

1,1-Bis(phenylsulfonyl)-1-(pyridinio)-methanide

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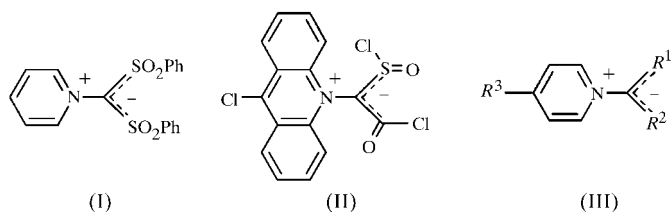
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The title disulfonyl-stabilized pyridinium ylide, $C_5H_5N^+-C^-(SO_2C_6H_5)_2$ or $C_{18}H_{15}NO_4S_2$, contains a near planar NCS_2 core. The structure suggests that the formal negative charge of the ylide C atom is delocalized to the S atoms rather than the N atom. Structural features of pyridinium ylides are briefly discussed.

Comment

The title compound, (I), provides the first structural example of a pyridinium ylide in which the negative charge on the ylide C atom is stabilized by electron-withdrawing sulfonyl groups.



	R^1	R^2	R^3	Reference
(IIIa)	$COCF_3$	$COCF_3$	H	Wittmann <i>et al.</i> (1983)
(IIIb)	$COCCl_3$	$COCCl_3$	H	Wittmann <i>et al.</i> (1983)
(IIIc)	$C(CF_3)_2$	$C(CF_3)_2$	NMe_2	Farnham <i>et al.</i> (1986)
(III d)	$COPh$	CS_2Me	H	Tominaga <i>et al.</i> (1979)
(IIIe)	CHO	CO_2H	H	Grunefeld <i>et al.</i> (1996)

In (I), ylide atom C13 is bonded to the pyridinium (py) N atom and to two S atoms, and lies only 0.053 (2) Å from the NS_2 plane (Fig. 1). The bond lengths and the molecular conformation indicate that C13–N1 is essentially a single bond and that the negative charge formally associated with atom C13 is substantially delocalized to atoms S1 and S2. Thus, significant $p\pi-p\pi$ overlap across N1–C13 is precluded by the near orthogonality of the relevant p orbitals of atoms

N1 and C13 [the C14–N1–C13–S1 torsion angle is 73.2 (3)°]. Consistent with this, the N1–C13 distance is 0.09 Å longer than the aromatic N1–C_{py} bond lengths; indeed, the N1–C13 bond length of 1.445 (3) Å is substantially longer than any mean value in the compilation of Orpen *et al.* (1992) for a bond between a Csp^2 atom and a three-coordinate N atom. The C13–S bonds are, on average, 0.08 Å shorter than the S–C_{Ph} distances, signalling the transfer of charge from atom C13 to the S atoms. This conclusion is consistent with hydrogen-bond basicity and IR spectroscopic studies on sulfonyl-stabilized nitrogen ylides; these studies have shown that sulfonamidates, $-SO_2N^+NMe_3$, are amongst the strongest sulfonyl bases known as a result of electron release from the negatively charged N atom to the sulfonyl group. The mechanism of this electron release is thought to be mainly inductive (see Chardin *et al.*, 1996, and references therein).

The closest comparison to (I) among known structures is provided by the acridinium ylide, (II) (Ning *et al.*, 1976), in which a chlorosulfonyl substituent is one of the two stabilizing groups. The S–C_{ylide} distance in (II) of 1.668 (8) Å is only slightly shorter than the corresponding distances in (I), while the N–C_{ylide} distance (1.447 Å) is nearly identical to that in (I).

A search of the Cambridge Structural Database (Allen, 2002), using the program *QUEST* to recalculate geometric parameters not given explicitly in the primary score, reveals that in the other pyridinium ylides, *viz.* (IIIa)–(IIIe) (see Scheme), which have been characterized by diffraction methods, the ylide C atom participates in two C–C bonds. In these structures, the bonds radiating from the ylide C atom are nearly coplanar, the pyridinium and ylide planes are roughly normal to one another ($C_{py}-N-C_{ylide}-C$ torsion angles are in the range 61–84°), the N–C_{ylide} distances (1.454–1.474 Å) are on average slightly longer than the corresponding values in (I) and (II), and the C–C_{ylide}–C bond angles (127.4–129.6°) are all much larger than 120°. This last feature may have a steric origin; the corresponding angles in (I) [124.7 (1)°] and (II) [123.3 (1)°] deviate less from 120°.

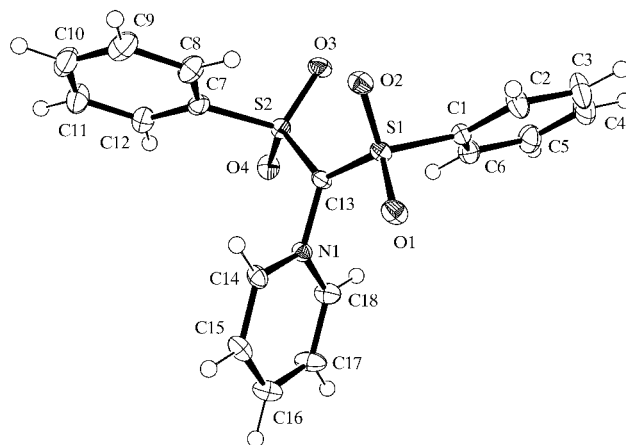


Figure 1
View of (I), with ellipsoids drawn at the 20% probability level.

