

1-(1-Pyridinio)-1-benzoyl-2-methylthio-2-thioxo-1-ethanide

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(Received 21 November 1978; accepted 7 June 1979)

Abstract. $C_{15}H_{13}NOS_2$, monoclinic, $P2_1/c$, $a = 9.533$ (2), $b = 13.710$ (2), $c = 11.284$ (2) Å, $\beta = 106.6$ (3)°, $Z = 4$. The pyridinium betaine $N^+-C(5)$ bond length is 1.470 Å. The intramolecular $S^- \cdots N^+$ distance is 2.937 Å.

Discussion. The eight central atoms, S(2), C(3), S(4), C(5), C(6), O(7), N(8) and C(14) (plane *A*), are almost planar; the deviations of the atoms from this plane are listed in Table 4, the largest deviation (0.108 Å) being observed at N(8). The dihedral angles between

Introduction. Although a considerable amount of research has been carried out on the synthetic chemistry of betaine compounds (Johnson, 1966), little information has been published concerning their crystal structures (Speziale & Ratts, 1965; Stephens, 1965*a,b*; Kawamoto, Hata, Kishida & Tamura, 1971, 1972). The title compound was synthesized by the reaction of Krohnke salt with carbon disulphide followed by addition of dimethyl sulphate (Krohnke & Gerlach, 1962). The three-dimensional intensities were collected on a Rigaku four-circle automatic diffractometer up to $2\theta = 55^\circ$ with Mo $K\alpha$ radiation and the $2\theta/\theta$ scan mode at a scan speed of 2° min^{-1} .

A total of 2925 independent reflexions were corrected for Lorentz and polarization factors but not for absorption. The usual heavy-atom technique using the S atoms was applied for the phase determination and all except the H atoms could be detected in the first Fourier map. After three cycles of full-matrix least-squares refinement with isotropic thermal parameters the *R* factor was reduced to 0.11. Positions for hydrogen atoms, whose peaks could not be obviously resolved, were calculated assuming a C–H bond distance of 1.05 Å. In the final cycle of block-diagonal least-squares refinement, all atoms were refined with anisotropic thermal parameters except for H; the *R* factor was reduced to 0.054.* The positional parameters and the bond lengths and angles are given in Tables 1, 2 and 3. A stereographic view (*ORTEP*; Johnson, 1965) is given in Fig. 1.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34527 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ($\times 10^4$, except for H $\times 10^3$) and bond lengths (Å) involving H atoms

Estimated standard deviations are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	
C(1)	181 (4)	897 (3)	3055 (4)	
S(2)	1932 (1)	1451 (1)	3775 (1)	
C(3)	3076 (3)	939 (2)	2952 (3)	
S(4)	2387 (1)	229 (1)	1701 (1)	
C(5)	4574 (3)	1160 (2)	3405 (3)	
C(6)	5265 (4)	1778 (2)	4404 (3)	
O(7)	4579 (3)	2177 (2)	5061 (3)	
N(8)	5517 (3)	633 (2)	2793 (2)	
C(9)	5994 (4)	−269 (3)	3215 (3)	
C(10)	6731 (4)	−841 (3)	2590 (4)	
C(11)	6971 (4)	−485 (3)	1519 (4)	
C(12)	6498 (4)	438 (3)	1114 (3)	
C(13)	5749 (4)	987 (3)	1751 (3)	
C(14)	6894 (4)	1980 (2)	4717 (3)	
C(15)	7832 (4)	1580 (3)	5777 (4)	
C(16)	9303 (5)	1850 (4)	6146 (4)	
C(17)	9827 (4)	2527 (3)	5488 (4)	
C(18)	8901 (4)	2934 (3)	4441 (4)	
C(19)	7434 (4)	2658 (3)	4041 (4)	
	<i>x</i>	<i>y</i>	<i>z</i>	X–H
H(C1a)	−26 (5)	72 (3)	369 (4)	0.97 (4)
H(C1b)	−39 (5)	129 (3)	244 (4)	0.93 (4)
H(C1c)	35 (5)	25 (3)	256 (4)	1.08 (5)
H(C9)	582 (4)	−46 (3)	406 (3)	1.05 (3)
H(C10)	707 (4)	−152 (3)	294 (3)	1.04 (4)
H(C11)	758 (4)	−88 (3)	103 (3)	1.06 (3)
H(C12)	665 (4)	69 (3)	31 (3)	1.02 (4)
H(C13)	533 (4)	163 (3)	146 (3)	0.98 (4)
H(C15)	738 (4)	110 (3)	629 (3)	1.05 (4)
H(C16)	996 (4)	162 (3)	695 (3)	1.00 (3)
H(C17)	1086 (4)	275 (3)	579 (3)	0.99 (3)
H(C18)	927 (4)	344 (3)	391 (3)	1.04 (4)
H(C19)	676 (4)	297 (3)	320 (3)	1.07 (3)

Table 2. Bond lengths (Å)

Standard deviations are in parentheses.

