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trans-Di-1,2-(6-methyl-2-thio-3-*p*-tolyl-1,2,3,4-tetrahydro-1,3,2-benzodiazaphosphorine)

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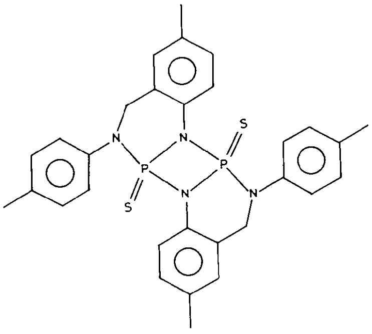
Abstract. $(C_{15}H_{15}N_2PS)_2$, monoclinic, $P2_1/b$; $a = 11{\cdot}94\,(1)$, $b = 22{\cdot}44\,(2)$, $c = 7{\cdot}00\,(1)$ Å, $\beta = 106{\cdot}9\,(1)°$; $Z = 2$, $D_c = 1{\cdot}23$, $D_m = 1{\cdot}23$ g cm^{-3}; μ(Mo $K\alpha$) = 2·7 cm^{-1}, $\lambda = 0{\cdot}7107$ Å. The crystals are poor diffractors of X-rays and slowly decompose on irradiation. The structure was determined from 529 independent reflexions measured on a linear diffractometer, and was refined by constrained full-matrix least squares to $R = 0{\cdot}14$. The molecule contains two N atoms with pyramidal configurations and P—N bond lengths between 1·74 and 1·80 Å.

Introduction. The title compound (I) contains two N atoms in different environments, one in a phosphazane ring and the other, also bonded to P, in a six-membered heterocycle. The structure of the compound was determined in order to examine the effect of the different environments upon the N atoms.

The crystals are very thin needles and have an approximate square cross-section of side ~ 0·05 mm. Several crystals were mounted about the needle axis (001) inside capillary tubes and the dimensions of the unit cell were determined from oscillation and Weissenberg photographs. Systematic extinctions $0kl$, $k = 2n + 1$; $00l$, $l = 2n + 1$ uniquely indicated space group $P2_1/b$. Only one crystal was found that gave a reasonable number of X-ray reflexions. From this, 529 unique reflexions were measured on a Hilger & Watts linear diffractometer ($hk0$–7). This is about 13% of those available with Cu radiation.

The crystal steadily decomposed in the X-ray beam and there was a 30% reduction of the intensity of the $hk0$ reflexions between the start and end of data collection. There did not, however, appear to be any appreciable difference in the relative intensities of the reflexions. The data were corrected for Lorentz and polarization factors but not for absorption.



(I)

The positions of the P and S atoms were determined from a Patterson function sharpened to 'point atoms at rest'; the remaining atoms were found from successive F maps.

The trial structure with individual isotropic temperature factors was refined by full-matrix least squares with the additional condition that certain bond lengths and interbond angles have reasonable values (Waser, 1963).

In the phenyl groups the C—C and C—Me lengths were constrained to be 1·39 and 1·51 Å respectively, and the distances betwen the non-bonded atoms were also restricted to such lengths that the interbond angles were 120°. No conditions were placed upon the P—N and N—C lengths. In the refinement it was found that when e.s.d.'s of 0·02 and 0·04 Å were applied (Rollett, 1970) to the bonded and non-bonded distances respectively, the refinement converged at $R = 0{\cdot}21$; convergence occurred at $R = 0{\cdot}17$ when the e.s.d.'s were adjusted for each distance so that the total addition from the constraints to any diagonal element of the normal matrix was initially never greater than a quarter of the term derived from the minimization of $(F_o - F_c)^2$. This was progressively reduced as the refinement proceeded until the constraints were contributing no more than a tenth to each element. The given e.s.d.'s at the end were approximately 0·05 and 0·1 Å for the bonded and non-bonded distances respectively.

Any attempt at least squares without constraints caused the refinement to diverge; when shifts (a tenth of those calculated) were applied to the parameters, the refinement still diverged, though the progress was somewhat more stately.

