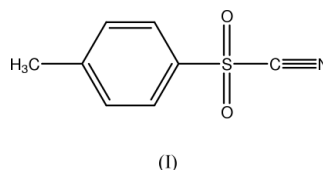
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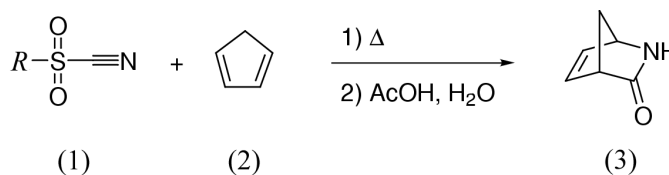
Online 31 January 2002

**Comment**

Herein we report the first example of the solid-state structure of a sulfonyl cyanide, (I).



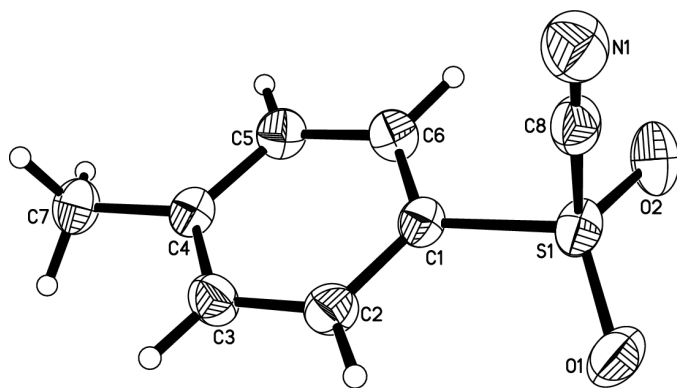
Sulfonyl cyanides (1) are important functional groups since they are used as dienophiles in nitrile cycloaddition reactions, *e.g.* in aza-Diels-Alder reactions with cyclopentadiene (2) (see reaction Scheme below) to yield cycloadduct (3) after hydrolysis (Jagt & van Leusen, 1974; Morgan *et al.*, 1996). More recently, Lewis-acid-catalysed and asymmetric cycloaddition reactions have also been reported (Katagiri *et al.*, 1996).



racemic

- (a)  $R = \text{phenyl}$   
(b)  $R = \text{benzyl}$   
(c)  $R = \text{methyl}$   
(d)  $R = \textit{p}$ -chlorophenyl  
(e)  $R = \textit{p}$ -tolyl

The conformation of the molecule is the usual one for aryl sulfones (Kalman *et al.*, 1981), with the CN group almost perpendicular to the Ph ring [torsion angle  $\text{C}8-\text{S}1-\text{C}1-\text{C}6$  is  $94.1$  (2)°]. However, in comparison with *p*-tolylsulfonyl-ethyne (Tykwinski *et al.*, 1993), the  $\text{S}-\text{C}_{\text{sp}^2}$  bond in (I) is much shorter (1.737 *versus* 1.757 Å) and the  $\text{S}-\text{C}_{\text{sp}}$  bond is significantly longer (1.772 *versus* 1.711 Å, respectively). This difference can be explained by a strong  $\pi-\sigma^*$  interaction between the aromatic ring and the cyano group.

