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The Crystal Structure of 2-Fluoro-1,3-dimethyl-1,3,2-diazaphospholidine 2-Sulfide*

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The structure of $\mathrm{CH_3\underline{NCH_2CH_2N(CH_3)P}F(S)}$ has been determined by single-crystal X-ray diffraction techniques. This compound crystallizes with four molecules in a monoclinic unit cell of $P2_1/c$ symmetry and of dimensions a = 10·213 (6), b = 6·418 (3), c = 12·829 (6) Å, and β = 103·66 (6)°. The structure was solved by direct methods and refined by full-matrix least-squares techniques to an unweighted residual of 0·048 for 734 independent diffractometer-collected reflections with $I \geq 3\sigma(I)$. The P atom of this molecule is bonded to a F atom, a S atom and two N atoms of the dimethylethylenediamine backbone. The five-membered ring contains P—N bond distances of 1·613 (5) and 1·603 (6) Å with both N atoms lying in a plane defined by the three N-atom substituent groups. The P—S and P—F bond distances are 1·901 (3) and 1·560 (6) Å, respectively.

Introduction

As part of a general study of the interactions of small molecules such as CO_2, COS, CS_2, and SO_2 with phosphines, several structurally interesting new cyclic phosphine compounds were isolated (Light & Paine, 1978). One of these compounds, 2-fluoro-1,3-dimethyl-1,3,2-diazaphospholidine 2-sulfide, was also isolated from the interaction of 2-fluoro-1,3-dimethyl-1,3,2-diazaphospholidine with sulfur. The structure of the title thiophosphoryl compound was determined from a crystal obtained from the direct reaction of sulfur with the aminophosphine ligand.

Crystals were grown from the oil of $\mathrm{CH_3\underline{NCH_2CH_2N(CH_3)P}F(S)}$ at 10°C. A colorless crystal (0·25 × 0·30 × 0·75 mm) was selected and mounted on the long dimension in a glass capillary. Precession and Weissenberg photographs revealed systematic absences $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$ which led to the identification of the space group as $P2_1/c$. Intensity data were collected at 23°C with an automated Picker diffractometer using Zr-filtered, Mo $K\alpha$ radiation and a scintillation detector employing pulse-height discrimination. The intensities were measured in the 2θ-scan mode for one hemisphere of reflections with $3{\cdot}0 \leq 2\theta \leq 40{\cdot}0°$ for a total of 2198 reflections. Equivalent reflections (with an average deviation of less than 2%) were averaged resulting in 1174 unique reflections of which 734 had $I \geq 3\sigma(I)$. Background radiation was measured for 10 s at the beginning and the end of each scan with the counter and crystal held stationary. The intensities of standard reflections, counted after every 50 reflections, showed no significant change during data collection. Atomic scattering factors (Cromer & Mann, 1968) and the real part of the anomolous dispersion corrections for the P and S atoms (*International Tables for X-ray Crystallography*, 1968) were applied. No absorption or extinction corrections were required.

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Crystal data

$C_4H_{10}FN_2PS$, $M_r = 168{\cdot}16$, m.p. = 40°C, monoclinic, $P2_1/c$, $a = 10{\cdot}213\,(6)$, $b = 6{\cdot}418\,(3)$, $c = 12{\cdot}829\,(6)$ Å, $\beta = 103{\cdot}66\,(6)°$, $V = 817{\cdot}11\,(2)$ Å^3, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 5{\cdot}21$ cm^{-1}, $Z = 4$, $D_c = 1{\cdot}374$ g cm^{-3}.

The lattice parameters were determined by least-squares refinement (*LATCON*) (Stewart, 1976) of the setting angles of 18 high-angle reflections.

