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Structure of 1-Dimethylamino-3-methyl-3*H*-2,1λ^5-benzoxaphosphole 1-Sulfide at 105 K

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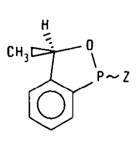
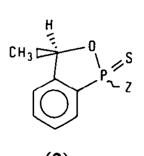
Abstract. $C_{10}H_{14}NOPS$, $M_r = 227{\cdot}27$, orthorhombic, $P2_12_12_1$ at 105 K, $a = 11{\cdot}654\,(3)$, $b = 13{\cdot}301\,(4)$, $c = 7{\cdot}193\,(3)$ Å, $V = 1115{\cdot}0\,(11)$ Å^3, $Z = 4$, $D_m(293\text{ K}) = 1{\cdot}26\,(1)$, $D_x(105\text{ K}) = 1{\cdot}354\,(1)$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71073$ Å, $\mu(\text{Mo }K\alpha) = 3{\cdot}88$ cm^{-1}, $F(000) = 480$, $T = 105\,(1)$ K, $R = 0{\cdot}032$ for 2645 observed reflections. On crystallization the compound spontaneously resolves into enantiomers. The absolute configuration found (*R,R*) confirms previous interpretations of NMR data. The heterocyclic five-membered ring is only slightly puckered. The P—S and P—N bond lengths are 1·9382 (5) and 1·6536 (14) Å respectively. Comparisons with similar structures show that these exocyclic bond lengths correlate inversely with the endocyclic *X*—P—*Y* angle.

Introduction. The stereochemistry of substitution reactions at trivalent phosphorus in a series of cyclic compounds has been investigated by Nielsen & Dahl (1984). From the magnitude of certain NMR coupling constants an assignment of the configuration around P was made. For the compounds (1) the diastereomers with small NMR coupling constants $^3J_{\text{POCH}}$ were assigned a structure with the substituent on P *trans* to the methyl group of the five-membered ring.



(1)



(2)

To verify this assignment it was necessary to obtain information about the stereochemistry around P by other experimental methods.

All the compounds (1) investigated are liquids at room temperature but their 1-sulfides (2) are crystalline. It has been shown (Mikolajczyk, 1980) that reactions of trivalent phosphorus compounds with S_8 occur stereospecifically with retention of the configuration at P. The present paper reports the structure determination for (2), $Z = N(CH_3)_2$.

Experimental. The title compound was prepared from (1) [$Z = N(CH_3)_2$], 97% diastereomerically pure according to ^{31}P NMR ($\delta_P = 131{\cdot}2$, $^3J_{\text{POCH}} < 1$ Hz), and S_8 in $CHCl_3$ (exothermic). It was recrystallized from hexane, m.p. 372–373 K, $\delta_P = 91{\cdot}7$ ($CDCl_3$, one signal). Found: C 53·01; H 6·42; N 6·11; S 14·08%. Calculated for $C_{10}H_{14}NOPS$; C 52·85; H 6·21; N 6·16; S 14·11%. The density was determined by flotation using an aqueous solution of KI. Transparent crystals elongated along the *c* axis. Systematically absent reflections: *h*00 for *h* odd, 0*k*0 for *k* odd and 00*l* for *l* odd. Crystal size for data collection 0·2 × 0·3 × 0·4 mm. Enraf–Nonius CAD-4 diffractometer and low-temperature device, graphite-monochromatized Mo $K\alpha$ radiation. Temperature recorded with a thermocouple, variations within 1 K. Cell parameters and orientation matrix from 22 reflections ($9 \le \theta \le 20°$). Maximum scan time 150 s. No corrections for absorption or secondary extinction. Three intensity control reflections measured every 10 000 s; the variations were not systematic and less than 1%. Intensity data measured by ω–2θ scan; $\Delta\omega = 1{\cdot}0° + 0{\cdot}35\tan\theta$, $\theta_{\max} = 37{\cdot}5°$; $0 \le h \le 19$, $0 \le k \le 20$, $0 \le l \le 12$. 3322 unique reflections measured, 2645 with $I > 2\sigma(I)$ used in structure solution and refinement. Non-hydrogen atoms localized by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Structure refinement by least squares minimizing $\sum w(|F_o| - |F_c|)^2$. All calculations performed on a PDP11/23 using the Enraf–Nonius *Structure Determination Package* (Frenz, 1982). The scattering factors by Cromer & Waber (1974) were used as contained in the program. f' and f'' calculated by Cromer & Liberman (1970) included for P, S, O, N and C. Hydrogen positions from $\Delta\rho$. Weights in final cycle $w^{-1} = \sigma^2(F) + p^2/4\,F^2$, $p = 0{\cdot}05$ chosen to make $\langle wF^2\rangle$ uniformly distributed in F_o. Number of variables 183 (anisotropic thermal parameters for heavy atoms, isotropic for H). In final cycle $R = 0{\cdot}032$, $wR = 0{\cdot}038$, $S = 1{\cdot}07$; largest $\Delta/\sigma = 0{\cdot}03$. Peaks in $\Delta\rho$ between $\pm 0{\cdot}5$ e Å^{-3}, larger positive peaks in bonding and lone-pair regions. Polarity of the crystal established as described by Rogers (1981).

