

Structure of 4-Methyl-2-(*N*-methyl-*N*-phenylamino)-1,3,2λ⁵-dioxaphosphorinane 2-Sulphide

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Abstract. C₁₁H₁₆NO₂PS, *M_r* = 257.3, monoclinic, *P*2₁/*c*, *a* = 8.735 (3), *b* = 12.776 (3), *c* = 11.666 (3) Å, β = 91.70 (3)°, *V* = 1301.3 Å³, *Z* = 4, *D_x* = 1.313, *D_m* = 1.29 Mg m⁻³, μ(Cu Kα) = 3.18 mm⁻¹, θ_{max} = 72°. The structure was solved by direct methods and refined by least-squares calculations to a final *R* of 6.2%. The intensities of 1760 independent reflections were collected by the counter method. The structure determination shows the 1,3,2-dioxaphosphorinane ring to have a chair conformation with the S in the axial and the 4-methyl in the equatorial position.

Introduction. 1,3,2-Dioxaphosphorinane is a widely used model system for the systematic X-ray study of the effect of substituent groups on the conformation of the ring (Beineke, 1969; Bukowska-Strzyżewska, Michalski, Młotkowska & Skoweranda, 1976; Cook & White, 1976; Corbridge, 1974; Drew & Rodgers, 1972; Grand & Robert, 1975; Mazhar-ul-Haque, Caughlan, Hargis & Bentrude, 1970; Killean, Lawrence & Magennis, 1971; Saenger & Mikołajczyk, 1973; Silver & Rudman, 1972). The present study was undertaken as a continuation of the investigation.

Plate-like crystals of the compound were crystallized from methanol. Intensities and cell dimensions were measured on a Syntex four-circle diffractometer with a crystal of diameter about 0.3 mm. The intensities of 1760 reflections (1295 with *I* > 2σ) were recorded to a maximum 2θ value of 144.0° with monochromated Cu radiation. The structure was solved by direct methods (*MULTAN*, Germain, Main & Woolfson, 1971) and refined anisotropically by the least-squares method with *CRYLSQ* of the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). H atom positions were calculated

with *XANADU* and refined with isotropic temperature factors in three cycles. In the final four cycles of refinement all the parameters were grouped into two blocks, H atom parameters in one block, non-hydrogen atoms in the other. These calculations resulted in *R* = 0.062.* The weights were σ⁻². Neutral-atom scattering factors (Doyle & Turner, 1968) were employed.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35411 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters with *e.s.d.*'s in parentheses

Positional coordinates for nonhydrogen atoms are × 10⁴, and for H atoms × 10³.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso} (Å ²)
S	5018 (1)	10067 (1)	7898 (1)	4.5 (1)
P	6969 (1)	9403 (1)	7760 (1)	3.0 (1)
N	8045 (4)	9854 (2)	6761 (2)	3.5 (2)
O(1)	6908 (3)	8190 (2)	7464 (2)	4.9 (2)
O(3)	8015 (3)	9423 (2)	8887 (2)	4.5 (2)
C(1)	9562 (5)	9400 (4)	6566 (3)	4.3 (3)
C(3)	8689 (5)	8921 (4)	10815 (3)	4.7 (3)
C(4)	7540 (5)	8735 (3)	9846 (3)	4.8 (3)
C(5)	7474 (5)	7626 (3)	9418 (3)	4.0 (3)
C(6)	6429 (5)	7496 (3)	8400 (4)	5.2 (4)
C(11)	7703 (4)	10831 (3)	6166 (3)	3.3 (3)
C(12)	8169 (5)	11768 (4)	6650 (3)	4.4 (3)
C(13)	7885 (6)	12696 (4)	6068 (4)	5.4 (4)
C(14)	7181 (5)	12679 (4)	4995 (4)	5.4 (4)
C(15)	6710 (5)	11748 (5)	4520 (3)	4.7 (3)
C(16)	6982 (5)	10801 (3)	5104 (3)	4.4 (3)
H(1,1)	971 (4)	928 (3)	576 (3)	3.3 (8)
H(1,2)	1045 (5)	982 (3)	675 (3)	5.8 (11)
H(1,3)	980 (5)	865 (3)	705 (3)	8.1 (13)
H(3,1)	843 (4)	846 (3)	1151 (3)	4.3 (9)
H(3,2)	975 (5)	874 (4)	1053 (4)	6.9 (13)
H(3,3)	862 (6)	962 (4)	1083 (4)	10.2 (17)
H(4,1)	644 (3)	903 (2)	1011 (2)	1.2 (7)
H(5,1)	872 (5)	736 (3)	925 (3)	7.2 (13)
H(5,2)	710 (4)	716 (3)	1006 (3)	5.6 (11)
H(6,1)	532 (4)	767 (3)	856 (3)	5.9 (11)
H(6,2)	650 (4)	678 (3)	803 (3)	4.2 (9)
H(12)	876 (4)	1179 (3)	747 (2)	3.7 (9)
H(13)	823 (4)	1341 (3)	647 (3)	5.8 (11)
H(14)	693 (4)	1344 (3)	452 (3)	4.6 (10)
H(15)	627 (4)	1171 (3)	383 (3)	3.6 (9)
H(16)	660 (3)	1013 (2)	484 (2)	1.7 (7)

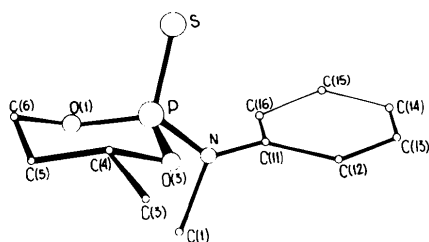


Fig. 1. A view of the molecule and the numbering system.

