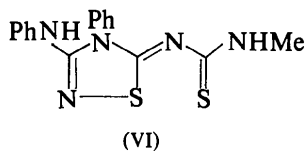
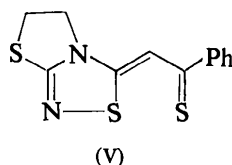
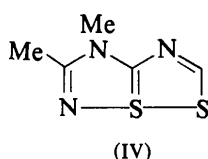
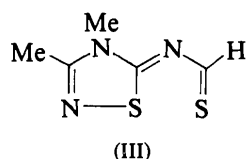


This confirms the structure (as III) proposed on the basis of ^1H NMR data (Mitchell, 1979).



The S—N and S...S distances are similar to those in (V) [S—N 1.727, S...S 2.750 Å (Glidewell, Holden & Liles, 1980)] and (VI) [S—N 1.697 (10) and S...S 2.822 (5) Å (Cuthbertson & Glidewell, 1981)], but the S—N distance is shorter, and the S—S distance longer

Table 5. The geometries of 1,2,4-thiadiazoline rings (Å)

	R_1	R_2	R_3		
VII	PhNH	Ph	H		
VIII	Ph	PhCH ₂	SO ₂ C ₆ H ₄ CH ₃		
IX	MeNH	Me	COMe		
	a	b	c	d	e
III	1.67 (1)	1.34 (1)	1.38 (1)	1.36 (1)	1.74 (1)
V	1.73 (1)	1.30 (1)	1.39 (1)	1.37 (1)	1.72 (1)
VI	1.697 (10)	1.303 (17)	1.403 (16)	1.407 (14)	1.754 (13)
VII	1.691 (3)	1.294 (4)	1.386 (4)	1.402 (4)	1.761 (4)
VIII	1.68	1.30	1.39	1.36	1.73
IX	1.685	1.29	1.39	1.36	1.725

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Structure of 3-Methyl-6-(5-phenyl-1,2-dithiol-3-ylideneamino)pyridine

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Abstract. C₁₅H₁₂N₂S₂, orthorhombic, *Pbca*, $a = 11.918$ (1), $b = 30.751$ (5), $c = 7.196$ (1) Å, $U = 2634.8$ Å³, $M_r = 284.40$, $D_c = 1.432$ Mg m⁻³ for $Z = 8$, $F(000) = 1184$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 0.337$ mm⁻¹; $R = 0.0700$ for 682

than in compounds containing a hypervalent S atom in the centre of an NSS chain; S—N range 1.779–1.863, S—S range 2.435–2.497 Å (see Glidewell *et al.*, 1980). The geometry of the 1,2,4-thiadiazoline ring is similar to those reported for (V), (VI), (VII) (Butler, Glidewell & Liles, 1978), (VIII) (L'Abbé, Verhelst, Toppet, King & Briers, 1976) and (IX) (Sato, Kinoshita, Hata & Tamura, 1972) (Table 5).

We thank the SRC for support, and Professor D. H. Reid and Dr J. A. Mitchell for the crystals.

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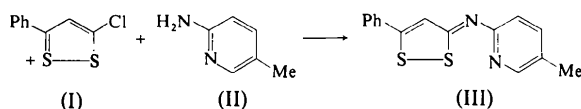
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reflections. The title compound does not contain a hypervalent S atom.

Introduction. The title compound (III) was obtained from the reaction of 3-chloro-5-phenyl-1,2-dithiol-1-ium chloride (I) with 2-amino-5-methylpyridine (II) (Mitchell, 1979). Crystals suitable for X-ray in-

vestigation were provided by Professor D. H. Reid and Dr J. A. Mitchell.



The intensities of 810 reflections in the octant $+h, +k, +l$ with $2^\circ \leq \theta \leq 30^\circ$, $l = 0-8$ ($0 \leq \mu \leq 23.365^\circ$), were measured, using a Stoe STADI-2 automatic two-circle diffractometer in the $\omega-2\theta$ scan mode, with graphite-monochromatized Mo $K\alpha$ radiation, for a crystal of dimensions $0.2 \times 0.05 \times 0.3$ mm, mounted about c . Each reflection was scanned using 100 steps of width 0.01° and a time of 2.0 s per step. Backgrounds were measured at each end of the scan for 100 s. Standard reflections were measured every 30 reflections and showed only small random deviations from their means. No corrections for absorption were made.

