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Vibrational Spectra and Structure of 2,2,2,4,4,4-Hexafluoro-1,3-dimethyl-1,3-diaza-2,4-diphosphacyclobutane $(CH_3NPF_3)_2$

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The vibrational spectrum of $(CH_3NPF_3)_2$ has been investigated by analyzing the vapor- and liquid-state infrared spectra (30–3200 cm^{-1}) and liquid-state Raman spectrum (100–3200 cm^{-1}). Existing vibrational data for $(CH_3NPCl_3)_2$ have been confirmed, and, in addition, the far-infrared spectrum in solution (30–450 cm^{-1}) has been recorded. It has been found that the vibrational data of both molecules may be satisfactorily interpreted in terms of a C_{2h} or a C_i structure. An approximate normal-coordinate calculation has been carried out and used to support the vibrational assignments for $(CH_3NPF_3)_2$ and $(CH_3NPCl_3)_2$.

Introduction

Several structural studies have recently been done on molecules containing the four-membered ring $(PN)_2$, in which the N and P atoms are three- and five-coordinated, respectively. X-Ray diffraction data[2] of N-methyltrichlorophosphinimine dimer, $(CH_3NPCl_3)_2$, show that the molecule is centrosymmetric with a planar ring of alternate P and N atoms. The coordination of each phosphorus atom is approximately a trigonal bipyramid with one apical and two equatorial chlorine atoms and one apical and one equatorial nitrogen atom. The coordination of the nitrogen atoms is planar trigonal. Infrared and Raman spectra for $(CH_3NPCl_3)_2$ in solution have also been reported.[3] The conclusion that the molecule is centrosymmetric was also reached on the basis that the two spectra are mutually exclusive.

More recently several fluoro-1,3,2,4-diazadiphosphetidine compounds were prepared and characterized by Schmutzler.[4] The molecule of 2,2,4,4-tetrafluoro-1,3-dimethyl-2,4-diphenyl-1,3,-diaza-2,4-diphosphacyclobutane, $(CH_3PF_2C_6H_5)_2$, has been shown[5] by X-ray measurements to possess a center of symmetry. The coordinations of the phosphorus and nitrogen atoms are similar to those reported for the $(CH_3NPCl_3)_2$ molecule.

In this communication we report the complete infrared (3500–30 cm^{-1}) and Raman spectra (3200–100 cm^{-1}) of the N-methylfluorophosphinimine dimer, $(CH_3NPF_3)_2$, in the condensed and the vapor phase. An interpretation of the spectra is given and several conclusions are drawn concerning the geometrical form of the molecule. As an aid to the interpretation of the spectra, we also investigated the vibrational spectra of the related molecule $(CH_3NPCl_3)_2$. Tentative assignments of the fundamentals have been made for both compounds.

Experimental Section

The sample of $(CH_3NPF_3)_2$ was furnished by Dr. R. Schmutzler of Du Pont and it was used without further purification.

Infrared spectra for the gas, liquid, and CS_2–CCl_4 solutions were recorded on a Perkin-Elmer Model 521 spectrophotometer (4000–250 cm^{-1}) calibrated with polystyrene. The gas-phase spectra were taken in a standard 10-cm gas cell fitted with KBr or CsI windows at different pressures in the range 48–0.1 mm. The far-infrared gas-phase spectra, over the range 300–30 cm^{-1}, were taken in a 30-cm gas cell at 48 mm pressure with a Jarrell-Ash far-infrared double-beam spectrophotometer.

The liquid samples were run as films between CsI plates and as CS_2–CCl_4 solutions in standard liquid cells in the region 4000–250 cm^{-1}. The far-infrared liquid spectra were obtained in polyethylene cells of 0.2-mm path length with a Fourier 520 interferometer equipped with a liquid helium cooled detector.

Raman spectra of the pure liquid were obtained in a 7-mm Raman tube on a Cary 81 Raman spectrophotometer. Depolarization factors were determined by the method of Edsall and Wilson.[6]

$(CH_3NPCl_3)_2$ was prepared as described by Chapman, *et al.*[3] Good agreement was obtained with their reported infrared and Raman spectra. Their infrared spectrum did not extend below 450 cm^{-1} and the results reported herein are new in that range. The infrared spectra of $(CH_3NPCl_3)_2$ were obtained in CS_2 and CCl_4 solutions and the Raman spectra in CS_2 and benzene solutions. The far-infrared spectrum was taken in *n*-hexane solution in polyethylene cells of 10-mm path length with the Fourier 520 interferometer.

