

Assignment of ^{31}P Chemical Shifts to Isomers of 2,3-Dialkoxy- λ^3 -diazadiphosphetidines – Crystal and Molecular Structure of *trans*-[PhNP(OCH₂CF₃)]₂

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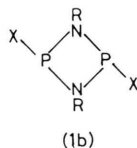
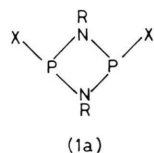
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Trifluoroethoxydiazadiphosphetidine, *cis-trans* Isomerisation, Crystal Structure, ^{31}P NMR Spectra

Geometrical isomers of λ^3 -diazadiphosphetidines show large differences in their ^{31}P chemical shifts. Trifluoroethoxylation of *cis*-(PhNPCl)₂ gives only the 'low-field' isomer initially, for which the crystal structure is determined. The compound crystallises in the triclinic space group $P\bar{1}$ with $a = 9.624(4)$, $b = 10.107(4)$, $c = 11.140(7)$ Å; $\alpha = 105.65(4)$, $\beta = 110.59(4)$, $\gamma = 93.82(3)^\circ$; and $Z = 2$. The structure was solved by direct methods and refined to $R = 0.045$. The alkoxy groups are *trans* to each other. On standing in solution, *trans*-[PhNP(OCH₂CF₃)]₂ transforms slowly and almost completely into its *cis* analogue with a high field ^{31}P chemical shift.

There has been considerable interest in the geometrical isomers of λ^3 -diazadiphosphetidines, **1a** *cis* and **1b** *trans* [1–7]. Large differences in the properties of geometrical isomers **1a** and **1b** have been observed.



For example, their ^{31}P chemical shifts differ by 50–80 ppm. For halogeno and amino derivatives, the resonances have been assigned unambiguously to the two isomers; the low field shift corresponds to the *trans* isomer [2, 4, 7]. We now report the correct assignment of shifts for the (alkoxy)diazadiphosphetidines by synthesising the pure 'low-field' isomer of **1** ($R = \text{Ph}$, $X = \text{OCH}_2\text{CF}_3$) and by determining its crystal structure.

Results and Discussion

The reactions of **1a** ($R = \text{Bu}'$ or Ph ; $X = \text{Cl}$) with primary alcohols in the presence of triethylamine as a

hydrogen chloride acceptor afford 2,4-dialkoxy-1,3,2 λ^3 ,4 λ^3 -diazadiphosphetidines (**1a** and **1b**; $X = \text{alkoxy}$). The ^{31}P NMR spectra of the products show two signals, one in the range 130–145 ppm and the other in the range 175–225 ppm corresponding to two geometrical isomers [2, 3]. Zeiss *et al.* have assigned the *trans* structure to the 'high-field' isomer [3]. The crystal structure of *trans*-[PhNP(OMe)]₂ has been determined [6] but a correlation between the geometrical disposition of the alkoxy groups and the ^{31}P chemical shift is not available. The assignment of the *trans* structure to the 'high-field' isomer and of the *cis* structure to the 'low-field' isomer has also been favoured by Kawashima and Inamoto [8], since it is expected that in the *cis* isomer steric repulsion between two alkoxy groups would cause a repulsion of the lone pair of electrons on the two phosphorus atoms and thereby lead to a deshielding of the phosphorus nuclei. On the other hand, Keat *et al.* [2] favour the assignment of the *cis* structure to the 'high-field' isomer from IR and Raman spectroscopic data and dipole moment measurements for the isomeric forms of **1** ($R = \text{Bu}'$, $X = \text{OMe}$).

We have determined the X-ray crystal structure of [PhNP(OCH₂CF₃)]₂, formed exclusively as its 'low-field' isomer in the reaction of **1a** ($R = \text{Ph}$, $X = \text{Cl}$) [7, 9] with trifluoroethanol in the presence of triethylamine. The compound has proven to be the isomer with the *trans* configuration of the trifluoroethoxy groups (see below for X-ray structure). The

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^{31}P NMR spectrum of the reaction mixture shows only a single peak at 189.8 δ . The crystals of **1b** ($\text{R} = \text{Ph}$, $\text{X} = \text{OCH}_2\text{CF}_3$) isolated from the reaction mixture can be preserved unchanged in a sealed ampoule for several months. In solution, however, the *trans* isomer gets slowly converted into the *cis* form (~ 10 days). Attempts to isolate the pure *cis* isomer have been unsuccessful. The NMR data for the two isomers are shown in Table I. The higher value of $^3J_{\text{PH}}$ and the ^{31}P NMR signal at a high-field indicate that the electron density around the phosphorus atoms is greater in the *cis* isomer than in the *trans* analogue.