C(1)—S(2)	1.802 (3)	C(9)—C(10)	1.374 (5)
S(2)—C(3)	1.767 (3)	C(10)—C(11)	1.382 (6)
C(3)—S(4)	1.686 (3)	C(11)—C(12)	1.378 (6)
C(3)—C(5)	1.405 (3)	C(12)—C(13)	1.374 (5)
C(5)—C(6)	1.414 (5)	C(14)—C(15)	1.385 (5)
C(5)—N(8)	1.470 (3)	C(14)—C(19)	1.392 (5)
C(6)—O(7)	1.246 (4)	C(15)—C(16)	1.394 (5)
C(6)—C(14)	1.516 (4)	C(16)—C(17)	1.369 (6)
N(8)—C(9)	1.357 (4)	C(17)—C(18)	1.375 (6)
N(8)—C(13)	1.347 (4)	C(18)—C(19)	1.393 (4)

Table 3. Bond angles (°)

Standard deviations are in parentheses.

C(1)—S(2)—C(3)	103.1 (0)	N(8)—C(9)—C(10)	120.7 (3)
S(2)—C(3)—S(4)	121.2 (2)	C(9)—C(10)—C(11)	118.9 (3)
S(2)—C(3)—C(5)	116.1 (2)	C(10)—C(11)—C(12)	119.7 (3)
S(4)—C(3)—C(5)	122.8 (2)	C(11)—C(12)—C(13)	120.0 (3)
C(3)—C(5)—C(6)	127.7 (3)	N(8)—C(13)—C(12)	119.9 (3)
C(3)—C(5)—N(8)	114.7 (2)	C(6)—C(14)—C(15)	119.6 (2)
C(6)—C(5)—N(8)	117.4 (2)	C(6)—C(14)—C(19)	120.6 (3)
C(5)—C(6)—O(7)	122.2 (3)	C(15)—C(14)—C(19)	119.3 (3)
C(5)—C(6)—C(14)	120.5 (2)	C(14)—C(15)—C(16)	119.9 (3)
O(7)—C(6)—C(14)	117.3 (3)	C(15)—C(16)—C(17)	120.6 (4)
C(5)—N(8)—C(13)	120.5 (2)	C(16)—C(17)—C(18)	119.8 (3)
C(5)—N(8)—C(9)	118.2 (2)	C(17)—C(18)—C(19)	120.4 (3)
C(9)—N(8)—C(13)	120.8 (2)	C(14)—C(19)—C(18)	119.9 (4)

plane *A* and the pyridine and benzene rings are 89.7 and 102.6°, respectively, whereas in acetophenone desaurin the angle between the pyridine ring and the plane of the dicyanomethylidene carbanion system is 3.0° (Bugg & Sass, 1965), or 11.4° (Lynch, Mellor & Nyburg, 1971). Therefore, in the present compound, the π -electron overlap between plane *A* and the pyridine and benzene rings seems to be so small, compared to the latter compound, that the C(5)—N(8) and C(6)—C(14) bonds exhibit normal single-bond distances.

The C(3)=S(4) length of 1.686 Å is in good agreement with the average of 1.675 Å found for a C=S bond in a half double bond of a thiocarbonyl group (Tamura, 1971). The C(3)—C(5) bond of 1.405 Å is slightly longer than the $C_{sp^2}-C_{sp^2}$ double bond in acetophenone desaurin (1.324 Å) (Lynch *et al.*, 1971), or bis(methylthio)methyleneacetophenone (1.378 Å) (Mellor & Nyburg, 1971*a*), whereas the C(5)—C(6) bond of 1.414 Å is shorter than the $C_{sp^2}-C=O$ single bond of 1.462 Å in acetophenone desaurin (Lynch *et al.*, 1971). Bugg & Sass (1965) reported the C—N bond length in a pyridinium ylide as 1.42 Å. However, in the title compound, the C(5)—N(8) length of 1.470 Å is almost equal to the $C_{sp^2}-N$ single bond of 1.48 Å observed in the diethylamine derivative (Bonamico, Mazzone, Vaciago & Zambonelli, 1973).

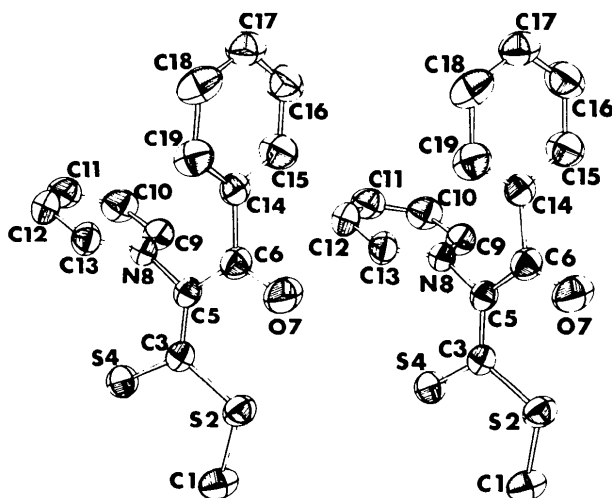


Fig. 1. Stereoscopic view of the molecule showing the atomic numbering used.