Results and Discussion

Infrared absorption frequencies and Raman displacement frequencies, relative intensities, and depolarization factors for $(CH_3NPF_3)_2$ and $(CH_3NPCl_3)_2$ are reported in Tables I and II. The infrared spectra of $(CH_3NPF_3)_2$ as obtained in the vapor phase and in solution are given in Figures 1 and 2. Analysis of the spectra indicates that except for a few lines which may be assigned with certainty to the CH_3 group vibrations, the Raman frequencies have no infrared counterparts. This implies the existence of an inversion center in the frame $(YNPF_3)_2$ and planarity of the $(PN)_2$ ring in the $(CH_3NPF_3)_2$ molecule. The fact that the strongly polarized Raman lines of the methyl group vibrations apparently coincide with certain infrared bands may be ascribed to a weak coupling of the two CH_3 groups, which leads to accidental degeneracy of the respective Raman- and infrared-active vibrations.

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[1] Fellow of the Consejo Nacional de Investigaciones Cientificas y Tecnicas, Argentina, 1965–1966.

[2] L. G. Hoard and R. A. Jacobson, *J. Chem. Soc., Sect. A*, 1203 (1966).

[3] A. C. Chapman, W. S. Holmes, N. L. Paddock, and H. T. Searle, *J. Chem. Soc.*, 1825 (1961).

[4] R. Schmutzler, *Chem. Commun.*, 19 (1965).

[5] J. W. Cox and E. R. Corey, *ibid.*, 123 (1967).

[6] J. T. Edsall and E. B. Wilson, *J. Chem. Phys.*, **6**, 124 (1939).

TABLE I

VIBRATIONAL SPECTRUM OF $(CH_3NPF_3)_2$[a]

Raman			Infrared			
Cm⁻¹	*I*	≃ρ	Cm⁻¹ (liq film)	Cm⁻¹ (gas)	*I*	Tent. assignment
				3073	vvw	
3033	15		3030	3041	vw	
2966	100	0.2	2965	2969	m	CH_3 str
2918	20	0.2	2914	2921	w	CH_3 str
2883	1					
2849	40	0.2	2849	2853	w	N–CH_3 str
				2770	vvw	
1473	12	0.7	1468	1468	w	CH_3 def modes
1446	12	0.5				
			1434	1435	w	
			1415	1415	vw	POF_3?
			1379	1378	vw	CH_3 def modes
1336	5	0.3				
			1257 br	1263	vs	ν_{27}
≃1200	1					ν_1
			1202 sh			CH_3 rock modes
			1190	1199	m–s	
			1173	1175	m–w	
			1137		vw	
			1123	1123	vw	
			1085	1093	vw	
			1023	1015	vw	
962	10	0.6				ν_2 or ν_{13}
			927 br	935	vs	ν_{17}
906	5	0.7				ν_2 or ν_{13}
			847	857	vs	ν_{22}
840	3	0.3				ν_7
			795	806	vs	ν_{23} and ν_{24}
				765	w	ν_{18}
741	20	0.3				ν_3
			739		w	?
			707		vw	627 + 75, 477 + 228, 564 + 142
			660		vw	359 + 315, 564 + 99
627	100	0.2				ν_8
			615	615	vw	477 + 142
564	20	0.3				ν_4
			532 br	535	s–vs	ν_{28}
477	10	0.5				ν_{11}
			474		vw	242 + 228
			458	455	vw	359 + 99
442	6	0.5				2 × 228, 142 + 315
418	4	0.5				315 + 99
				405	vw	106 + 315, 268 + 142
359	25	0.3				ν_5
			314	315	m–w	ν_{25}
268	16	0.7				ν_9 and ν_{14}
242	30	0.5				ν_{10}
			230	228	m[b]	ν_{19} and ν_{29}
			151	142	s[b]	ν_{20}, ν_{26}?, and ν_{30}
106	m[b]	0.8				ν_6
			103	99	s[b]	ν_{16}
			82	75	w[b]	ν_{21}

[a] s, strong; m, medium; w, weak; v, very; br, broad. [b] Obtained on a different scale; see text.

TABLE II

VIBRATIONAL SPECTRUM OF $(CH_3NPCl_3)_2$[a]