Determination of the structure and refinement

The structure was solved with *MULTAN* (Main, Woolfson & Germain, 1971) and subsequent Fourier syntheses. All calculations following *MULTAN* were accomplished using the XRAY 76 system (Stewart, 1976). Least-squares refinement of the nonhydrogen atoms with isotropic temperature factors converged to an unweighted R factor, $R = \sum||F_o| - |F_c||/\sum |F_o|$, of 0·114. H atoms were placed in idealized positions and anisotropic refinement of the nonhydrogen atoms resulted in a final convergence at $R = 0{\cdot}048$. All least-squares refinements were based upon the minimization of $\sum w_i||F_o| - |F_c||^2$ with individual weights $w_i = 1/\sigma(F_o)^2$. A final difference Fourier map revealed no maxima greater than 0·1 e Å^{-3}. The final fractional coordinates of the atoms are listed in Tables 1 and 2.*

Table 1. *Fractional coordinates of non-hydrogen atoms with standard deviations*

	x	y	z
P	0·7389 (2)	−0·0191 (3)	0·1836 (1)
S	0·7956 (2)	−0·1035 (4)	0·0592 (1)
F	0·6334 (5)	−0·1830 (8)	0·2107 (4)
N(1)	0·8471 (5)	0·0048 (10)	0·2969 (4)
N(2)	0·6681 (6)	0·2018 (9)	0·1905 (4)
C(1)	0·9502 (8)	−0·1450 (13)	0·3407 (5)
C(2)	0·5739 (8)	0·2991 (13)	0·1040 (6)
C(3)	0·8118 (7)	0·1668 (13)	0·3626 (5)
C(4)	0·7109 (8)	0·3036 (14)	0·2918 (6)

Table 2. *Fractional coordinates of the calculated positions for the hydrogen atoms*

H(1) to H(3) bonded to C(1), H(4) to H(6) bonded to C(2), H(7), H(8) bonded to C(3), and H(9), H(10) bonded to C(4). U_{iso} was arbitrarily set at 0·0633 Å^2 and not refined.

	x	y	z
H(1)	0·9623	−0·2477	0·2842
H(2)	1·0395	−0·0743	0·3702
H(3)	0·9265	−0·2268	0·4013
H(4)	0·5525	0·2078	0·0379
H(5)	0·4857	0·3325	0·1236
H(6)	0·6017	0·4360	0·0825
H(7)	0·8948	0·2485	0·4006
H(8)	0·7714	0·1053	0·4217
H(9)	0·6329	0·3365	0·3255
H(10)	0·7550	0·4460	0·2830

Results and discussion

Chemical and spectroscopic characterization data for $CH_3NCH_2CH_2N(CH_3)PF(S)$ previously established the formulation and basic connectivity of the molecule, but the details of the molecular structure were not provided by this initial data (Light & Paine, 1978). The molecular structure as determined in the X-ray study is shown in Fig. 1, and the pertinent bond distances and bond angles are summarized in Tables 3 and 4, respectively. The structure (Fig. 1) consists of a five-membered ring containing one P atom, two N atoms and two C atoms linked in a fashion NCCNP. The five atoms defining the ring are nearly coplanar. A slight puckering results in a least-squares-plane standard deviation of only 0·082 Å from the five-atom system (Table 5, plane 1). Atoms C(1) and C(2) lie on the S side of the ring, and they are distorted away from the P(S)F group [*e.g.*, angle P—N(2)—C(2) is greater than angle C(2)—N(2)—C(4)]. The bond angles about the N atoms show that these atoms have trigonal-planar geometry. This stereochemistry is also indicated by the small deviations of the N atoms from calculated least-squares planes defined by the three atoms surrounding each N (Table 5, planes 2 and 3).

