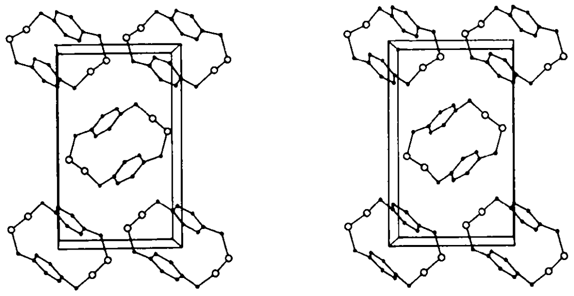

Fig. 3. Stereoview of the molecular packing in compound (VI). The origin of the unit cell lies at the upper left corner, with **a** pointing towards the reader, **b** downwards, and **c** from left to right. Hydrogen atoms have been omitted for clarity. Compound (V) has a similar mode of molecular packing.

A stereoview of the molecular packing in (VI) is illustrated in Fig. 3; compound (V) has a similar mode of herringbone arrangement of structural units in the unit cell with no unusual van der Waals interactions. Finally, we conclude with the observation that para-cyclophanes of inherent $\bar{1}$ molecular symmetry generally occupy an inversion center in the crystalline state. Besides compounds (V), (VI), (VII), (X) and (XI), many more examples are found in the literature (Keehn, 1983).

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Structure of an Eight-Membered CN_4S_3 Ring with a $Ph_3P{=}N$ Substituent

BY RENÉ T. BOERÉ, GEORGE FERGUSON AND RICHARD T. OAKLEY

Guelph–Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

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Abstract. 7-Phenyl-3-(triphenylphosphinimino)-1,3,5,-2,4,6,8-trithiatetrazocine, $C_{25}H_{20}N_5PS_3$, $M_r = 517{\cdot}64$, monoclinic, $P2_1/c$, $a = 13{\cdot}957\ (3)$, $b = 9{\cdot}242\ (3)$, $c = 19{\cdot}473\ (4)$ Å, $\beta = 102{\cdot}80\ (2)°$, $V = 2449{\cdot}4$ Å^3, $Z = 4$, $D_x = 1{\cdot}40\ \text{g cm}^{-3}$, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 3{\cdot}8\ \text{cm}^{-1}$, $F(000) = 1072$, $T = 293\ (1)$ K, final $R = 0{\cdot}038$ for 2430 observed reflections. The molecule has a phenyl ring substituted at a planar carbon, and a $Ph_3P{=}N$ group substituted at S in the 3-position. The CN_4S_3 ring is folded by 114·5°, with an almost planar SNCNS fragment, and an *endo*-S-envelope SNSNS fragment (dihedral 145·0°). The $Ph_3P{=}N$ substituent at S is *endo* and the transannular S···S contact is 2·415 (1) Å.

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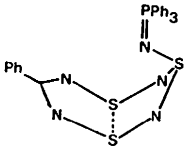
Introduction. In the course of our studies of reactions of the bicyclic molecule PhCN$_5$S$_3$ (I) (Boeré, Cordes & Oakley, 1985) with nucleophiles, we isolated the compound PhC(NSN)$_2$SN=PPh$_3$ (II) in essentially quantitative yield from the reaction of (I) with triphenylphosphine.



(II)

Eight-membered sulfur–nitrogen heterocycles commonly exist both in planar and folded conformations. We have determined by a single-crystal X-ray diffraction study that (II) is of the folded type.

Experimental. Yellow plates crystallized from CH$_2$Cl$_2$/CH$_3$CN, data crystal $0{\cdot}15 \times 0{\cdot}20 \times 0{\cdot}36$ mm. Enraf–Nonius CAD-4 diffractometer, Mo radiation, graphite monochromator, ω–2θ scans. Unit cell determined from 25 reflections, $7 < \theta < 12°$. Data collected with $2 < \theta < 27°$, $h\,0\rightarrow17$, $k\,0\rightarrow21$, $l\,-24\rightarrow24$, 6040 reflections measured, 5155 unique ($R_{\rm int} = 0{\cdot}021$), 2430 reflections with $I > 3\sigma(I)$ used in refinement. Standard reflections $4\bar{1}1$, $5\bar{3}0$, $20\bar{8}$, negligible decay, no correction; absorption correction applied, with transmission coefficients from 0·926 to 0·960. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), and refined by full-matrix least-squares techniques which minimized $\sum w(\Delta F)^2$. The 20 H atoms appeared as top 20 peaks in difference map, and included in idealized positions (C—H = 0·95 Å) with fixed isotropic thermal parameters. 307 parameters refined to give $R = 0{\cdot}038$, $wR = 0{\cdot}044$ and goodness-of-fit $S = 1{\cdot}34$. Final $(\Delta/\sigma)_{\rm max} = 0{\cdot}000$, $\Delta\rho = 0{\cdot}18$ e Å^{-3}. Weighting scheme based on counting statistics ($p = 0{\cdot}04$), and plots of $\sigma(F)$ *versus* F, order of data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974), all calculations performed with Enraf–Nonius *SDP-Plus* package (Enraf–Nonius, 1982). Atomic coordinates and equivalent isotropic temperature factors are given in Table 1.* Selected bond distances and angles are presented in Table 2. An *ORTEP*II illustration (Johnson, 1976) of the molecule is given in Fig. 1.