This work		Chapman, *et al.*[3]			
Infrared,[b] cm⁻¹	*I*	Raman line,[c,d] cm⁻¹	Infrared, cm⁻¹	*I*	Tentative assignment
2999	m	2999 vw	2996	m	CH_3 str
2950	m	2946 m	2941	m	CH_3 str
2830	w		2812	w	N–CH_3 str
1457	m		1461	m	CH_3 def modes
1425	m		1429	m	
1289	vw				
1210	s		1210	s	ν_{27}
1187	s		1184	s	CH_3 rock modes
1166	s		1162	s	
1118	vw				
925	vw				268 + 660
847	vs		847	vs	ν_{22}
747	vw		747	vw	544 + 212
700	m		700	m	ν_{17}
660	s		658	s	ν_{18}
576	s		575	s	ν_{28}
		544 s, dp			ν_8
		458 m, dp			ν_3 and ν_{11}
429	m		434	m	ν_{23}
		412 w, dp			2 × 212, 2 × 204
400	m				ν_{24}
391	m				
		352 vs, p			ν_4
336	m				268 + 62, 204 + 122?
288	w				?
275	w				?
		268 s, dp			ν_5
212[e]	s				ν_{25}
		240 ms, dp			ν_9 and ν_{14}
175[e]	vw				?
122[e]	vw				ν_{19}, ν_{20}, ν_{26}, and ν_{29}
62[e]	m				ν_{21} and ν_{30}

[a] s, strong; m, medium; w, weak; v, very. [b] Solutions in CS_2 and CCl_4. [c] Solutions in CS_2 and benzene. [d] Since our results are in complete agreement with those of Chapman, *et al.*, only their results are included in the table. [e] Solution in *n*-hexane.

The molecule has a total of 48 normal vibrations, of which 18 are methyl-group vibrations and 30 are skeletal vibrations. In order to simplify the treatment, we have assumed throughout that the hydrogen atom motions are not coupled appreciably with the motions of the other groups in the molecule and may be treated separately from the skeletal vibrations. Thus the CH_3 groups were regarded as point masses in the analysis of the skeletal vibrations, $(YNPF_3)_2$.

If the carbon atoms lie in the plane of the $(PN)_2$ ring, as is actually the case in the crystals of $(CH_3NPCl_3)_2$ and $(CH_3NPC_6H_5F_2)_2$, a D_{2h}, C_{2h}, or C_i structure is possible, depending on the orientation of the fluorine atoms around the phosphorus. If the carbon atoms are not in the plane of the ring, the structure must be C_{2h} or C_i. However, the D_{2h} structure, which requires that each phosphorus atom be coplanar with its coordinated fluorine atoms, is considered unlikely because the number of polarized Raman lines observed is larger than the number expected (six) for D_{2h} symmetry. In the following analysis we shall assume that the carbon atoms are coplanar with the ring, that each nitrogen atom is coordinated in the axial configuration to one phosphorus atom and in the equatorial configuration to the other, and that the fluorine atoms fill the remaining axial and equatorial positions of the trigonal bipyramid about the phosphorus.

The distributions of the various skeletal vibrations

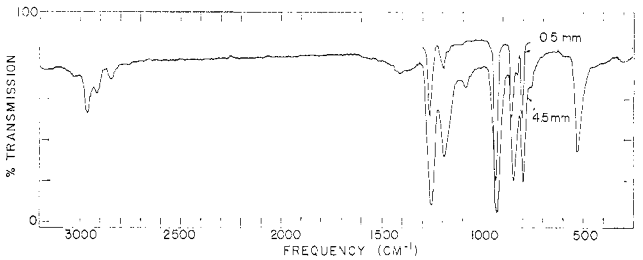

Figure 1.—Infrared spectrum of $(CH_3NPF_3)_2$ vapor at pressures of $\simeq$4.5 and $\simeq$0.5 mm.

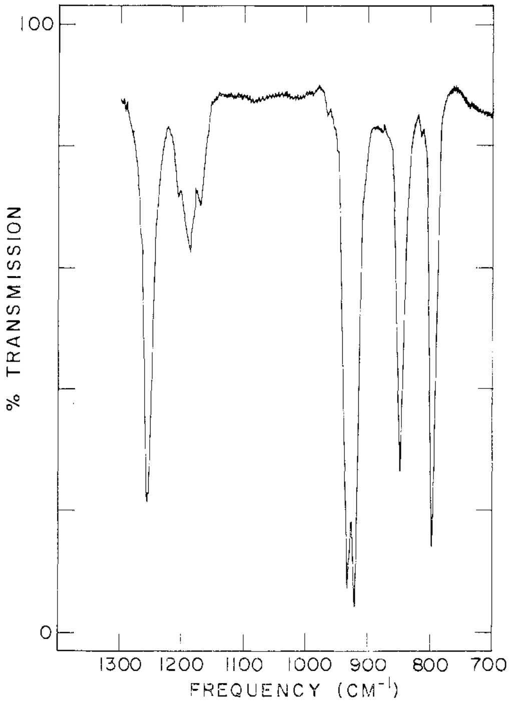

Figure 2.—Infrared spectrum of $(CH_3NPF_3)_2$ in CS_2 solution ($\simeq$5%); cell thickness 0.025 mm.