Crystal Structure Analysis

Crystal data for *trans*-[PhNP(OCH₂CF₃)₂] and the details of the structure determination are summarised in Table II. The structure was solved by direct methods (Mulan-80) and refined in blocks using SHELX-76. In the crystal, the asymmetric unit con-

Table II. Crystal data for *trans*-[PhNP(OCH₂CF₃)₂] and details of structure determination.

Molecular formula	C ₁₆ H ₁₄ F ₆ N ₂ O ₂ P ₂
M	442.3
Space group	P1
<i>a</i> [Å]	9.624(4)
<i>b</i> [Å]	10.107(4)
<i>c</i> [Å]	11.140(7)
α [°]	105.65(4)
β [°]	110.59(4)
γ [°]	93.82(3)
<i>V</i> [Å ³]	960.9(9)
<i>Z</i>	2
<i>d</i> _c [g cm ⁻³]	1.528(1)
μ [cm ⁻¹]	3.065
Crystal size [mm]	0.8 × 0.4 × 0.4
<i>F</i> (000)	448
Number of reflections collected	3437
Unique	2668
Observed [<i>I</i> > 3 σ (<i>I</i>)]	2106
Maximum 2 θ [°]	46
<i>R</i>	0.045
<i>R</i> _w	0.048
Weight (ω)	1.818/[σ^2 (<i>F</i>) + 0.0006 <i>F</i> ²]

Isomer	$\delta(^1\text{H})^b$	$\delta(^{31}\text{P})$	Isomer percentage in solution ^c		
			Immediately after dissolution	After 2 days	After 9 days
1b	4.20 (dq) $^3J_{\text{PH}} = 5.7$ $^3J_{\text{FH}} = 8.3$	189.8	100	75	10
1a	4.43 (dq) $^3J_{\text{PH}} = 7.9$ $^3J_{\text{FH}} = 8.3$	142.2	0	25	90

Table I. ^1H and ^{31}P NMR spectral data^a for isomers **1a** and **1b** ($\text{R} = \text{Ph}$, $\text{X} = \text{OCH}_2\text{CF}_3$).

^a δ in ppm, *J* in Hz, solvent CDCl₃, dq = doublet of quartets; ^b for the -OCH₂CF₃ protons; virtual coupling is also seen; ^c by ^{31}P NMR.

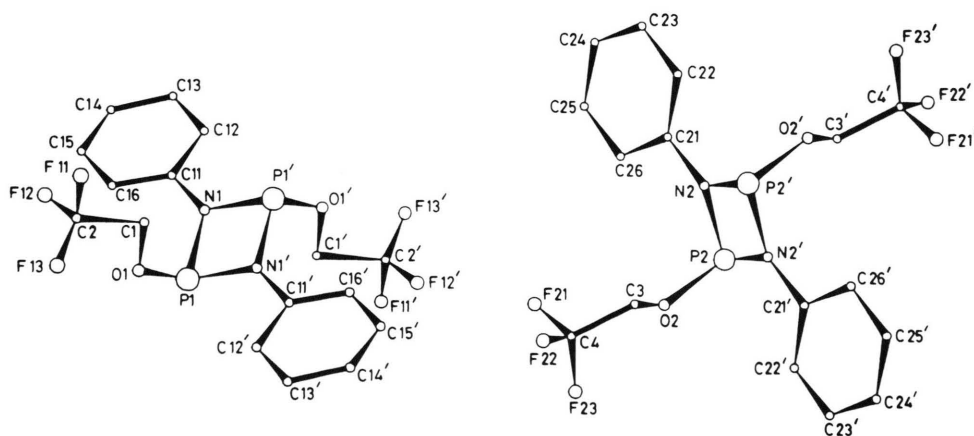


Fig. 1. The stereo view of both the molecules of *trans*-[PhNP(OCH₂CF₃)₂] (**1b**), in the unit cell. Hydrogen atoms are omitted for clarity.

tains two separate half-molecules. Both molecules in the unit cell are centrosymmetric. A stereo view of both the molecules and the numbering scheme are shown in Fig. 1. Atomic coordinates and isotropic thermal parameters are given in Table III and the molecular dimensions are summarised in Table IV. The bond lengths and bond angles for the corresponding bonds in the two separate half-molecules of the asymmetric unit are the same within the experimental error. The two molecules differ in the conformation of exocyclic trifluoroethoxy substituents with respect to the P–N ring. The four-membered rings in both molecules of the unit cell are virtually planar, phenyl rings are slightly inclined with respect to the four-membered ring in both molecules, 21° in one and 24° in the other. The nitrogen atoms of the ring are trigonal planar, the angles around nitrogen atoms summing up to *ca.* 360°. The bond distances and angles are close to those observed for *trans*-[PhNP(OMe)]₂ [6] and *trans*-[PhNP(NPh₂)]₂ [7].