Discussion. Atomic positional parameters and isotropic temperature factors are given in Table 1; Tables 2 and 3 list bond lengths and angles. The numbering system is shown in Fig. 1. Most values are in good agreement with the mean literature ones and will not be discussed in detail. The P–N bond is significantly shorter than the accepted single-bond length of 1.77 Å, the value of 1.624 (3) Å indicating partial π character. In various 2-amino-1,3,2-dioxaphosphorinanes the length of the bond varies from 1.61 to 1.66 Å (Wagner, Jensen, Wadsworth & Johnson, 1973; Grand & Robert, 1978; Bartczak, Christensen, Kinas & Stec, 1975, 1976; Cameron, Galdecki & Karolak-Wojciechowska, 1976). On the other hand, in dithia-cyclophosphazenes the P–N bond lengths range up to 1.95 Å (Engelhardt & Hartl, 1975; Ibrahim *et al.*, 1971; Cameron, Prout & Howlett, 1975*a*; Peterson & Wagner, 1973). Although the dependence of the P–N distance on the electronegativity of the substituents is well known (Ahmed, Singh & Barnes, 1969), in the compounds mentioned above other effects also occur, mainly of a spatial nature connected with better or worse overlapping of *d* phosphorus and *p* nitrogen orbitals (d_{π} - p_{π} coupling). One can risk stating that the P–N bond should be slightly shorter in the case of the equatorial position of N. Unfortunately, there are no more known structures to verify this suggestion. Appropriate investigations have now been undertaken (Galdecki & Głowska, 1979). The P=S bond length of 1.915 (2) Å is in good agreement with those observed in similar compounds (Grand & Robert, 1978; Grand, Robert & Filhol, 1977; Cameron, Prout & Howlett, 1975*a,b*; Ibrahim *et al.*, 1971; Peterson & Wagner, 1973).

The 1,3,2-dioxaphosphorinane ring adopts a chair conformation which deviates only slightly from C_s symmetry. The asymmetry parameters (Duax & Norton, 1975) are: $\Delta C_s^2 = 0.6$ (5), $\Delta C_s^3 = 3.2$ (5), $\Delta C_s^{3,4} = 3.8$ (5) Å, $\bar{\phi} = 56.3$ (5)°. The dihedral angles defined by the best least-squares plane through the four central

Table 2. Bond lengths (Å)

P–S	1.915 (2)	H(1,1)–C(1)	0.97 (3)
P–N	1.624 (3)	H(1,2)–C(1)	0.96 (4)
P–O(1)	1.589 (3)	H(1,3)–C(1)	1.13 (4)
P–O(3)	1.579 (2)	H(3,1)–C(3)	1.03 (3)
N–C(1)	1.471 (5)	H(3,2)–C(3)	1.02 (5)
N–C(11)	1.455 (5)	H(3,3)–C(3)	0.90 (6)
O(1)–C(6)	1.477 (5)	H(4,1)–C(4)	1.09 (3)
O(3)–C(4)	1.491 (5)	H(5,1)–C(5)	1.16 (5)
C(3)–C(4)	1.509 (6)	H(5,2)–C(5)	1.02 (4)
C(4)–C(5)	1.503 (6)	H(6,1)–C(6)	1.02 (4)
C(5)–C(6)	1.486 (6)	H(6,2)–C(6)	1.01 (3)
C(11)–C(12)	1.380 (6)	H(12)–C(12)	1.07 (3)
C(12)–C(13)	1.384 (7)	H(13)–C(13)	1.06 (4)
C(13)–C(14)	1.379 (7)	H(14)–C(14)	1.15 (3)
C(14)–C(15)	1.370 (7)	H(15)–C(15)	0.89 (3)
C(15)–C(16)	1.405 (7)	H(16)–C(16)	0.97 (3)
C(16)–C(11)	1.374 (5)		

Table 3. Valency angles (°)