Discussion. PhC(NSN)$_2$SN=PPh$_3$ has a folded shape, and the overall geometry is similar to that reported for the related molecules ^{t}BuC(NSN)$_2$SCl (Boeré, Oakley & Cordes, 1985) and Me$_2$NC(NSN)$_2$SCl (Chivers, Richardson & Smith, 1985). The dihedral angle between the essentially planar SNCNS fragment and

Table 1. *Atomic positional and equivalent isotropic thermal parameters*

	x	y	z	$B_{\rm eq}$(Å^2)
S(1)	0·10631 (6)	0·0757 (1)	0·40757 (5)	4·04 (2)
S(2)	0·16831 (8)	0·0587 (1)	0·55377 (5)	5·80 (3)
S(3)	0·03822 (6)	0·2294 (1)	0·50989 (5)	5·24 (2)
P	0·22146 (6)	0·2080 (1)	0·32490 (4)	3·15 (2)
N(1)	0·0172 (2)	0·1600 (3)	0·4333 (2)	4·52 (7)
N(2)	0·1572 (2)	−0·0161 (3)	0·4788 (2)	5·10 (8)
N(3)	0·2463 (2)	0·1923 (3)	0·5690 (2)	5·03 (8)
N(4)	0·1196 (2)	0·3587 (3)	0·5226 (1)	4·29 (7)
N(5)	0·1840 (2)	0·1980 (3)	0·3967 (1)	3·78 (6)
C(1)	0·2123 (2)	0·3245 (4)	0·5499 (2)	3·96 (8)
C(11)	0·2841 (2)	0·4450 (4)	0·5608 (2)	3·73 (8)
C(12)	0·2543 (3)	0·5888 (4)	0·5542 (2)	5·2 (1)
C(13)	0·3224 (3)	0·6971 (5)	0·5628 (2)	6·7 (1)
C(14)	0·4201 (3)	0·6657 (5)	0·5769 (3)	7·2 (1)
C(15)	0·4497 (3)	0·5264 (5)	0·5832 (3)	7·6 (1)
C(16)	0·3830 (3)	0·4154 (5)	0·5752 (2)	5·6 (1)
C(21)	0·2486 (2)	0·3944 (4)	0·3127 (2)	3·05 (7)
C(22)	0·2541 (3)	0·4474 (4)	0·2471 (2)	4·86 (9)
C(23)	0·2804 (3)	0·5899 (4)	0·2395 (2)	5·7 (1)
C(24)	0·3000 (3)	0·6790 (4)	0·2964 (2)	4·8 (1)
C(25)	0·2936 (3)	0·6292 (4)	0·3608 (2)	5·0 (1)
C(26)	0·2675 (3)	0·4868 (4)	0·3694 (2)	3·99 (8)
C(31)	0·3343 (2)	0·1090 (4)	0·3310 (2)	3·30 (7)
C(32)	0·3753 (3)	0·0359 (4)	0·3922 (2)	4·13 (9)
C(33)	0·4624 (3)	−0·0379 (4)	0·3980 (2)	5·1 (1)
C(34)	0·5096 (3)	−0·0391 (4)	0·3435 (2)	5·5 (1)
C(35)	0·4692 (3)	0·0320 (5)	0·2822 (2)	5·9 (1)
C(36)	0·3821 (1)	0·1052 (4)	0·2753 (2)	4·83 (9)
C(41)	0·1355 (2)	0·1445 (4)	0·2488 (2)	3·23 (7)
C(42)	0·0532 (3)	0·2279 (4)	0·2209 (2)	4·56 (9)
C(43)	−0·0199 (3)	0·1736 (5)	0·1677 (2)	5·4 (1)
C(44)	−0·0114 (3)	0·0360 (5)	0·1421 (2)	5·2 (1)
C(45)	0·0697 (3)	−0·0455 (4)	0·1689 (2)	5·0 (1)
C(46)	0·1422 (3)	0·0077 (4)	0·2221 (2)	4·34 (9)

Equivalent isotropic thermal parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ac\cos\beta B(1,3)]$.

