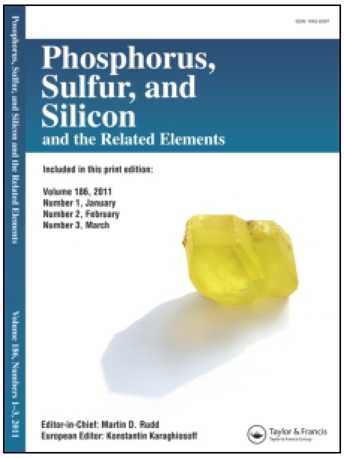

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CRYSTAL STRUCTURES OF TWO FLUORODIAZADIPHOSPHETIDINES

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To cite this Article Jones, Peter G. and Schmutzler, Reinhare(1991) 'CRYSTAL STRUCTURES OF TWO FLUORODIAZADIPHOSPHETIDINES', Phosphorus, Sulfur, and Silicon and the Related Elements, 56: 1, 173 — 177
To link to this Article: DOI: 10.1080/10426509108038080
URL: http://dx.doi.org/10.1080/10426509108038080

Phosphorus, Sulfur, and Silicon, 1991, Vol. 56, pp. 173–177
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CRYSTAL STRUCTURES OF TWO FLUORODIAZADIPHOSPHETIDINES

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(Received July 6, 1990)

The crystal structures of the difluorodiazadiphosphetidines $[RF_2PNR']_2$ (**1e**; R = R′ = Me and **1a**; R = Ph, R′ = Me) have been determined at −95°C. **1e**: $P2_1/n$, $Z = 2$, $R = 0.031$ and **1a**: $Pbca$, $Z = 4$, $R = 0.032$. Both molecules are associated with crystallographic inversion centres, and the P_2N_2 rings are therefore exactly planar. The bond lengths follow the usual pattern for trigonal bipyramidal phosphorus.

Key words: Fluorodiazadiphosphetidines; X-ray structure.

INTRODUCTION

The syntheses of certain fluorodiazadiphosphetidines, $[R_nF_{3-n}PNR']_2$ (R, R′ = hydrocarbon moiety; $n = 0,1,2$] have been reported.[1] Such compounds are formally dimers of fluorophosphine imides $R_nF_{3-n}PNR'$ (cf. Reference 2). The phosphorus atoms in such compounds are pentacoordinate. Therefore, fluorodiazadiphosphetidines may be considered as phosphoranes involving two pentacoordinate phosphorus (λ^5P) centres; as such, they would be expected to display static and dynamic stereochemistry typical of phosphoranes.[3,4] Structural information on such compounds is therefore of interest. Here we restrict ourselves to compounds with n = 1, *viz.* $[RF_2PNR']_2$ (**1**).

The first X-ray crystal structure determination of such a compound, **1a** (R = Ph; R′ = Me) was reported in 1967.[5] Two further studies involved **1b** (R = CCl_3; R′ = Me)[6] and **1c** (R = C_6F_5; R′ = Me).[7] The structure of the volatile hexafluorodiazadiphosphetidine $[F_3PNMe]_2$ **1d** (n = 0, R′ = Me) has been determined by electron diffraction.[8]

We report the low-temperature crystal structure of **1e** (R = R′ = Me) and a redetermination of the structure of **1a** (R = Ph; R′ = Me).

DISCUSSION

The redetermination of the structure of compound **1a** confirms the qualitative features observed in the 1967 study,[1] but the use of modern methods and low temperature techniques necessarily leads to a far more accurate determination. The axial P—N bond length, for instance, is now 2 pm shorter than in Reference 1, and this is now a significant difference (10σ). Some earlier discussions[7] of variation of P—N bond length with electronegativity of the substituent at phosphorus may be based on non-significant differences.

The molecules of compounds **1e** and **1a** (see Figures 1 and 2) both display crystallographic symmetry centres, and the four-membered P_2N_2 rings are therefore exactly planar. The bond lengths and angles of both compounds are closely similar (Tables IV and V). The geometry at phosphorus is trigonal bipyramidal. The axial positions are occupied by one fluorine and one ring nitrogen, whereas the carbon, the second fluorine and the second ring nitrogen are equatorial. There are some distortions from ideal angles, presumably attributable to the presence of the small ring; e.g., F_{ax}-P—N is 169.5, 168.9°. The maximum deviation is this 11.1°, and other deviations >10° are observed for F_{ax}-P—C and the acute ring angle P—N—P (*cf.* N—P—N 100.8, 100.5°).