S–P–N	116.0 (1)	N–C(1)–H(1,1)	111 (2)
S–P–O(1)	115.2 (1)	N–C(1)–H(1,2)	118 (2)
S–P–O(3)	114.7 (1)	N–C(1)–H(1,3)	114 (2)
N–P–O(1)	101.9 (2)	O(1)–C(6)–H(6,1)	107 (2)
N–P–O(3)	105.0 (2)	O(1)–C(6)–H(6,2)	102 (2)
O(1)–P–O(3)	102.2 (1)	O(3)–C(4)–H(4,1)	106 (1)
P–N–C(1)	121.0 (3)	C(3)–C(4)–H(4,1)	108 (1)
P–N–C(11)	122.1 (3)	C(4)–C(3)–H(3,1)	110 (2)
C(1)–N–C(11)	116.0 (3)	C(4)–C(3)–H(3,2)	108 (2)
P–O(1)–C(6)	115.7 (2)	C(4)–C(3)–H(3,3)	97 (3)
P–O(3)–C(4)	116.6 (2)	C(4)–C(5)–H(5,1)	108 (2)
O(1)–C(6)–C(5)	110.1 (3)	C(4)–C(5)–H(5,2)	108 (2)
O(3)–C(4)–C(3)	106.0 (3)	C(5)–C(4)–H(4,1)	113 (2)
O(3)–C(4)–C(5)	108.4 (3)	C(5)–C(4)–H(4,2)	113 (2)
C(3)–C(4)–C(5)	114.6 (4)	C(5)–C(6)–H(6,2)	113 (2)
C(4)–C(5)–C(6)	112.8 (3)	C(6)–C(5)–H(5,1)	113 (2)
N–C(11)–C(12)	119.7 (3)	C(6)–C(5)–H(5,2)	109 (2)
N–C(11)–C(16)	119.3 (3)	C(11)–C(12)–H(12)	121 (2)
C(11)–C(12)–C(16)	119.8 (4)	C(11)–C(16)–H(16)	117 (2)
C(12)–C(13)–C(14)	120.0 (4)	C(12)–C(13)–H(13)	118 (2)
C(13)–C(14)–C(15)	120.1 (4)	C(13)–C(14)–H(14)	120 (2)
C(14)–C(15)–C(16)	120.5 (4)	C(13)–C(12)–H(12)	119 (2)
C(15)–C(16)–C(11)	118.7 (4)	C(14)–C(13)–H(13)	122 (2)
C(16)–C(11)–C(12)	120.9 (4)	C(14)–C(15)–H(15)	123 (2)
		C(15)–C(14)–H(14)	120 (2)
		C(15)–C(16)–H(16)	124 (2)
		C(16)–C(15)–H(15)	117 (2)
		H(1,1)–C(1)–H(1,2)	100 (3)
		H(1,1)–C(1)–H(1,3)	109 (3)
		H(1,2)–C(1)–H(1,3)	103 (3)
		H(3,1)–C(3)–H(3,2)	111 (3)
		H(3,1)–C(3)–H(3,3)	122 (4)
		H(3,2)–C(3)–H(3,3)	107 (4)
		H(5,1)–C(5)–H(5,2)	106 (3)
		H(6,1)–C(6)–H(6,2)	110 (3)

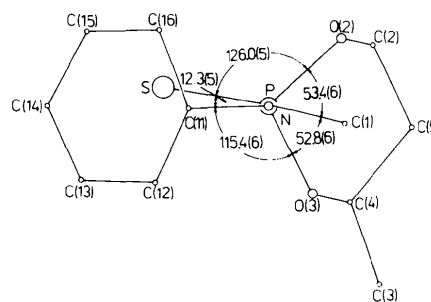


Fig. 2. The Newman projection of the molecule along the P–N(exocyclic) bond.

atoms of the ring and the O–P–O plane on the one hand and the plane of the C atoms on the other are 46.2 (5) and 52.6 (5)° respectively. The flattening of the ring at the P end is very similar to that found in other 1,3,2-dioxaphosphorinanes (Corbridge, 1974), though values less than 42° have been reported more frequently. The N and its bonded atoms form a planar system perpendicular to the plane of the phosphorinane ring (Fig. 2). The positions of the axial S and the equatorial C(4) methyl groups have been predicted and found.

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The Structure of the Precursor of Phosphafuranoses: 2-Hydroxy-5-hydroxymethyl-1-phenylphospholane 1-Oxide*

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Abstract. C₁₁H₁₅O₃P, *M_r* = 226.2, triclinic, *P*1̄, *a* = 8.711 (3), *b* = 8.014 (3), *c* = 8.782 (3) Å, *α* = 94.74 (4), *β* = 115.11 (5), *γ* = 99.97 (4)°, *V* = 538.3 Å³, *D_m* = 1.383 (floatation), *D_x* = 1.395 Mg m⁻³, *Z* = 2, *μ*(Cu Kα) = 2.12 mm⁻¹, *F*(000) = 240. The crystal structure of one of the two isomeric products formed in the intramolecular cyclization of the respec-

tive secondary δ-oxoalkylphosphine oxide has been determined from 1354 intensities collected on a four-circle diffractometer with copper radiation. The structure was solved by direct methods and refined by least squares to a final *R* of 0.042. The molecules are linked into chains along [010] by hydrogen bonds with O...O distances of 2.74 Å.

* The atom-numbering scheme adopted in the paper does not correspond to the numbering in the title which is in agreement with the IUPAC convention.

Introduction. It has been shown that intramolecular cyclization of secondary phosphine oxides containing a