

The Structure of 2,2,2,4,4,4-Hexafluoro-1,3-dimethyl-1,3-diaza-2,4-diphosphacyclobutane, [MeN·PF₃]₂

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As an empirical rule the axial sites of the trigonal bipyramid framework of substituted fluorophosphoranes are occupied by the most electronegative ligands.¹ However, the steric restrictions imposed by the four-membered P-N ring of 1,3-diaza-2,4-diphosphacyclobutane derivatives² of the type [RN·PR'₂]₂ may well result in violation of this rule. Recent investigations of the vibrational spectra of substituted fluorophosphoranes³ have now been extended to the compound 2,2,2,4,4,4-hexafluoro-1,3-dimethyl-1,3-diaza-2,4-diphosphacyclobutane, [MeN·PF₃]₂, the infrared and Raman spectra of which have been recorded in the range 30–3500 cm.⁻¹.

The vibrational modes likely to be most sensitive as indices of the overall geometry of the [MeN·PF₃]₂ molecule are those associated with the motions of the [CN·PF₃]₂ skeleton. To simplify matters, vibrational features due principally to internal vibrations of the methyl groups have first been eliminated (notwithstanding the coupling of certain modes of the same symmetry class, *e.g.*, C–N stretching and CH₃ rocking⁴); the remaining bands attributable to fundamental modes of the heavy-atom skeleton are listed in Table 1. The conspicuous lack of coincidences between infrared

and Raman frequencies, taken in conjunction with the relative simplicity of the spectra, is compelling evidence for a centrosymmetric molecule. This reduces the possible molecular structures for [MeN·PF₃]₂ to (I) and (II) (point groups C_{2h} and D_{2h}, respectively). The vibrational selection rules appropriate to the frameworks of the two models are summarized in Table 2. Despite the relatively

TABLE 2

Selection rules for the skeletal modes of [MeN·PF₃]₂

Point group	Model		Observed spectra
	(I)	(II)	
C _{2h}	D _{2h}	—	
Raman-active fundamentals	15	15	14
Polarized Raman lines	10	6	>5
I.r.-active fundamentals	15	14	13

fine distinctions between the two structures, the following details favour (I):

(i) Although no more than five polarized lines are clearly identifiable, there must be at least *two* more totally symmetric skeletal modes (approximating to C–N stretching and skeletal deformation) irrespective of the symmetry of the system. For

TABLE 1

Vibrational frequencies of the skeleton of [MeN·PF₃]₂

Infrared (vapour)		Raman (liquid)		Approximate description of mode
cm. ⁻¹	Intensity	cm. ⁻¹	Intensity	
1264	s	~1202	vw, br	C–N antisym. stretch
~964	w, sh	960	m, dp	C–N sym. stretch
934	vs	904	mw, dp	Equat. P–F antisym. stretch
858	vs	839.5	mw, p	Equat. P–F sym. stretch
807	vs	741.5	m, p	Axial P–F stretch
614	m	626	s, p	Equat. P–N stretch
535	vs	563	ms, p	Axial P–N stretch
457	m	478	m, dp	} Deformation and rocking modes of skeleton
321	s	442	mw, dp	
~283	w, sh	418	w, dp	
221	m	356	m, p	
137	m	267	m, sh, dp	
99	mw	243	ms, dp	
		104.5	m, dp	

s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder, p = polarized, dp = depolarized, equat. = equatorial. Descriptions of modes refer to co-ordination environment of the phosphorus atom.

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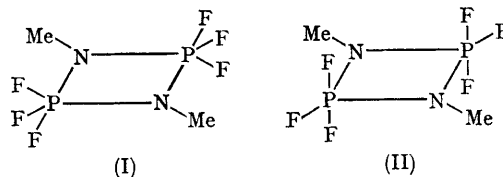
the P-N and P-F stretching modes model (I) implies four polarized lines (as observed at 563, 626, 742, and 840 cm^{-1}), whereas model (II) implies only three such lines.

(ii) In the vapour-phase infrared spectrum the band envelopes of the absorptions due to P-N and P-F stretching vibrations comply well with expectations based on model (I).

(iii) Comparison of the frequencies with those of other substituted fluorophosphoranes³ also indicates that of the three fluorine atoms attached to each phosphorus two are in equatorial sites and only one is in an axial site of the trigonal bipyramid skeleton. As usual,³ the P-N and P-F axial bonds are markedly weaker than the corresponding equatorial bonds.

We conclude, then, that the $[\text{MeN}\cdot\text{PF}_3]_2$ molecule has a structure analogous to that⁵ of

$[\text{MeN}\cdot\text{PCl}_3]_2$ with the effective symmetry C_{2v} . As in the phenyl derivative, $[\text{MeN}\cdot\text{PPhF}_2]_2$, for which preliminary X-ray diffraction results have recently been reported,⁶ the stereochemical properties of the P-N four-membered ring appear to favour five-co-ordinate phosphorus atoms for which the electronegativity principle is inapplicable.



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² R. Schmutzler, *Chem. Comm.*, 1965, 19.

³ A. J. Downs and R. Schmutzler, *Spectrochim. Acta*, 1965, **21**, 1927; *ibid.*, 1967, **23**, A, 681.

⁴ See, for example, M. J. Buttler and D. C. McKean, *Spectrochim. Acta*, 1965, **21**, 465.

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⁶ J. W. Cox and E. R. Corey, *Chem. Comm.*, 1967, 123.