The bond lengths follow the usual pattern for trigonal bipyramidal phosphorus, in that the axial bonds are longer; P—N_{ax} 176.3, 176.0, P—N_{eq} 163.0, 163.2, P—F_{ax} 163.8, 163.8, P—F_{eq} 158.0, 157.8°. The largest bond length difference is 1.6 pm for P—C (179.0, 180.6 pm), which may be attributed to the different chemical nature of the carbon substituents. There are few significant differences from the

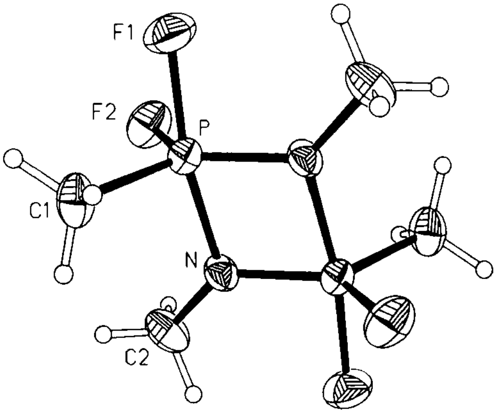

FIGURE 1 The centrosymmetric molecule of compound **1e** in the crystal, showing the numbering scheme of the asymmetric unit. Thermal ellipsoids represent 50% probability. H atom radii are arbitrary.

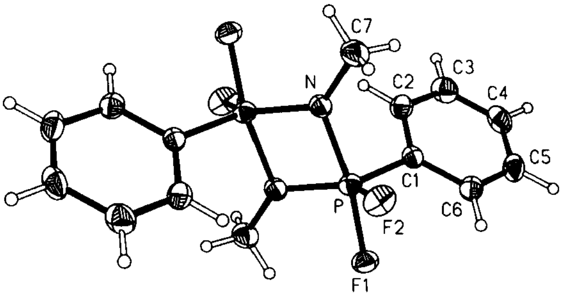

FIGURE 2 The centrosymmetric molecule of compound **1a** in the crystal, showing the numbering scheme of the asymmetric unit. Thermal ellipsoids represent 50% probability. H atom radii are arbitrary.

previously determined structures,[6,7] except that compound **1b** displays a very long P—C_{eq} bond and correspondingly wide N—P—F angle (188.8 pm, 134.3°), presumably because of the bulky CCl_3 group.

TABLE I

Summary of crystal data

	Compound	
	1e	**1a**
Formula	$C_4H_{12}N_2F_4P_2$	$C_{14}H_{16}N_2F_4P_2$
M_r	226.1	350.2
Crystal form	Colourless tablet	Colourless tablet
Crystal size (mm)	0.8 × 0.7 × 0.3	0.55 × 0.45 × 0.15
Space group	$P2_1/n$	$Pbca$
Cell constants:		
a (pm)	562.4 (2)	753.2 (3)
b (pm)	625.5 (2)	1835.5 (8)
c (pm)	1319.3 (6)	1105.0 (5)
β (°)	95.50 (5)	
V (nm^3)	0.4620	1.5276
Z	2	4
D_x (Mg m^{-3})	1.625	1.523
F (000)	232	720
μ (mm^{-1})	0.475	0.316
Temperature (°C)	−95	−95
$2\vartheta_{max}$ (°)	55	55
No. of reflections:		
measured	2796	4933
independent	1057	1751
R_{int}	0.016	0.016
observed [$>4\sigma(F)$]	990	1384
R	0.031	0.032
wR_w	0.047	0.041
g	0.0002	0.00005
No. of parameters	61	103
S	4.1	1.8
Max. Δ/σ	0.022	0.001
Max. $\Delta\rho$ (e pm^{-3})	0.33×10^{-6}	0.27×10^{-6}

TABLE II

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (pm^2) for compound (**1e**)

	x	y	z	U(eq)
P	5476.4(6)	4506.3(7)	5961.1(3)	237(1)
N	6007(2)	6477(2)	5054(1)	247(4)
F(1)	5059(2)	2365(2)	6636(1)	430(4)
F(2)	8250(2)	4195(2)	6244(1)	399(4)
C(1)	4289(3)	6216(3)	6877(1)	380(5)
C(2)	7695(3)	8257(3)	5176(2)	374(5)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

EXPERIMENTAL

Single crystals in the form of colourless tablets were obtained for **1e** [after distillation (b.p. 60°/4 mm Hg)] from acetone and for **1a** from toluene. Because of their sensitivity to moisture, crystalline samples were immersed in inert oil for optical inspection and the chosen crystals then rapidly transferred to the cold gas stream of the diffractometer (Siemens R3 fitted with LT-2 cooling device). Data were collected using monochromated Mo-$K\alpha$ radiation. Cell constants were refined from diffractometer angles of 49 strong reflections in the 2ϑ range 20–24°. The structures were solved using direct methods and subjected to anisotropic full-matrix least-squares refinement on F. Rigid methyl groups were employed, with C—H 96 pm, H—C—H 109.5°. Weighting schemes were of the form $w^{-1} = \sigma^2(F) + gF^2$. Further details of data collection and structure refinement are given in Table I, atomic coordinates in Tables II and III and derived bond lengths and angles in Tables IV and V. For compound **1e** a rigid-body libration correction was applied (R_{lib} 0.083), but the extra torsional degree of freedom in **1a** precludes such a correction; we therefore discuss only uncorrected bond lengths. The crystallographic program system was "Siemens SHELXTL PLUS."