A difference synthesis calculated when R was 0·17 suggested marked anisotropy of the P, S and methyl C atoms. Refinement was continued with anisotropic temperature factors for these four atoms and with the constraints unchanged. The refinement converged at $R = 0{\cdot}14$. A Hamilton (1965) test indicated that the decrease in R was significant. At this stage there was no significant change in parameters when the constraints were removed. The weights were given by $w = [F_o + 0{\cdot}04(F_o)^2]^{-1}$.

All calculations were performed with Sheldrick's (1975) system on the University of Ulster's 1903A computer.

The final atomic parameters are given in Table 1.*

Table 2. *Interatomic distances* (Å) *and interbond angles* (°)

P(1)—S(1)	1·906 (12)	C(4)—C(5)	1·39 (4)
P(1)—N(1)	1·75 (2)	C(4)—C(7)	1·47 (5)
P(1)—N(2)	1·74 (2)	C(5)—C(6)	1·40 (4)
P(1)—N(2)′	1·80 (2)	C(11)—C(12)	1·41 (4)
N(1)—C(1)	1·38 (3)	C(11)—C(16)	1·37 (4)
N(1)—C(21)	1·45 (4)	C(12)—C(13)	1·41 (4)
N(2)—C(11)	1·33 (4)	C(13)—C(14)	1·39 (4)
C(1)—C(2)	1·38 (2)	C(14)—C(15)	1·41 (4)
C(1)—C(6)	1·40 (3)	C(14)—C(17)	1·47 (4)
C(2)—C(3)	1·42 (4)	C(15)—C(16)	1·42 (4)
C(3)—C(4)	1·40 (4)	C(16)—C(21)	1·53 (4)

N(1)—P(1)—S(1)	113 (1)	C(5)—C(4)—C(3)	115 (3)
N(2)—P(1)—S(1)	125 (1)	C(7)—C(4)—C(3)	123 (3)
N(2)′—P(1)—S(1)	111 (1)	C(5)—C(4)—C(7)	122 (3)
N(1)—P(1)—N(2)	100 (1)	C(6)—C(5)—C(4)	122 (3)
N(1)—P(1)—N(2)′	117 (1)	C(12)—C(11)—N(2)	117 (2)
N(2)—P(1)—N(2)′	89 (1)	C(16)—C(11)—N(2)	120 (2)
C(1)—N(1)—P(1)	112 (1)	C(12)—C(11)—C(16)	122 (2)
C(21)—N(1)—P(1)	118 (2)	C(13)—C(12)—C(11)	117 (2)
C(21)—N(1)—C(1)	123 (2)	C(14)—C(13)—C(12)	122 (2)
C(11)—N(2)—P(1)	124 (2)	C(15)—C(14)—C(13)	120 (2)
P(1)′—N(2)—P(1)	91 (1)	C(17)—C(14)—C(13)	116 (2)
C(11)—N(2)—P(1)′	126 (2)	C(15)—C(14)—C(17)	124 (2)
C(2)—C(1)—N(1)	123 (2)	C(16)—C(15)—C(14)	119 (2)
C(6)—C(1)—N(1)	121 (2)	C(21)—C(16)—C(11)	120 (2)
C(2)—C(1)—C(6)	113 (2)	C(15)—C(16)—C(11)	119 (2)
C(3)—C(2)—C(1)	123 (2)	C(21)—C(16)—C(15)	119 (2)
C(4)—C(3)—C(2)	121 (3)	C(16)—C(21)—N(1)	110 (2)

Table 1. *Final atomic parameters* (×10⁴)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P(1)	*1073 (7)*	*293 (4)*	*149 (11)*	*121*	232	*154*	38	*−33*	*108*
S(1)	1827 (8)	1125 (4)	941 (14)	306	165	426	−73	6	32
C(7)	5664 (30)	1056 (23)	−5885 (67)	309	794	1714	395	432	−155
C(17)	1145 (37)	−2214 (16)	5331 (51)	760	552	454	26	−474	−283