Finally, we note that the structures of 1,1-dicyano-1-pyridinomethanide compounds differ from those of (I)–(III) in that the angle between the C(CN)₂ and pyridinium planes is close to 0°, permitting conjugation across the N–C_{ylide} bonds. These, in consequence, are shorter (1.416–1.427 Å) than those in (I)–(III) (see, for example, Matsumoto *et al.*, 1998; Baert *et al.*, 1982). The angles at the ylide C atom in these dicyano compounds do not show the large deviations from 120° typical of (III).

Experimental

Crystals of (I) were prepared according to the method of Hadjiarapoglou & Varvoglis (1988) and recrystallized from a CH₂Cl₂ melt at 543–546 K. The specimen used in the diffraction experiment was recrystallized from ethyl acetate.

Crystal data

C ₁₈ H ₁₅ NO ₄ S ₂	Mo K α radiation
$M_r = 373.43$	Cell parameters from 3666 reflections
Orthorhombic, <i>Pca</i> 2 ₁	$\theta = 1.0\text{--}35.0^\circ$
$a = 8.9402$ (2) Å	$\mu = 0.33$ mm ⁻¹
$b = 17.2777$ (5) Å	$T = 100$ (2) K
$c = 11.3437$ (4) Å	Needle, yellow
$V = 1752.22$ (9) Å ³	0.33 × 0.12 × 0.07 mm
$Z = 4$	
$D_x = 1.416$ Mg m ⁻³	

Data collection

Bruker–Nonius KappaCCD diffractometer	6736 independent reflections
Thick-slice φ scans	5207 reflections with $I > 2\sigma(I)$
Absorption correction: Gaussian (Coppens <i>et al.</i> , 1965)	$R_{\text{int}} = 0.061$
$T_{\text{min}} = 0.924$, $T_{\text{max}} = 0.977$	$\theta_{\text{max}} = 35.0^\circ$
13 541 measured reflections	$h = 0 \rightarrow 14$
	$k = -27 \rightarrow 0$
	$l = -18 \rightarrow 17$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0$
$R(F) = 0.056$	$\Delta\rho_{\text{max}} = 0.45$ e Å ⁻³
$wR(F^2) = 0.116$	$\Delta\rho_{\text{min}} = -0.46$ e Å ⁻³
$S = 1.02$	Absolute structure: Flack & Bernardinelli (2000), 2756
6736 reflections	Friedel pairs
226 parameters	Flack parameter = -0.15 (7)
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0305P)^2 + 1.5610P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

H atoms were located initially in difference maps. In the final refinement, their positions were determined by the HFIX instruction in *SHELXL97* (Sheldrick, 1997) and they were then allowed to ride on their parent C atoms, with C–H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The data set used in these calculations contained 3980 unique reflections when Friedel pairs were averaged.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*;

Table 1

Selected geometric parameters (Å, °).

S1–C13	1.691 (2)	N1–C18	1.352 (3)
S1–C1	1.774 (2)	N1–C14	1.357 (3)
S2–C13	1.695 (2)	N1–C13	1.445 (3)
S2–C7	1.778 (2)		
N1–C13–S1	117.13 (18)	S1–C13–S2	124.69 (13)
N1–C13–S2	117.85 (17)		
C13–S1–C1–C6	−7.9 (3)	O1–S1–C13–N1	−6.0 (2)
C13–S2–C7–C8	57.7 (2)	O4–S2–C13–N1	−35.8 (2)
C14–N1–C13–S1	73.2 (3)		

program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1169). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Baert, F., Coppens, P., Stevens, E. D. & Devos, L. (1982). *Acta Cryst.* **A38**, 143–151.
- Chardin, A., Laurence, C., Berthelot, M. & Morris, D. G. (1996). *J. Chem. Soc. Perkin Trans. 2*, pp. 1047–1051.
- Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.
- Farnham, W. B., Middleton, W. J., Fultz, W. C. & Smart, B. E. (1986). *J. Am. Chem. Soc.* **108**, 3125–3127.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Flack, H. D. & Bernardinelli, G. (2000). *J. Appl. Cryst.* **33**, 1143–1148.
- Grunefeld, J. & Jones, P. G. (1996). *J. Prakt. Chem.* **338**, 718–724.
- Hadjiarapoglou, L. & Varvoglis, A. (1988). *Synthesis*, pp. 913–915.
- Matsumoto, K., Katsura, H., Okada, A., Uchida, T. & Kakehi, A. (1998). *Heterocycl. Commun.* **4**, 501–506.
- Ning, R. Y., Madan, P. B., Blount, J. F. & Fryer, R. I. (1976). *J. Org. Chem.* **41**, 3406–3409.
- Nonius (2000). *KappaCCD Control Software*. Nonius BV, Delft, The Netherlands.
- Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1992). *International Tables for Crystallography*, Vol. C, Table 9.5.1.1. Dordrecht: Kluwer Academic Publishers.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Tominaga, Y., Kobayashi, G., Tamura, C., Sata, S. & Hata, T. (1979). *Acta Cryst.* **B35**, 2443–2445.
- Wittmann, H., Ziegler, E., Peters, K., Peters, E. M. & von Schnering, H. G. (1983). *Monatsh. Chem.* **114**, 1097–1106.