Further details of the structure determinations (H atom coordinates, structure factors, temperature factors) have been deposited at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote a full literature citation and the reference number CSD 54801.

TABLE III

Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (pm^2) for compound **(1a)**

	x	y	z	U(eq)
P	800.9(6)	4527.9(2)	5693.7(4)	210(1)
N	1216(2)	5273.2(8)	4733(1)	228(4)
F(1)	120(2)	3936.5(6)	6701(1)	303(4)
F(2)	1901(2)	4896.9(6)	6743(1)	340(4)
C(1)	2167(3)	3860(1)	4937(2)	213(5)
C(2)	2176(3)	3822(1)	3677(2)	274(6)
C(3)	3158(3)	3292(1)	3090(2)	336(6)
C(4)	4168(3)	2800(1)	3752(2)	347(7)
C(5)	4188(3)	2841(1)	5002(2)	322(6)
C(6)	3184(3)	3363(1)	5599(2)	263(6)
C(7)	2894(3)	5652(1)	4552(2)	318(6)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE IV

Bond lengths (pm) and angles (°) for compound **(1e)**

P—N	176.3 (2)	177.1	P—F(1)	163.8 (1)	164.5
P—F(2)	158.0 (1)	158.7	P—C(1)	179.0 (2)	179.7
P . . . P(i)	261.5 (2)	262.7	P—N(i)	163.0 (1)	163.7
N—C(2)	146.2 (2)	146.8			
N—P—F(1)	169.5 (1)		N—P—F(2)	91.1 (1)	
F(1)—P—F(2)	87.7 (1)		N—P—C(1)	98.0 (1)	
F(1)—P—C(1)	92.3 (1)		F(2)—P—C(1)	109.7 (1)	
N—P—N(i)	79.2 (1)		F(1)—P—N(i)	92.8 (1)	
F(2)—P—N(i)	124.3 (1)		C(1)—P—N(i)	125.9 (1)	
P—N—C(2)	127.5 (1)		P—N—P(i)	100.8 (1)	
C(2)—N—P(i)	130.8 (1)				

Symmetry operator: (i) 1−x, 1−y, 1−z.

Libration-corrected bond lengths are given without esd's.

TABLE V

Bond lengths (pm) and angles (°) for compound (**1a**)

P—N	176.0 (2)	P—F(1)	163.8 (1)
P—F(2)	157.8 (1)	P—C(1)	180.6 (2)
P. . . P(i)	260.9 (2)	P—N(i)	163.2 (2)
N—C(7)	145.6 (3)	C(1)—C(2)	139.5 (3)
C(1)—C(6)	139.7 (3)	C(2)—C(3)	138.3 (3)
C(3)—C(4)	138.9 (3)	C(4)—C(5)	138.4 (3)
C(5)—C(6)	138.8 (3)		
N—P—F(1)	168.9 (1)	N—P—F(2)	90.9 (1)
F(1)—P—F(2)	87.1 (1)	N—P—C(1)	98.5 (1)
F(1)—P—C(1)	92.5 (1)	F(2)—P—C(1)	109.4 (1)
N—P—N(i)	79.5 (1)	F(1)—P—N(i)	93.0 (1)
F(2)—P—N(i)	127.2 (1)	C(1)—P—N(i)	123.3 (1)
P—N—C(7)	127.5 (1)	P—N—P(i)	100.5 (1)
C(7)—N—P(i)	131.4 (1)	P—C(1)—C(2)	119.9 (1)
P—C(1)—C(6)	120.9 (1)	C(2)—C(1)—C(6)	119.2 (2)
C(1)—C(2)—C(3)	120.4 (2)	C(2)—C(3)—C(4)	120.2 (2)
C(3)—C(4)—C(5)	119.8 (2)	C(4)—C(5)—C(6)	120.3 (2)
C(1)—C(6)—C(5)	120.1 (2)		

Symmetry operator: (i) −x, 1−y, 1−z.

ACKNOWLEDGEMENTS

We thank the Fonds der Chemischen Industrie for financial support.

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