Table III. Atomic coordinates and isotropic thermal parameters for the two half-molecules of *trans*-[PhNP(OCH₂CF₃)]₂ constituting the asymmetric unit (Fig. 1).

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U(<i>iso</i>)
P(1)	0.3647(1)	0.4683(1)	0.9031(1)	0.0539
N(1)	0.4562(4)	0.4501(4)	1.0590(3)	0.0541
O(1)	0.3432(3)	0.3175(3)	0.7957(3)	0.0599
C(1)	0.4519(6)	0.2289(5)	0.8062(5)	0.0739
C(2)	0.4197(8)	0.1294(6)	0.6738(6)	0.0888
F(11)	0.4292(7)	0.1916(5)	0.5889(4)	0.1431
F(12)	0.5117(5)	0.0399(4)	0.6785(4)	0.1306
F(13)	0.2814(6)	0.0580(4)	0.6203(5)	0.1381
C(11)	0.4049(5)	0.3786(4)	1.1316(4)	0.0522
C(12)	0.4849(5)	0.4085(5)	1.2695(5)	0.0649
C(13)	0.4404(7)	0.3335(6)	1.3399(5)	0.0767
C(14)	0.3117(7)	0.2309(6)	1.2757(6)	0.0791
C(15)	0.2312(6)	0.2052(5)	1.1414(6)	0.0778
C(16)	0.2764(6)	0.2771(5)	1.0673(5)	0.0645
P(2)	0.0871(1)	0.4114(1)	0.4718(1)	0.0545
N(2)	−0.0183(4)	0.4477(4)	0.5690(3)	0.0564
O(2)	−0.0141(3)	0.2756(3)	0.3462(3)	0.0570
C(3)	−0.1742(5)	0.2570(5)	0.2856(5)	0.0642
C(4)	−0.2246(7)	0.1488(6)	0.1539(5)	0.0734
F(21)	−0.1789(5)	0.0341(4)	0.1591(4)	0.1154
F(22)	−0.3729(4)	0.1217(4)	0.0954(3)	0.1067
F(23)	−0.1770(5)	0.1902(5)	0.0708(4)	0.1331
C(21)	−0.0520(5)	0.3731(5)	0.6485(4)	0.0553
C(22)	−0.0387(6)	0.2340(5)	0.6264(5)	0.0683
C(23)	−0.0712(7)	0.1621(6)	0.7041(6)	0.0831
C(24)	−0.1192(7)	0.2255(8)	0.8030(6)	0.0895
C(25)	−0.1323(7)	0.3650(7)	0.8266(6)	0.0899
C(26)	−0.1000(6)	0.4388(5)	0.7499(5)	0.0739

Table IV. Selected mean bond lengths (Å) and angles (°) for *trans*-[PhNP(OCH₂CF₃)]₂.

P(1)–N(1)	1.716(3)	N(1)–P(1)–N(1')	79.8(2)
P(1')–N(1)	1.715(3)	N(1)–P(1)–O(1)	105.6(2)
P(1)–O(1)	1.611(3)	N(1')–P(1)–O(1)	105.5(2)
N(1)–C(11)	1.402(4)	P(1)–N(1)–P(1')	100.2(2)
O(1)–C(1)	1.416(6)	P(1)–N(1)–C(11)	130.7(3)
C(1)–C(2)	1.456(6)	P(1')–N(1)–C(11)	128.9(3)
C(2)–F	1.30(1)		

Further details of the investigations on crystal structures may be received at: "Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2". The Registry-No., CSD 51955, the name of the author, and the reference should be given.

Recently several generalisations have been made regarding the isomer preference for diazadiphosphetidines [7]. The 2,4-dichloro derivatives, [RNPCI]₂, (R = Ph or Bu') exist as *cis* isomers with no evidence for a *trans* form. The 2,4-diamino substituted N(ring)-aryl diazadiphosphetidines appear to behave differently from the N(ring)-alkyl analogues. *Trans* isomers are favoured for the former when the exo-amino groups are relatively bulky; with the smaller amino substituents (particularly with one primary amino substituent), the *cis* form is preferred. On the other hand, for the N(ring)-alkyl substituted diazadiphosphetidines, the *cis* isomers are preferred exclusively in several instances [7].