Systematic absences: $hk0$, $h \neq 2n$; $h0l$, $l \neq 2n$; $0kl$, $k \neq 2n$ showed the space group to be $Pbca$ (D_{2h}^{12} , No. 61).

The structure was solved using the fast centrosymmetric direct-methods program in *SHELX 76* (Sheldrick, 1976). Full-matrix least-squares refinement with anisotropic temperature factors for all non-H atoms, and with the H atoms in calculated positions ($C-H = 1.08$ Å) with a common isotropic temperature parameter, converged to give R ($= \sum \Delta / \sum F_o$, $\Delta = |F_o - |F_c||$) of 0.0700 and R_G ($= (\sum w\Delta^2 / \sum wF_o^2)^{1/2}$) of 0.0798 for 682 independent reflections with $F_o \geq 4\sigma(F_o)$. Weighting schemes with $w = [\sigma(F_o)^2 + gF_o^2]^{-1}$

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature parameters ($\times 10^3$)

The equivalent isotropic temperature parameters are defined as the geometric mean of the diagonal components of the diagonalized matrix of U_{ij} .

	x	y	z	U_{eq} (Å ²)
S(1)	2244 (3)	3928 (1)	1374 (8)	37 (2)
S(2)	2827 (3)	3266 (1)	1277 (8)	35 (3)
N(1)	5072 (9)	3156 (3)	1398 (20)	26 (7)
N(2)	3727 (9)	2612 (3)	1230 (23)	21 (7)
C(1)	4233 (12)	3436 (4)	1377 (25)	28 (9)
C(2)	4417 (9)	3881 (4)	1404 (23)	15 (7)
C(3)	3539 (12)	4158 (4)	1432 (27)	28 (9)
C(4)	4807 (12)	2717 (4)	1384 (26)	31 (9)
C(5)	5616 (12)	2386 (5)	1448 (29)	39 (11)
C(6)	5278 (15)	1964 (5)	1466 (32)	46 (12)
C(7)	4161 (15)	1859 (5)	1256 (33)	45 (11)
C(8)	3403 (13)	2183 (4)	1218 (27)	29 (10)
C(9)	3772 (15)	1388 (5)	1261 (34)	45 (13)
C(10)	3645 (11)	4628 (4)	1523 (21)	19 (8)
C(11)	4588 (13)	4828 (4)	2376 (30)	30 (10)
C(12)	4667 (16)	5280 (4)	2458 (33)	38 (11)
C(13)	3864 (14)	5550 (5)	1755 (26)	32 (12)
C(14)	2919 (13)	5355 (4)	0954 (24)	32 (10)
C(15)	2837 (14)	4908 (4)	0855 (21)	38 (10)

Table 2. Bond lengths (Å)

a	2.155 (5)	h	1.405 (18)	o	1.456 (17)
b	1.759 (14)	i	1.363 (19)	p	1.421 (19)
c	1.389 (18)	j	1.380 (21)	q	1.397 (18)
d	1.350 (17)	k	1.349 (18)	r	1.365 (21)
e	1.700 (14)	l	1.378 (15)	s	1.402 (21)
f	1.321 (15)	m	1.332 (15)	t	1.381 (18)
g	1.389 (15)	n	1.520 (18)	u	1.379 (18)

Table 3. Bond angles ($^\circ$)

ab	91.5 (4)	gh	123.3 (13)	lm	120.3 (12)
ae	95.7 (4)	gm	117.1 (12)	op	121.2 (13)
bc	116.4 (10)	hi	119.2 (14)	ou	123.0 (13)
bf	122.0 (10)	hm	119.6 (12)	pq	120.2 (16)
cd	120.0 (11)	ij	120.6 (15)	pu	115.7 (12)
cf	121.6 (12)	jk	118.5 (14)	qr	123.0 (17)
de	116.3 (9)	jn	121.2 (15)	rs	117.1 (13)
do	124.1 (13)	kl	121.5 (14)	st	120.4 (15)
eo	119.5 (10)	kn	120.1 (15)	tu	123.7 (15)
fg	117.5 (11)				

