

1,21 Å. C(2)—O(1) [1,382 (3) Å], C(8a)—O(1) [1,379 (3) Å] et C(7)—O(11) [1,367 (3) Å] diffèrent peu des liaisons semblables rencontrées dans la méthyl-4 ombelliférone (Shimizu, Kashino & Haisa, 1975), dans l'avicennine (Lai & Marsh, 1974) et dans l'esculétine (Ueno & Saito, 1977). La différence de longueurs entre les deux liaisons issues de O(11) [1,367 (3) et 1,416 (3) Å] n'est pas fortuite puisqu'on observe une différence du même ordre entre les mêmes liaisons dans l'avicennine déjà citée.

Comme prévu, C(12), C(13) et C(14) sont alignés. La liaison C(13)—C(14), longue de 1,157 (4) Å, paraît légèrement courte si on la compare aux liaisons acétyléniques rencontrées dans C₂H₂ (1,204 Å) (*International Tables for X-ray Crystallography*, 1968), dans le butyne-2 (1,211 Å) (Wyckoff, 1966a) ou dans l'acide butyne-2 dioïque dihydraté (1,19 Å) (Wyckoff, 1966b). Dans la mesure où ce raccourcissement possède une signification physique, il peut indiquer une mobilité importante de l'atome H(14). C(12)—C(13) [1,454 (4) Å] est comparable aux liaisons C—C voisines d'une liaison acétylénique. Par exemple, dans le butyne-2 la même liaison mesure 1,457 Å.

Les angles entre les liaisons homologues présentes dans la coumarine, la daphnétine (Ueno & Saito, 1976), l'esculétine, l'avicennine, la méthyl-4 ombelliférone et le composé étudié ont, compte tenu des incertitudes, les mêmes valeurs, à de rares exceptions près.

Dans l'étude des contacts intermoléculaires, il a été admis pour rayons de van der Waals 1,70 et 1,77 Å pour les atomes de carbone aliphatique et aromatique et 1,50 Å pour les atomes d'oxygène (Bondi, 1964). Des rayons égaux à 1,72 Å ont été attribués aux atomes de carbone éthylénique et acétylénique. Il y a contact entre les atomes des cycles *A* et *B* et les atomes des cycles qui

s'en déduisent par les translations $\pm c$. La distance entre les plans moyens de l'ensemble des cycles *A* et *B* de deux molécules voisines est de 3,459 (5) Å, c'est-à-dire à peine supérieure à la distance de deux plans consécutifs d'atomes de carbone dans le graphite. Il y a aussi contact entre O(9) et C(12ⁱ) [3,327 (3) Å] [(i): $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$] et entre C(14) et son homologue C(14ⁱⁱ) [3,488 (5) Å] [(ii): $-\frac{1}{2}-x, -y, \frac{1}{2}+z$].

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Structure of 1-Dimethylamino-2,2,3,4,4-pentamethyl-1λ⁵-phosphetane 1-Sulphide, C₁₀H₂₂NPS, at 105 K

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Abstract. $M_r = 219.33$, orthorhombic, $Pnam$, $a = 1.12(1) \text{ g cm}^{-3}$ (by flotation at 293 K), $Mo K\alpha$, $\lambda = 12.106(2)$, $b = 8.481(1)$, $c = 12.239(4) \text{ Å}$, $V = 0.71073 \text{ Å}^3$, $\mu = 3.36 \text{ cm}^{-1}$, $F(000) = 480$, 105 K, $Z = 4$, $D_x = 1.159(1)$, $D_m = R = 0.026$ for 2622 unique reflections with $I > 2\sigma(I)$.

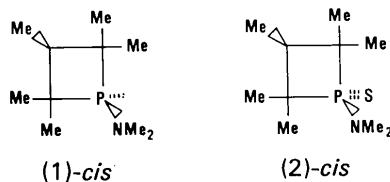
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The molecule lies on a crystallographic mirror plane through the SPN unit. The phosphetane ring is puckered with a dihedral angle of 28.75 (5)°. The P—S bond length is 1.9577 (4) Å, and P—N is 1.6797 (8) Å. There are no intermolecular distances significantly shorter than the sums of the van der Waals radii.

Introduction. During a study of the stereochemistry of nucleophilic substitution at P in cyclic three-coordinate P compounds (Nielsen & Dahl, 1984) it proved essential to know the configuration at the asymmetric P atom, relative to that of the asymmetric C atom in 1-dimethylamino-2,2,3,4,4-pentamethylphosphetane (1).

The main isomer had, according to ¹H and ³¹P NMR, the C(3)-Me and NMe₂ groups *cis*, which was unexpected from considerations of the thermodynamic stabilities of the (1)-*cis* and (1)-*trans* isomers. In order to obtain detailed knowledge of the molecular geometry the crystal structure of (2)-*cis* has been determined. (2) was formed from (1) and sulphur with retention at phosphorus (Horner & Winkler, 1964).