The results of the present study put the assignment of *cis* and *trans* structures to 2,4-di(alkoxy) or di(aryloxy) substituted diazadiphosphetidines on a firm basis. It is intriguing to note that with smaller alkoxy groups (OMe, OEt, or OCH₂CF₃), the initial product is the *trans*-isomer which transforms into its *cis* counterpart on standing in solution, whereas with a more bulky group such as OBu' or OPh [2, 3, 10], only the *cis* isomer is formed. This behaviour is observed for both N(ring)-alkyl and N(ring)-aryl diazadiphosphetidines. Apparently the factors that govern the relative stability of the isomers of diazadiphosphetidines are far more subtle than have been recognised and need to be investigated in more detail.

Experimental

The infrared spectrum (4000–400 cm^{−1}) was recorded with a Carl-Zeiss UR-10 spectrometer; ¹H NMR spectra were obtained from a Bruker FT 270 (270 MHz), with TMS as internal standard.

^{31}P NMR spectra were recorded at 32.2 MHz on a Varian FT-80A spectrometer. Chemical shifts downfield from the external standard 85% H_3PO_4 , are assigned positive values. Elemental analyses were performed at City University, London, UK, by Dr. S. A. Matlin. The mass spectrum was obtained from a VG ZAB2F Spectrometer (EI conditions, 70 eV, 200 μA ; source temperature 200 $^\circ\text{C}$). The sample was introduced via the direct inlet system without any heating. X-ray diffraction data were collected using a CAD-4 diffractometer (MoK_α radiation, $\lambda = 0.70926 \text{ \AA}$) equipped with a graphite monochromator.

Preparation of 2-trans-4-bis(trifluoroethoxy)-1,3-diphenyl-1,3,2 λ^3 ,4 λ^3 -diazadiphosphetidine

Trifluoroethanol (Fluka) (3.2 g, 32 mmol) and triethylamine (3.3 g, 33 mmol) were added dropwise at 25 $^\circ\text{C}$ in an atmosphere of dry N_2 to a stirred solution of **1a** ($\text{R} = \text{Ph}$, $\text{X} = \text{Cl}$) [7, 9] (5.0 g, 16 mmol) in light petroleum ether (b.p. 60–80 $^\circ\text{C}$) (200 cm^3). Stirring was continued for 6 h. The solution was then heated under reflux (0.5 h) and filtered. The filtrate was concentrated to $\sim 50 \text{ cm}^3$ and cooled to 0 $^\circ\text{C}$ to obtain **1b** ($\text{R} = \text{Ph}$, $\text{X} = \text{OCH}_2\text{CF}_3$) (4.3 g, 61%), m.p. 95 $^\circ\text{C}$. MS: $m/e = 442$. $\text{C}_{16}\text{H}_{14}\text{F}_6\text{N}_2\text{O}_2\text{P}_2$ requires $m/e = 442$. IR (KBr): 1595 (s), 1580 (s), 1490 (s),

1445 (m), 1405 (m), 1280 (vs), 1265 (vs), 1170 (vs), 1160 (vs), 1050 (vs; $\nu_{\text{P-O-C}}$), 960 (s), 905 (vs; $\nu_{\text{asym P-N-P}}$), 880 (m), 845 (m), 785 (s), 750 (s), 685 (br), 655 (br) cm^{-1} .

$\text{C}_{16}\text{H}_{14}\text{F}_6\text{N}_2\text{O}_2\text{P}_2$ (442)

Calcd C 43.4 H 3.2 N 6.3,

Found C 44.6 H 3.2 N 6.6.

Crystals for the X-ray diffraction study were obtained by crystallising the compound from light petroleum ether (b.p. 60–80 $^\circ\text{C}$) within one day. Examination of the crystals by ^{31}P and ^1H NMR spectra showed that they were of pure 'low-field' isomer. The crystal was sealed in a 0.5 mm capillary.

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- [10] The phenoxy derivative, $[\text{PhNP}(\text{OPh})_2]$ [Ref. 9] shows only the 'high-field' signal [$\delta(^{31}\text{P}) = 137.6$ in CH_2Cl_2] in its ^{31}P NMR spectrum.