	x	y	z	U_{iso}		x	y	z	U_{iso}
N(1)	2070 (23)	−113 (13)	−480 (36)	354	C(11)	319 (28)	−759 (14)	2321 (37)	236
N(2)	87 (27)	−270 (15)	−1514 (42)	398	C(12)	−191 (29)	−947 (15)	4120 (41)	349
C(1)	2879 (19)	214 (12)	−1789 (27)	218	C(13)	88 (31)	−1452 (15)	5006 (47)	461
C(2)	2719 (25)	149 (15)	−3739 (32)	240	C(14)	827 (28)	−1749 (14)	4150 (37)	299
C(3)	3575 (26)	470 (20)	−5088 (45)	683	C(15)	1313 (31)	−1551 (14)	2344 (40)	418
C(4)	4735 (25)	753 (18)	−4530 (42)	460	C(16)	1130 (26)	−1009 (13)	1519 (36)	188
C(5)	4946 (28)	725 (21)	−2583 (43)	544	C(21)	1661 (31)	−787 (16)	−433 (45)	260
C(6)	4049 (22)	471 (16)	−1269 (41)	432					

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* The observed structure amplitudes and structure factors calculated from the final atomic parameters listed in Table 1 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31964 (5pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The scattering factors were those given in *International Tables for X-ray Crystallography* (1974) and were corrected for dispersion. The bond distances and angles are given in Table 2. Fig. 1 shows the unique molecule and Fig. 2 the packing. The diagrams were drawn by *STRPL* (Cameron, 1973).

Discussion. The cell contains two isolated molecules of the dimer on centres of symmetry at (0,0,0) and $(\frac{1}{2},0,\frac{1}{2})$. This requires that the cyclodiphosphazane ring P(1), N(2), P(1)′, N(2)′ be planar with the two S atoms in the *trans* configuration. The molecules pack with the plane of the phenyl group C(11)–C(16) approximately parallel to (140). A stack of these phenyl groups is formed parallel to the *a* face down the centre of the unit cell. The other phenyl group C(1)–C(6) packs along **b** with the edge of one group against the plane of the centrosymmetrically related group translated along the axis by the *b* glide.

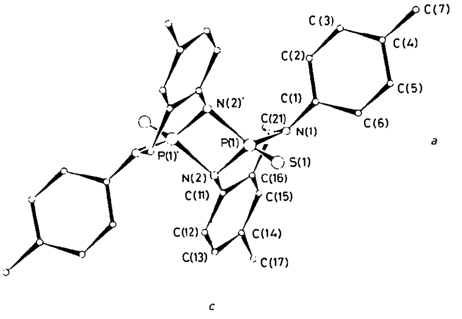

Fig. 1. The molecule projected along **b**.

The fragment of the structure N(1)–P(1)–N(2)–C(11) is approximately planar and the least-squares best plane through these four atoms makes an angle of 123° with the P_2N_2 plane. The torsion angle between the plane of the phenyl ring C(1)–C(6) and the P(1)–N(1) bond, about the N(1)–C(1) bond, is 92°; that of the phenyl ring C(11)–C(16) and the P(1)–N(2) bond, about the N(2)–C(11) bond, is 28°.

Within the molecule the various C–C, C–N and P=S lengths (and interbond angles) are not significantly different from the expected values.

The P–N lengths, however, are unusual. Those in the phosphazane ring are 1·740 (18) and 1·798 (18) and that in the heterocycle 1·753 (19) Å. Normally the P–N lengths in diphosphazanes are much shorter, *e.g.* 1·688 Å in $[PhP(S)NCH_3]_2$ (Cameron, Howlett & Prout, 1975). In these compounds, though, the N atom has always been sp^2, while in the present compound, with N(2) 0·37 Å from the plane of the three atoms bonded to it and with the sum of the bond angles only 342°, it is predominantly sp^3. N(1) also has considerable sp^3 character since it is 0·24 Å from the plane of its bonded atoms and the sum of the interbond angles is 352°. The distortion about the two N atoms is probably the result of the steric requirements within the heterocycle P(1), N(1), C(21), C(16), C(11) and N(2).

These long P–N bonds in the present compound could well explain the surprising instability of the crystal; $[PhP(S)NPh]_2$, for example, is quite stable (Peterson & Wagner, 1973).