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

S(1)–N(1)	1·638 (3)	P–C(21)	1·791 (3)
S(1)–N(2)	1·647 (3)	P–C(31)	1·803 (3)
S(1)–N(5)	1·612 (2)	P–C(41)	1·787 (3)
S(2)–N(2)	1·591 (3)	N(3)–C(1)	1·334 (4)
S(2)–N(3)	1·630 (3)	N(4)–C(1)	1·323 (4)
S(3)–N(1)	1·589 (3)	C(1)–C(11)	1·481 (4)
S(3)–N(4)	1·629 (3)	C–C ring (min.)	1·350 (6)
S(2)···S(3)	2·415 (1)	C–C ring (max.)	1·392 (4)
P–N(5)	1·601 (2)	C–C ring (ave.)	1·374
N(1)–S(1)–N(2)	101·6 (2)	S(1)–N(1)–S(3)	118·9 (2)
N(1)–S(1)–N(5)	106·6 (1)	S(1)–N(2)–S(2)	119·0 (2)
N(2)–S(1)–N(5)	107·1 (1)	S(2)–N(3)–C(1)	117·5 (2)
N(2)–S(2)–N(3)	115·0 (2)	S(3)–N(4)–C(1)	118·2 (3)
N(1)–S(3)–N(4)	114·6 (1)	S(1)–N(5)–P	121·0 (2)
N(5)–P–C(21)	107·0 (1)	N(3)–C(1)–N(4)	125·9 (3)
N(5)–P–C(31)	111·3 (1)	N(3)–C(1)–C(11)	117·5 (3)
N(5)–P–C(41)	114·6 (1)	N(4)–C(1)–C(11)	116·6 (3)
C(21)–P–C(31)	106·8 (1)	C–C–C ring (min.)	118·4 (3)
C(21)–P–C(41)	109·2 (1)	C–C–C ring (max.)	121·1 (4)
C(31)–P–C(41)	107·7 (1)	C–C–C ring (ave.)	120·0

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* Lists of structure factors, anisotropic temperature factors, H-atom positional parameters, complete interatomic distances and angles, and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42834 (59 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the *endo*-S(1)-envelope-shaped SNSNS fragment is 114·5°, while the envelope flap has a dihedral of 145·0°. In ^{t}BuC(NSN)$_2$SCl the fold angle is approximately 113°, and there is an *endo*-envelope with a flap angle of 158°. The related dithiatetrazocine $Me_2NC(NSN)_2CNMe_2$ (Ernest, Holick, Rihs, Schomburg, Shoham, Wenkert & Woodward, 1981) has two planar fragments which are folded with a dihedral of 101°. On the other hand, the cation $CF_3C(NSN)_2S^+$ (Höfs, Hartmann, Mews & Sheldrick, 1984) has a planar CN_4S_3 ring.

The transannular S···S contact of 2·415 (1) Å is shorter than the range 2·45–2·58 Å observed in a series of folded sulfur–nitrogen ring compounds (see compilation in Boeré, Oakley & Cordes, 1985), but longer than the 2·378 Å reported for ^{t}BuC(NSN)$_2$SCl. The $Ph_3P{=}N$ substituent is *endo*, a conformation which may be stabilized by a 3·15 Å contact between N(5) and C(1), slightly less than the sum of the van der Waals radii. Similar conformations are observed in the structures of $Ph_3P{=}NS(NSN)_2SN{=}PPh_3$ (Bojes, Chivers, Cordes, Maclean & Oakley, 1981), $Me_2NS(NSN)_2SNMe_2$ (Roesky, Pelz, Gieren & Hädicke, 1981) and $(Me_2N)_2C_2N_4S_2Cl^+$ (Boeré, Cordes, Oakley & Reed, 1985).

The chemically equivalent pairs of S–N bonds in the eight-membered ring can be averaged on a normal distribution (Stout & Jensen, 1968), and show an interesting long–short–long alternation around the ring from S(1) to N(3) [1·643 (5), 1·590 (1), 1·630 (5) Å]. By contrast, the alternation in the corresponding bonds in ^{t}BuC(NSN)$_2$SCl is short–long–short [1·577 (2), 1·635 (2), 1·601 (5) Å]. As expected the C–N bond lengths are essentially identical in the two structures [mean values 1·329 (6) and 1·330 (4) Å]. The induction of alternating bond lengths in delocalized sulfur–nitrogen compounds has been noted before, for example in $Me_2NS(NSN)_2SNMe_2$ (Roesky *et al.*, 1981), where the *endo* $Me_2N{-}S$ bond is virtually single, while the *exo* has marked double-bond character. We attribute the *opposite* inductions in the $Ph_3P{=}N$ and Cl substituted trithiatetrazocines to the better π-donor properties of the former substituent.

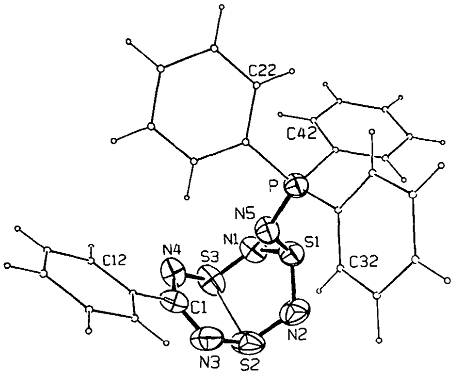

Fig. 1. An illustration of the molecule, showing the geometry and atom-numbering scheme.

The structures of two further $Ph_3P{=}N$ substituted sulfur–nitrogen compounds have been reported: $Ph_3P{=}NS_3N_3$ (Holt & Holt, 1974), and $Ph_3P{=}NSNSS$ (Chivers, Cordes, Oakley & Swepston, 1981). The exocyclic S–N and P=N bond lengths in (II), 1·612 (2) and 1·601 (2) Å, respectively, are within the ranges observed for these bonds in such compounds [1·599 (4) to 1·621 (4) Å for S–N; 1·592 (4) to 1·65 (1) Å for P=N].

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