Experimental. (2) prepared as mixture of 91% *cis* (δ_p 107.2 in CDCl₃) and 9% *trans* (δ_p 111.4) from (1) (89% *cis*, 11% *trans*; Oram & Trippett, 1973) and sulphur in benzene. Recrystallization from pentane gave pure (2)-*cis* (>99%, δ_p 107.2), m.p. 324.7–324.9 K.

Prismatic crystals 0.55 × 0.25 × 0.20 mm. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo K α radiation. Lattice parameters from 18 reflections ($18 \leq \theta \leq 20^\circ$). 3402 reflections measured. ω -scan, variable scan rate, max. scan time 100 s, 2θ range 0 to 74° ($0 \leq h \leq 20$, $0 \leq k \leq 13$, $0 \leq l \leq 20$). Systematic absences $k + l = 2n + 1$ for $0kl$ and $h = 2n + 1$ for $h0l$. Three standard reflections measured every 10000 s, total decay of 0.02I during experiment. Intensities corrected for decay, Lorentz and polarization effects. No correction for absorption. 2622 reflections with $I > 2\sigma(I)$ used in structure refinement. Scattering factors from Cromer & Waber (1974); f' and f'' included for all atoms (Cromer, 1974). All crystallographic calculations performed on a PDP11/23 using Enraf–Nonius *Structure Determination Package* (Frenz, 1982). Intensity statistics indicated the non-standard centrosymmetric *Pnam* rather than *Pna2*₁ which was originally assumed with the molecule in a general position. The centrosymmetry gives $Z = 4$ and hence the molecule must possess a crystallographic mirror plane through the SPN unit. Structure solved by

Table 1. Atomic parameters and their estimated standard deviations

For non-H atoms $B_{eq} = \frac{1}{3}[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} or B_{iso} (Å ²)
S(9)	−0.06578 (2)	0.55272 (3)	0.250	1.356 (4)
P(1)	0.06060 (2)	0.40870 (3)	0.250	0.825 (3)
N(7)	0.18690 (6)	0.4907 (1)	0.250	1.11 (1)
C(2)	0.05354 (5)	0.24296 (8)	0.34860 (5)	1.010 (8)
C(3)	0.00882 (8)	0.1418 (1)	0.250	1.12 (1)
C(4)	−0.02840 (6)	0.26023 (9)	0.44206 (5)	1.50 (1)
C(5)	0.16495 (6)	0.18646 (9)	0.39277 (6)	1.51 (1)
C(6)	0.0375 (1)	−0.0326 (1)	0.250	1.79 (2)
C(8)	0.21435 (6)	0.58068 (9)	0.34881 (6)	1.56 (1)
H(31)	−0.071 (1)	0.155 (2)	0.250	0.8 (2)
H(41)	−0.0965 (9)	0.312 (1)	0.4188 (9)	2.2 (2)
H(42)	−0.0489 (9)	0.152 (2)	0.471 (1)	3.0 (3)
H(43)	0.003 (1)	0.315 (1)	0.5038 (8)	1.8 (2)
H(51)	0.2236 (8)	0.176 (1)	0.336 (1)	2.0 (2)
H(52)	0.1876 (8)	0.257 (1)	0.4491 (9)	2.0 (2)
H(53)	0.1565 (9)	0.084 (1)	0.4239 (9)	2.1 (2)
H(61)	0.113 (1)	−0.053 (2)	0.250	2.4 (3)
H(62)	0.007 (1)	−0.082 (1)	0.1890 (9)	2.6 (2)
H(81)	0.2956 (8)	0.597 (1)	0.353 (1)	2.6 (2)
H(82)	0.1926 (8)	0.522 (1)	0.4122 (9)	2.0 (2)
H(83)	0.1789 (9)	0.688 (1)	0.3513 (9)	2.1 (2)

Table 2. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

P(1)—C(2)	1.8545 (7)	N(7)—P(1)—S(9)	116.96 (4)
P(1)—N(7)	1.6797 (8)	P(1)—C(2)—C(3)	85.99 (4)
P(1)—S(9)	1.9577 (4)	P(1)—C(2)—C(4)	116.52 (5)
C(2)—C(3)	1.5767 (9)	P(1)—C(2)—C(5)	115.25 (5)
C(2)—C(4)	1.5211 (10)	C(3)—C(2)—C(4)	113.84 (6)
C(2)—C(5)	1.5301 (10)	C(3)—C(2)—C(5)	113.75 (6)
C(3)—C(6)	1.5193 (12)	C(4)—C(2)—C(5)	109.84 (5)
N(7)—C(8)	1.4684 (9)	C(2)—C(3)—C(2')	99.90 (6)
C(2)—P(1)—C(2')	81.20 (4)	C(2)—C(3)—C(6)	116.82 (6)
C(2)—P(1)—N(7)	110.83 (3)	P(1)—N(7)—C(8)	114.91 (5)
C(2)—P(1)—S(9)	115.90 (2)	C(8)—N(7)—C(8')	110.91 (8)

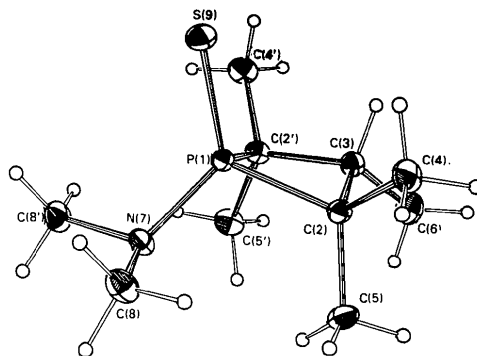


Fig. 1. An ORTEP drawing (Johnson, 1976) of the title compound, with the mirror plane approximately in the plane of the paper.