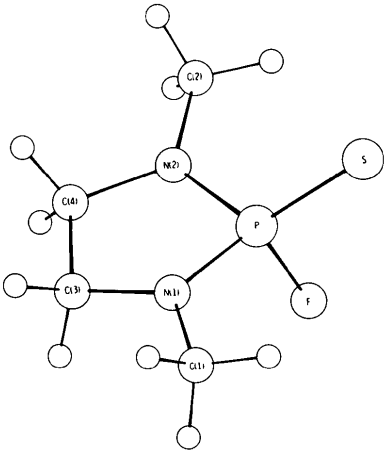

Fig. 1. A view of the $CH_3NCH_2CH_2N(CH_3)PF(S)$ molecule showing the atom-numbering scheme.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33840 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The P—N bond lengths of 1·613 (5) and 1·603 (6) Å in the title compound are of interest when compared with the P—N bond distances in related cyclic phosphoryl and thiophosphoryl compounds containing a N—P—N unit. The structures of 2-chloro-1,3-dimethyldiazaphospholidine oxide and sulfide compounds with a more complex *N,N'*-dimethyl-4-toluidine backbone have been determined. The P—N bond distances are 1·634 (5) and 1·636 (4) Å for the $N_2P(S)Cl$ complex (Cameron, Prout & Howlett, 1975) and 1·637 (6) and 1·650 (6) Å for the $N_2P(O)Cl$ complex (Cameron, 1972). The slightly shorter P—N distances in the title compound also closely compare with the distances in a variety of phosphonitrilic ring compounds (Corbridge, 1974). These distances are noticeably shorter than the single-bond P—N distance of 1·77 (2) Å in $NaPO_3NH_3$ (Cruickshank, 1964).

The short P—N distance may result from the increased electron withdrawal by a F atom compared to a Cl atom attached to P, the increased π overlap between P and N atoms in the F analog, steric factors, or some combination of these effects. The trigonal-planar bond angles observed in these compounds suggest that a π-overlap contribution to the P—N bonds is present. This overlap would involve delocalization of the N lone pairs, with predominantly *p* character, into vacant *d* orbitals localized on P. This overlap should be enhanced by electronegative substituents, such as F, attached to P; therefore, a combination of electronegativity and π-overlap effects seems to account for the P—N bond-distance trends. Similar arguments have been prepared in explanation of observed P—N bond shortening in phosphonitrilic rings as a function of substituent-group electronegativity (Corbridge, 1974). This trend in phosphonitrilic ring P—N distances is illustrated by the following series: 1·597 Å in a C_6H_5P—N group, 1·59 Å in a ClP—N group and 1·535 Å in a FP—N group (Corbridge, 1974).

Table 3. *Bond lengths* (Å) *with standard deviations*

P—S	1·901 (3)	N(1)—C(1)	1·439 (10)
P—F	1·560 (6)	N(1)—C(3)	1·437 (10)
P—N(1)	1·613 (5)	N(2)—C(2)	1·429 (9)
P—N(2)	1·603 (6)	N(2)—C(4)	1·427 (10)
		C(3)—C(4)	1·488 (11)

Table 4. *Bond angles* (°) *with standard deviations*

S—P—F	106·9 (2)	C(1)—N(1)—C(3)	121·0 (5)
N(1)—P—S	120·2 (2)	P—N(1)—C(3)	112·6 (4)
N(1)—P—F	106·3 (3)	P—N(2)—C(2)	124·9 (5)
N(2)—P—S	121·9 (3)	C(2)—N(2)—C(4)	120·8 (6)
N(2)—P—F	104·6 (3)	P—N(2)—C(4)	114·2 (5)
N(1)—P—N(2)	95·0 (3)	N(1)—C(3)—C(4)	107·6 (6)
P—N(1)—C(1)	124·9 (5)	N(2)—C(4)—C(3)	107·7 (7)

Table 5. *Least-squares planes*

Plane 1: P, N(1), N(2), C(3), C(4)

$$8·019x + 3·278y - 6·745z = 4·700$$

Distances of atoms from the plane (Å)

P	−0·078	C(3)	−0·089
S	0·941	C(4)	0·028
F	−1·582	C(1)	0·145
N(1)	0·106	C(2)	0·181
N(2)	0·033		

Plane 2: P, C(2), C(4)

$$8·595x + 2·866y - 6·340z = 5·131$$

Distance of N(2) from plane = −0·018 Å.

Plane 3: P, C(1), C(3)

$$7·346x + 3·743y - 6·886z = 4·091$$

Distance of N(1) from plane = 0·106 Å.

At the present time the structure of the cyclic aminophosphine $CH_3NCH_2CH_2N(CH_3)PF$ has not been determined, but the structure of the ligand coordination complex with an $Fe(CO)_4$ fragment has been completed (Bennett, Neustadt, Parry & Cagle, 1978). This complex shows P—N bond distances of 1·635 (6) and 1·642 (5) Å. These distances are longer than the corresponding distances in the title compound as would be expected for the comparison of trivalent and pentavalent P complexes of these types.