Discussion. The final atomic coordinates and isotropic thermal parameters are listed in Table 1.* Bond lengths and angles involving the non-hydrogen atoms are given in Table 2. The C—H bond distances are in the range 0·90 to 1·00 Å with e.s.d.'s of 0·03 Å. The stereochemistry of the molecule is illustrated by the *ORTEP*II (Johnson, 1971) drawing shown in Fig. 1. The two chiral atoms C(3) and P have the same absolute configuration *R*. This means that the parent molecule [(1), $Z = N(CH_3)_2$] has the methyl group *trans* to the $N(CH_3)_2$ group. This result confirms the stereochemical interpretation of the NMR data (Nielsen & Dahl, 1984). The compound crystallizes in the space group $P2_12_12_1$, so spontaneous resolution of the two enantiomers occurs by precipitation.

The five-membered heterocyclic ring is only slightly puckered with O displaced −0·094 (2) Å relative to the least-squares plane calculated for the benzene ring. The similar displacements of C(3) and P are −0·003 (2) and 0·006 (1) Å respectively. The C(5)—P—O angle of 94·52 (6)° is in the range 88 to 98° observed for other structures with P in a five-membered ring (Prange, Pascard, Devillers & Navech, 1977; Hellwinkel, Krapp, Schomberg & Sheldrick, 1976; Gałdecki, Bartczak, Wolf, Krawczyk & Majewski, 1985).

The exocyclic P—S and P—N bonds are longer than the similar distances observed in compounds containing P in a six-or seven-membered ring investigated by Grand & Robert (1978) but shorter than those found in a structure with a four-membered ring (Gajhede, Dahl & Nielsen, 1985). Since the endocyclic angles for P in these systems increase from 81·20 (4)° in the four-membered ring to 103·6 (2)° in the seven-membered it seems that the P—N and P—S bond lengths are inversely correlated with the endocyclic *X*—P—*Y* angle. A shortening of the exocyclic P—N bond with increasing endocyclic angle around P can be interpreted as an increase of its double-bond character. This is supported by an analysis of the geometry around N. In the compounds with the shortest P—N bonds, 1·612 (5) and 1·616 (8) Å (Grand & Robert, 1978), the N atom is planar since the sum of the angles is virtually 360·0°. The molecule with the longest P—N bond, 1·6779 (8) Å (Gajhede, Dahl & Nielsen, 1985), has a pyramidal N, the sum of the angles being 340·7 (2)°. The geometry around N in the present structure, with P—N = 1·634 (1) Å and a sum of angles around N of 350·4 (4)°, fits well with this interpretation.

Table 1. *Atomic parameters and their estimated standard deviations*

$$B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j U(i,j).$$

	x	y	z	B_{eq}(Å^2)
S	0·27702 (3)	0·15545 (3)	0·73916 (6)	1·340 (5)
P	0·36894 (3)	0·23535 (3)	0·57003 (5)	0·982 (5)
O	0·49913 (9)	0·25173 (8)	0·6402 (2)	1·39 (2)
N	0·3716 (1)	0·1900 (1)	0·3561 (2)	1·33 (2)
C(1)	0·4402 (2)	0·2452 (1)	0·2174 (2)	1·84 (3)
C(2)	0·3721 (2)	0·0812 (1)	0·3230 (2)	1·62 (2)
C(3)	0·5397 (1)	0·3560 (1)	0·6407 (2)	1·16 (2)
C(4)	0·4372 (1)	0·4206 (1)	0·5932 (2)	1·08 (2)
C(5)	0·3383 (1)	0·3664 (1)	0·5519 (2)	1·04 (2)
C(6)	0·2355 (1)	0·4140 (1)	0·5062 (2)	1·35 (2)
C(7)	0·2344 (2)	0·5186 (1)	0·5012 (2)	1·51 (2)
C(8)	0·3331 (2)	0·5734 (1)	0·5415 (2)	1·57 (2)
C(9)	0·4354 (1)	0·5255 (1)	0·5886 (2)	1·34 (2)
C(10)	0·5920 (1)	0·3782 (1)	0·8283 (3)	1·55 (2)