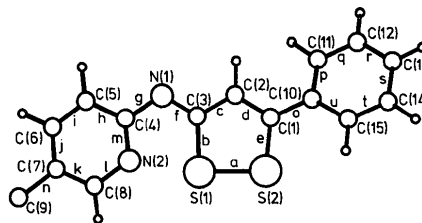


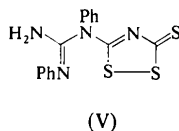
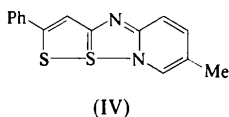
Fig. 1. The molecule showing the numbering scheme for the atoms and bonds.

were tried for various fixed values of g ($0 \leq g \leq 0.1$), but none gave as satisfactory results as unit weights. Therefore unit weights were used throughout the refinement. A final difference map showed no significant residual electron density. Complex neutral-atom scattering factors were used for all atoms (Cromer & Mann, 1968; Cromer & Liberman, 1970). The reductions in R_G at all stages of the refinement were significant at the 99.5% level (Hamilton, 1965). The final coordinates are given in Table 1.* These, together with the full covariance matrix, were used to calculate the bond lengths and bond angles given in Tables 2 and 3. Fig. 1 shows the molecule and the numbering scheme for atoms and bonds.

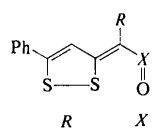
Discussion. The S—S distance of 2.155 (5) Å and the S(2)···N(2) distance of 2.282 (10) Å show that the

* Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36024 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

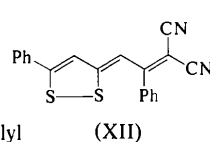
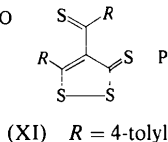
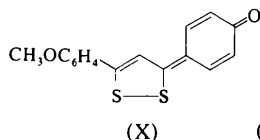
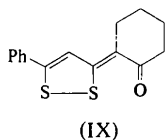
compound should be represented as (III), rather than containing a hypervalent S atom as in (IV).



The S—S and S...N distances are similar to those in (V) (2.121 and 2.324 Å respectively) (Butler, Glidewell & Liles, 1978), but the S—S distance is shorter, and the S...N distance is longer than for compounds containing a hypervalent S atom at the centre of a NSS chain: S—S range 2.435–2.497, S—N range 1.779–1.863 Å (see Butler, Glidewell & Liles, 1978; or Glidewell, Holden & Liles, 1980). Although it is too long to be regarded as a bond, the S...N distance is shorter than the sum of the van der Waals radii of S and N (3.35 Å, Pauling, 1960). This phenomenon is also observed in (V) and in a number of 3*H*-1,2-dithiole derivatives containing S—S...O chains (VI)–(IX), where the S—S and S...O distances are (VI) 2.178 (2) and 2.034 (5) Å (Johnson, Reid & Paul, 1971), (VII) 2.074 (3) and 2.373 (7) Å (Reid & Paul, 1971), (VIII) 2.106 (3) and 2.382 (6) Å (Hordvik, Sletten & Sletten, 1969), and (IX) 2.126 (4) and 2.255 (8) Å (Pinel, Mollier, Llaguno & Paul, 1971). The S...O distances are all less than the sum of the van der Waals radii of S and O (3.2 Å, Pauling, 1960). In most cases the S—S distances show a slight increase compared with the S—S distances in (X) (2.054 Å) (Wei, Paul, Le Coustumer, Pinel & Mollier, 1977), (XI) [2.044 (3) Å] (Cheng & Nyburg, 1977) and (XII) [2.072 (4) Å] (Nguyen-Huy-Dung & Etienne, 1978), where there are no exocyclic S...X contacts.



(VI) PhCo N
(VII) Br NO
(VIII) Ph CH



The geometries of the pyridyl and phenyl rings show no exceptional features and the geometry of the dithiole ring is similar to those in (VI)–(IX). The dithiole and pyridyl rings are nearly coplanar. The phenyl ring, however, is twisted with respect to the dithiole ring with a dihedral angle of 26.5 (8)°. This compares with the equivalent dihedral angles in (VI) (20.3°), (VIII) (23.4°) and (XII) (29.4°), but is greater than the equivalent dihedral angle in (VII) (9.9°) and the dihedral angle between the dithiole ring and the methoxyphenyl ring in (X) (9.4°).

We thank the SRC for support, and Professor D. H. Reid and Dr J. A. Mitchell for the crystals.

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