The remaining stereochemistry around P appears to be normal. The bond angles about the P atom, N(1)—P—S and N(2)—P—S, are greater than tetrahedral while N(1)—P—F, N(2)—P—F, and N(1)—P—N(2) are less than tetrahedral. Similar distortions have been observed in other five-membered P heterocyclic compounds (Lee & Goodacre, 1971*a,b*). The P—S bond length of 1·901 (3) Å is similar to that found in $PSCl_3$ [1·908 (6) Å] (Moritani, Kuchitsu & Morino, 1971) and in $[(CH_3)_2N]_3PS$ [1·91 (1) Å] (Subramanian & Trotter, 1969). The P—F bond length of 1·560 (6) Å is shorter than the distance in the aminophosphine $(CH_3)_2NPF_2$ [1·610 (4) Å] (Morris & Nordman, 1969), but longer than the distances in POF_3 [1·524 (3) Å] (Moritani, Kuchitsu & Morino, 1971) and PSF_3 (1·53 Å)

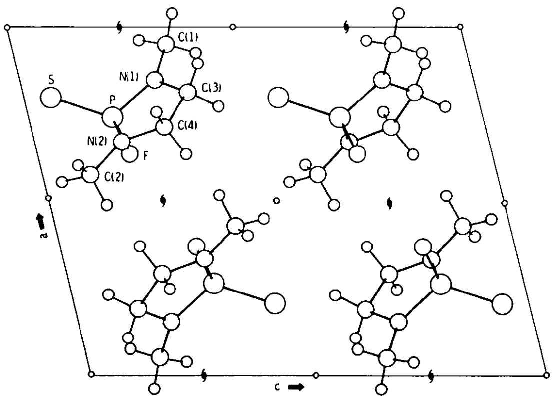

Fig. 2. [010] projection showing four $CH_3NCH_2CH_2N(CH_3)PF(S)$ molecules in a monoclinic cell of $P2_1/c$ symmetry.

(Williams, Sheridan & Gordy, 1952). The P—F bond length in the present compound agrees closely with the axial P—F distance (1·57 Å) in the novel dimer $(CH_3NPF_2C_6H_5)_2$ (Cox & Corey, 1967). The C—C and C—N distances and inner ring angles are not unusual for phosphorus five-membered-ring heterocyclic compounds (Lee & Goodacre, 1971*a*,*b*; Corbridge, 1974). No unusually short internuclear separations were detected between the nonhydrogen atoms. Fig. 2 shows an [010] projection of the unit cell.

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The Crystal Structure of (—)-Avenaciolide

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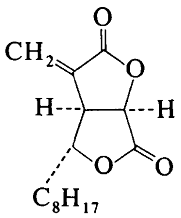
(—)-Avenaciolide, the naturally occurring antifungal metabolite of *Aspergillus avenaceus*, forms colourless, euhedral crystals which are orthorhombic, $P2_12_12_1$, with a = 7·006 (1), b = 33·475 (6), c = 6·279 (1) Å. The structure has been determined from diffractometer intensities (monochromated Mo $K\alpha$ radiation, $2\theta \leq 50°$, 1546 unique reflections) by direct methods. On refinement to convergence, R = 0·083 for all data. In the bislactone 'head', the ring with the methylene-group substituent has a twist conformation with the two bridgehead C atoms out-of-plane. The other ring has an envelope conformation. The octyl-group 'tail' is fully extended with torsion angles at all C—C bonds *ca* 180°. The crystal consists of stacked bilayers, with bands of the bislactone 'heads' and of close-packed, parallel, hydrocarbon chains which have an orthorhombic ($O_{\perp}$) subcell.

Introduction

(—)-Avenaciolide is a naturally occurring antifungal metabolite of *Aspergillus avenaceus*. Its formula, (I), determined by chemical and spectroscopic means (Brookes, Tidd & Turner, 1963), shows an unusual bislactone fused-ring 'head' system and a paraffinic octyl group as 'tail'.



(I)