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

S—P	1·9382 (5)	S—P—O	113·41 (5)
P—O	1·6141 (11)	S—P—N	113·22 (5)
P—N	1·6536 (14)	O—P—N	108·86 (7)
P—C(5)	1·7835 (14)	S—P—C(5)	118·10 (5)
O—C(3)	1·465 (2)	O—P—C(5)	94·52 (6)
N—C(1)	1·474 (2)	N—P—C(5)	107·01 (7)
N—C(2)	1·466 (2)	P—O—C(3)	115·58 (9)
C(3)—C(4)	1·510 (2)	P—N—C(1)	117·24 (11)
C(4)—C(5)	1·392 (2)	P—N—C(2)	120·76 (11)
C(3)—C(10)	1·511 (2)	C(1)—N—C(2)	112·35 (14)
C(4)—C(9)	1·396 (2)	O—C(3)—C(4)	106·43 (11)
C(9)—C(8)	1·394 (2)	O—C(3)—C(10)	108·52 (13)
C(8)—C(7)	1·392 (3)	C(4)—C(3)—C(10)	114·20 (13)
C(7)—C(6)	1·392 (2)	C(3)—C(4)—C(5)	114·11 (13)
C(6)—C(5)	1·394 (2)	C(3)—C(4)—C(9)	125·88 (14)
		C(5)—C(4)—C(9)	120·01 (14)
		P—C(5)—C(4)	108·97 (11)
		P—C(5)—C(6)	129·26 (12)
		C(4)—C(5)—C(6)	121·77 (13)
		C(5)—C(6)—C(7)	117·93 (15)
		C(6)—C(7)—C(8)	120·64 (15)
		C(7)—C(8)—C(9)	121·22 (14)
		C(8)—C(9)—C(4)	118·42 (15)

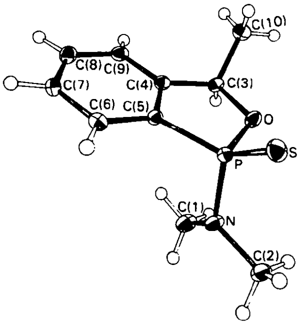


Fig. 1. Perspective drawing of the molecule illustrating the atomic labelling. The thermal ellipsoids are drawn at the 50% probability level, the H atoms are drawn as spheres with arbitrary radius.

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* Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43097 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

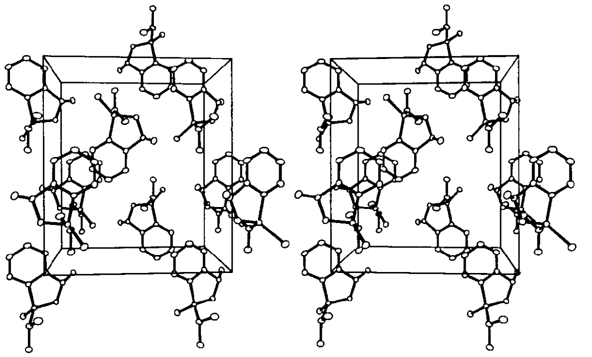

Fig. 2. A stereo pair illustrating the packing in the crystal viewed in the direction of the *c* axis.

The torsion angles S—P—N—C(1) and S—P—N—C(2) are −179·50 (11) and −36·03 (14)° respectively. This difference could be caused by steric interactions between S and C(2).

A stereo pair illustrating the packing in the crystal is shown in Fig. 2. All intermolecular contacts are larger than the sum of the van der Waals radii.

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Structure of a Sulfone that Reveals the Direction of Cleavage of a Camphor-based Thiirane 1,1-Dioxide by a Thiol*

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Abstract. 7,7-Dimethyl-1-[1-(2,4-dinitrophenylsulfonyl)-2-(*p*-tolylthio)ethyl]bicyclo[2.2.1]heptan-2-one, (V), $C_{24}H_{26}N_2O_7S_2$, $M_r = 518·6$, orthorhombic, $P2_12_12_1$, $a = 12·436\,(2)$, $b = 27·267\,(3)$, $c = 6·987\,(1)$ Å, $V = 2369·3$ Å^3, $Z = 4$, $D_m = 1·459$, $D_x = 1·454$ g cm^{-3}, Cu $K\beta$, $\lambda = 1·39217$ Å (cell constants), Mo $K\alpha$, $\lambda = 0·7107$ Å (intensity data), $\mu = 2·61$ cm^{-1}, $F(000) = 1088$, $T = 293$ K, $R = 0·061$ for 3926 independent reflections. Full-matrix least-squares refinement included isotropic hydrogen atoms. Bond distances ($\sigma = 0·004$ Å) and angles ($\sigma = 0·3°$) are given for the camphor moiety. The two phenyl rings in the molecule are parallel and in contact. Phenyl rings in adjacent molecules are also parallel and in contact. This structure shows that in the reaction of 2-(2-oxo-7,7-dimethyl-1-bicyclo[2.2.1]heptyl)thiirane 1,1-dioxide (I), *p*-toluenethiolate ion attacked the dioxide at the CH_2 site of the thiirane 1,1-dioxide ring.

Introduction. Protection of animals against ionizing radiation is afforded by salts of sulfinic acids (RSO_2H) of the type —SS—C_4—SO_2Na, where C_4 represents carbon atoms that either are in an acyclic chain or are wholly or partly in a benzenoid system (Srivastava, Field & Grenan, 1975; Bowman, Clement, Davidson, Eswarakrishnan, Field, Hoch, Musallam, Pick, Ravichandran & Srivastava, 1986). For chemical or biological details of the present report see Harmon

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* Paper 17 in the series 'Sulfinic acids and related compounds'. Paper 16: Chandra, R. & Field, L. (1986). *Phosphorus Sulfur*, **27**, 247–251.

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