The interbond angles in the phosphazane ring P–N–P, 91·0 (2), and N–P–N, 89·0 (2), compare with 98·1 (3) and 81·9 (2)° in *trans*-$[PhP(S)NPh]_2$

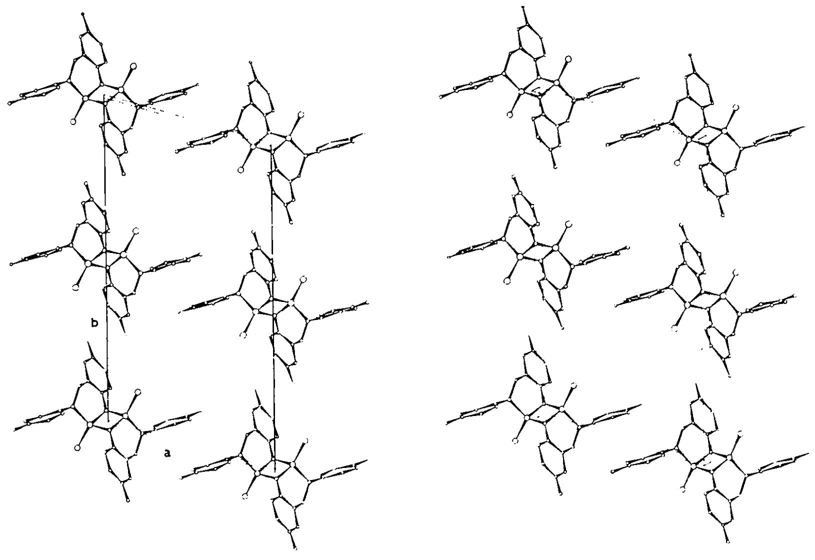

Fig. 2. A stereoscopic projection of the unit cell.

where, however, the P—N distances are much shorter [1·695 (4) Å], and the P···P (2·52) and N···N (2·25 Å) non-bonded interactions across the ring are said to distort its shape from a regular square. In the present compound the non-bonded distances are P(1)···P(1)′ (2·53) and N(2)···N(2)′ (2·48 Å). The longer N···N contact distance is consistent with the increased space required to accommodate an sp^3 rather than an sp^2 N atom (Coulson, 1961).

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6-*N*-Dimethylaminonaphthylsulphonylaziridine

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Abstract. $C_{14}H_{16}N_2O_2S$, monoclinic, space group $P2_1/a$, $Z = 4$, $a = 22{\cdot}277$ (2), $b = 7{\cdot}469$ (2), $c = 8{\cdot}001$ (1) Å, $\beta = 100{\cdot}18$ (8)°, final $R = 0{\cdot}040$ for 1233 intensities with $I > \sigma(I)$. The naphthalene system is not planar; the sulphone-group tetrahedron is very distorted with evidence of interaction between S d_{xy} and C $p\pi$ orbitals. The aziridene group shows the angles, but not bond lengths, expected from other measurements of systems containing this group. The *N*-dimethylamino group has the usual geometry.

Introduction. The commercial product (Pierce, Rockford, Illinois) was crystallized by cooling an ethanol–water solution. Intensities were collected on a Philips PW 1100 four-circle diffractometer. 1379 independent reflexions were measured in the Cu sphere in the $\theta/2\theta$ scan mode.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). The positions and anisotropic thermal factors of all non-hydrogen atoms were refined by full-matrix least squares. During the refinement it was possible to locate the H atoms on a difference synthesis; in the last cycle they were refined isotropically. Table 1 lists the fractional atomic coordinates and thermal parameters, Table 2 the bond angles and Table 3 the bond lengths.*

Discussion. The title compound (*N*-dansylaziridine) (Fig. 1) is an activated molecule belonging to the group of aziridines which easily react with nucleophiles. It is a fluorescent selective reagent towards thiolic groups and finds its main use in biochemistry as a marker of cysteines present in proteins (Scouten, Lubcher & Baughman, 1974).

Naphthalene system. The usual distribution of bond lengths is observed (Aleby, 1972; Cruickshank, 1957). The mean C_{sp^2}—C_{sp^2} length is 1·402 (3) and the mean C_{sp^2}—H distance 0·97 (9) Å.

The internal angle at the S-substituted C atom is 121·5 (3)° in good agreement with values reported for phenyl sulphones (Domenicano, Vaciago & Coulson, 1975). The naphthalene system is not planar: the

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31969 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.