*MULTAN*11/82 (Frenz, 1982; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$; $w^{-1} = \sigma^2(F_o) + (p/4)F_o^2$, $p = 0.04$ chosen to make $\sum w(\Delta F)^2$ uniformly distributed in $|F_o|$. H atoms from $\Delta\rho$ map. 130 parameters (anisotropic thermal parameters for heavy atoms, isotropic for H) refined in final cycle. $R = 0.026$, $wR = 0.036$, $S = 1.321$. Largest Δ/σ 0.08. Max. peak in $\Delta\rho$ map $0.38 \text{ e } \text{\AA}^{-3}$; all peaks above $0.15 \text{ e } \text{\AA}^{-3}$ found in bond regions.

Discussion. Atomic parameters are listed in Table 1.* Fig. 1 is an *ORTEP*II drawing of the title compound which clearly shows that the C(3)-Me is *cis* to the NMe₂ group, as indicated from the NMR data. The phosphetane ring is puckered with a puckering angle, defined as the dihedral angle between the planes C(2)-P(1)-C(2') and C(2)-C(3)-C(2'), of $28.75(5)^\circ$ and with the C(3)-Me and NMe₂ groups pseudoequatorial. Similar puckering angles ($17-30^\circ$) have been found for other phosphetanes, and the direction of puckering has always been such as to place the C(3)-Me pseudo-equatorial (Fitzgerald, Campbell, Smith, Caughlan & Cremer, 1978). Bond lengths and angles are listed in Table 2.

No correction for libration has been attempted. With respect to the phosphetane ring the bond lengths and angles are not significantly different from those of *cis*-2,2,3,4,4-pentamethyl-1-phenyl-1 λ^5 -phosphetane 1-oxide (Mazhar-ul-Haque, 1971), except for a smaller P(1)-C(2)-C(3) angle, this angle being $87.1(2)^\circ$ compared to $85.99(3)^\circ$ for (2). The puckering angles are 23.8 and $28.75(5)^\circ$ respectively, indicating that the puckering is dependent on the substituents on P.

The P-S bond is rather long in comparison with that of similar compounds, e.g. $1.918(1) \text{ \AA}$ in 3-methyl-2-phenoxy-1,3,2 λ^5 -oxazaphosphorinane 2-sulphide (Karolak-Wojciechowska, Wiczorek, Zwierzak & Zawadzki, 1979) and $1.937(1) \text{ \AA}$ in 1-dimethylamino-

3-methyl-3*H*-2,1 λ^5 -benzoxaphosphole 1-sulphide (S. Larsen, R. Fogh and O. Dahl, unpublished) but within the range of tertiary phosphine sulphides ($1.86-1.97 \text{ \AA}$) (Khaikin & Vilkov, 1971; Kerr, Boorman, Misoner & van Roodc, 1977). The NMe₂ group is pyramidal, sum of bond angles at N $340.7(6)^\circ$, but the P-N bond is much shorter than the accepted single-bond length of H₃N⁺-PO₃⁻ of $1.77(2) \text{ \AA}$ (Cruickshank, 1964). It is, however, close to the P-N bond length of *N,N*-dimethyldiphenylphosphinamide which was found to be $1.681(6) \text{ \AA}$ by Mazhar-ul-Haque & Caughlan (1976), who rationalize the short P-N bond and long P-O bond by some π interaction of the N lone-pair electrons with the P *d* orbitals.

Examination of the crystal packing reveals no intermolecular distances significantly shorter than the sum of the van der Waals radii. This suggests that packing effects on molecular conformation are of little importance. Fig. 2 shows a stereoscopic *ORTEP*II drawing of the unit cell.

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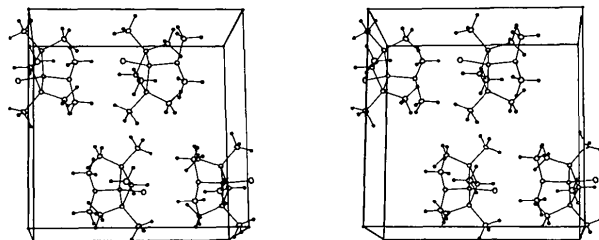


Fig. 2. Stereoscopic *ORTEP*II drawing of the unit cell, viewed down the *b* axis.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42060 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.