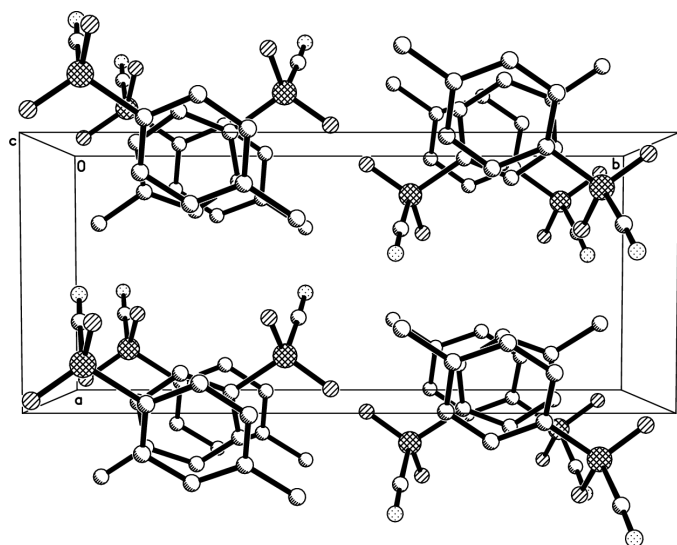


**Figure 1**  
The molecular structure of (I) (displacement ellipsoids are at the 50% probability level).

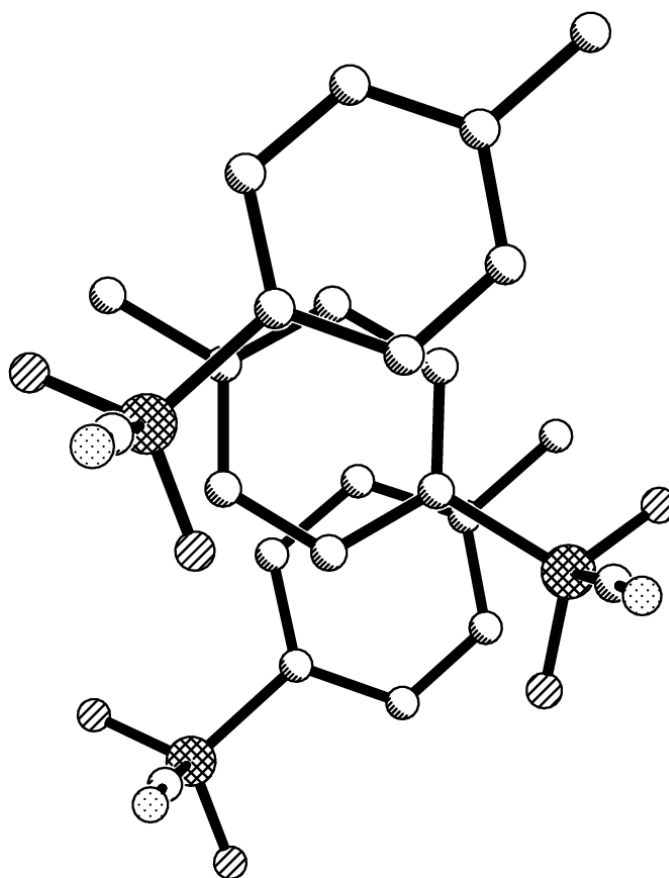
Molecules of (I) form stacks in the crystal, with a significant lateral displacement between molecules (Figs. 2 and 3). The shortest intermolecular contact between atoms in the stack is  $C2 \cdots C6(x, 3/2-y, 1/2+z)$ , at 3.684 (2) Å. The shortest contact between adjacent stacks [ $C5-H5 \cdots O1(2-x, 3/2+y, 1/2-z)$ :  $C \cdots O = 3.409$  (2) Å and  $C-H \cdots O = 138$  (2)°] corresponds to a weak  $C-H \cdots O$  bond.

## Experimental

Tosyl cyanide (500 mg) was gently warmed in 300 ml of petroleum ether (313–333 K) which had been freshly distilled from calcium hydride. The warm solution was filtered and evaporated over a water bath *in vacuo* to give an extremely concentrated solution. Crystallization was effected by slow evaporation under reduced pressure.



**Figure 2**  
Packing diagram viewed along the *c* axis.



**Figure 3**  
The stacking of molecules of (I) viewed perpendicular to the aromatic ring plane.

## Crystal data

$C_8H_7NO_2S$   
 $M_r = 181.21$   
Monoclinic,  $P2_1/c$   
 $a = 6.5810$  (4) Å  
 $b = 15.377$  (1) Å  
 $c = 8.3671$  (5) Å  
 $\beta = 93.49$  (1)°  
 $V = 845.15$  (9) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.424$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 1807 reflections  
 $\theta = 2.8$ – $30.5^\circ$   
 $\mu = 0.34$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
Prism, colourless  
 $0.40 \times 0.18 \times 0.10$  mm

## Data collection

Bruker SMART 6000 diffractometer  
 $\omega$  scans  
Absorption correction: none  
6296 measured reflections  
2542 independent reflections

1742 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.051$   
 $\theta_{max} = 30.5^\circ$   
 $h = -8 \rightarrow 9$   
 $k = -21 \rightarrow 21$   
 $l = -11 \rightarrow 11$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.130$   
 $S = 0.97$   
2542 reflections  
137 parameters

All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.001$   
 $\Delta\rho_{max} = 0.46$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.37$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

S1—O1	1.4217 (14)	C1—C2	1.390 (3)
S1—O2	1.4234 (14)	C2—C3	1.387 (2)
S1—C1	1.7368 (17)	C3—C4	1.391 (2)
S1—C8	1.772 (2)	C4—C5	1.394 (2)
N1—C8	1.132 (2)	C4—C7	1.503 (2)
C1—C6	1.387 (2)	C5—C6	1.382 (2)
O1—S1—O2	121.38 (9)	C3—C2—C1	118.22 (16)
O1—S1—C1	111.51 (9)	C2—C3—C4	121.33 (17)
O2—S1—C1	110.34 (8)	C3—C4—C5	118.78 (16)
O1—S1—C8	105.26 (9)	C3—C4—C7	120.52 (16)
O2—S1—C8	104.50 (9)	C5—C4—C7	120.70 (16)
C1—S1—C8	101.49 (8)	C6—C5—C4	121.17 (16)
C6—C1—C2	121.88 (16)	C5—C6—C1	118.62 (17)
C6—C1—S1	118.26 (13)	N1—C8—S1	177.09 (18)
C2—C1—S1	119.86 (13)		

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve

structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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