Table 4. Deviations (Å) from least-squares planes

Deviations of atoms not included in the calculations are given in parentheses.

	Plane A	Plane B	Plane C
C(1)	(−0.189)		
S(2)	−0.028		
C(3)	0.027	(1.512)	
S(4)	0.099		
C(5)	0.005	(0.175)	(0.900)
C(6)	0.007	(−0.992)	(−0.185)
O(7)	−0.039		(−1.320)
N(8)	−0.108	−0.001	
C(9)	(−1.348)	−0.002	
C(10)		−0.002	
C(11)		0.008	
C(12)		−0.011	
C(13)	(0.993)	0.007	
C(14)	0.065		−0.001
C(15)	(−1.057)		−0.007
C(16)			0.008
C(17)			−0.002
C(18)			−0.007
C(19)	(1.274)		0.008

The intramolecular non-bonded S(2)···O(7) distance is 2.715 Å which is shorter than the sum of the van der Waals radii for O and S (3.25 Å). Similar strong interactions have been reported for other compounds and the lengths are in the range 2.41–2.78 Å (Mammi, Bardi, Traverso & Bezzi, 1961; Williams, 1966; Lynch *et al.*, 1971; Mellor & Nyburg, 1971*a,b*). It is noticeable that the positively charged pyridine ring and the benzene ring come face to face, and the negatively charged S atom is above the plane of the pyridine ring as shown in Fig. 1. Thus, S(4) and N(8) which are on the *A* plane are a short distance apart (2.937 Å).

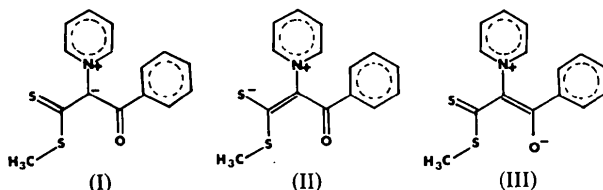
Table 5. Intermolecular contacts (Å) less than 3.8 Å

Standard deviations are in parentheses.

Symmetry code

(i)	$-1 + x,$	$y,$	z	(ii)	$1 - x,$	$\frac{1}{2} + y,$	$\frac{1}{2} - z$
(iii)	$1 - x,$	$-\frac{1}{2} + y,$	$\frac{1}{2} - z$	(iv)	$1 - x,$	$-y,$	$-z$
(v)	$1 - x,$	$-y,$	$1 - z$	(vi)	$x,$	$\frac{1}{2} - y,$	$\frac{1}{2} + z$
(vii)	$-1 + x,$	$\frac{1}{2} - y,$	$-\frac{1}{2} + z$				
C(1)···C(11) ⁱ	3.596 (5)			S(4)···C(18) ⁱⁱⁱ	3.487 (4)		
C(1)···C(12) ⁱ	3.623 (5)			S(4)···C(19) ⁱⁱⁱ	3.638 (4)		
C(1)···C(17) ^{vii}	3.552 (6)			O(7)···C(9) ^v	3.395 (5)		
C(1)···C(18) ⁱ	3.582 (6)			O(7)···C(10) ^v	3.717 (6)		
S(2)···C(9) ^v	3.772 (3)			O(7)···C(11) ⁱⁱ	3.759 (5)		
S(2)···C(17) ⁱ	3.487 (5)			O(7)···C(12) ^{vi}	3.769 (5)		
S(2)···C(18) ⁱ	3.781 (5)			O(7)···C(13) ^{vi}	3.163 (5)		
S(4)···C(12) ^{iv}	3.740 (4)						

From these data, three possible canonical forms of the title compound can be drawn: the pyridinium ylide structure (I) has sufficient negative charge on the central C(5) atom, but structures (II) and (III) may also make some contribution.



Acta Cryst. (1979). B35, 2445–2448

The 1:1 Salt from 2,2',6,6'-Tetramethyl-4^{4'}-bithiopyran (TMBTP) and 7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ)

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(Received 20 March 1979; accepted 12 June 1979)

Abstract. TMBTP–TCNQ, C₂₆H₂₀N₄S₂, triclinic, *P*1̄, *a* = 7.209 (1), *b* = 8.404 (1), *c* = 10.139 (2) Å, *α* = 107.21 (1), *β* = 97.33 (1), *γ* = 102.70 (1)°, *V* = 560.1 Å³, *D_m* = 1.35 ± 0.01, *D_c* = 1.342 Mg m⁻³. Full-matrix least-squares refinement with all atoms anisotropic based on 1752 reflections led a final *R* of 0.037

Intermolecular interatomic distances, less than 3.8 Å, are listed in Table 5, the shortest of which is O(7)···C(13) of 3.16 Å.

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and weighted *R* of 0.048. The TMBTP molecular ion is nearly planar except for the H atoms, while the TCNQ is slightly twisted about its long axis. The bond distances and angles observed for the TCNQ molecular ions are very close to literature values for TCNQ⁻. The molecular ions occur in an alternating (mixed) stack; least-squares planes of TMBTP and TCNQ are not quite parallel, deviating by 5.3°. The average distance from atoms of TMBTP to the plane of TCNQ is 3.4 Å.