among the different vibrational species of the point groups C_i and C_{2h} are $15A_g + 15A_u$ and $10A_g + 5B_g + 6A_u + 9B_u$, respectively. Thus, for both structures 15 Raman lines are expected, either all polarized (C_i) or 10 polarized (C_{2h}), and 15 infrared bands. The gas-phase infrared spectrum was insufficiently resolved to determine with certainty the envelopes for all of the bands, and the main difference to be expected in the spectra of the two structures is the number of polarized Raman lines. Of the 13 Raman lines observed below 1000 cm^{-1}, 10 have a depolarization factor, ρ, less than 0.7 and can be described as polarized, and among these only eight were assigned to skeletal fundamentals. Unfortunately the three lines at 906, 268, and 106 cm^{-1} have ρ values around 0.7–0.8, and owing to the uncertainty associated with their measurement, it is not possible to decide if they correspond to totally symmetrical or to nontotally symmetrical vibrations.

As is apparent the total number of observed Raman lines as well as of polarized lines assigned to skeletal fundamentals is slightly less than predicted for either structure. This may be due to the intrinsic weakness of the Raman lines or to the fact that several vibrations have very nearly the same frequency. Because of these difficulties and the similarity of the selection rules for C_{2h} and C_i structures, no conclusions can be drawn from the vibrational spectra alone regarding the relative orientations of the PF_3 groups in the molecule.

Assignment of Frequencies.—To assist in the assignment of the observed infrared and Raman frequencies to the actual vibrations of the molecule, an approximate normal coordinate calculation was carried out. Since no structural information is available for this molecule, several assumptions had to be made Bond lengths and angles for the fluorine compound were taken from the results of the crystal-structure study of $(CH_3NPCl_3)_2$.[2] The values used were: P–N = 1.70 A (mean value of the axial and equatorial P–N bonds), C–N = 1.48 A, N–P–N = 80.5°, and P–N–P = 99.5°. The P–F bond length was assumed to be 1.55 A[7] (average length in PF_5).

In order to facilitate the handling of the secular equations by reducing their order, a D_{2h} symmetry was assumed in the calculation with the PF_3 plane normal to the $(PN)_2$ ring (Figure 3). A complete set of internal vibrational coordinates was chosen and these were then grouped into combinations derived from the D_{2h} symmetry group in the usual way[8] (see Table V). The symmetrized G-matrix elements were calculated through the SD-9064-I program written by Schachtschneider.[9]

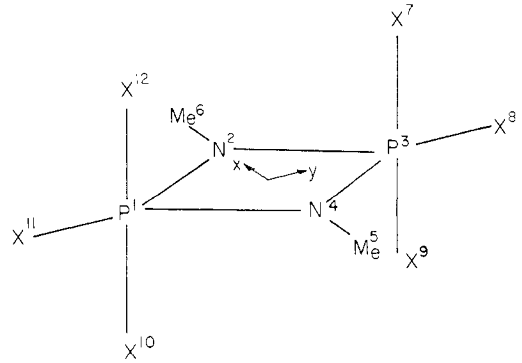

Figure 3.—Molecule of $(CH_3NPX_3)_2$ (X = F or Cl) (D_{2h} symmetry).

Initially a symmetrized valence-force field was assumed with stretching force constants for P–N, P–F, and C–N of 3.6, 5.5, and 5.0 mdynes/A and a single bending constant for all angles of 1.0 mdynes/A. The P–N bond stretching force constant is the same as that calculated in ref 10 for a single P–N bond by applying Gordy's rule, and the value given for the P–F bond stretching is a weighted average of the axial and equatorial A_1' constants in PF_5.[11] The C–N bond stretching constant is a mean value of that reported for different compounds.[8]

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(7) K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, **4**, 1775 (1965).

(8) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(9) J. H. Schachtschneider, Technical Report No. 210-61, Shell Development Co., Emeryville, Calif.

(10) A. C. Chapman and D. F. Carroll, *J. Chem. Soc.*, 5005 (1963).

(11) L. C. Hoskins and R. C. Lord, *J. Chem. Phys.*, **46**, 2402 (1967).

The normal coordinate calculation for the $(CH_3NPCl_3)_2$ molecule was carried out along with the help of assumptions similar to those made for the fluorine compound. The P–Cl bond distance was taken as 2.06 A[2] and the initial P–Cl stretching force constant as 2.9 mdynes/A.[10] The frequencies were calculated by Wilson's *FG*-matrix method through the program No. SD-9032-III.[12]

Comparison of the calculated and observed frequencies served as a guide for the assignment of the vibrational modes of the $(CH_3NPF_3)_2$ and $(CH_3NPCl_3)_2$ molecules given in Tables III and IV.

TABLE III

CALCULATED FREQUENCIES OF SKELETAL MODES IN $(CH_3NPF_3)_2$

Freq no.	Species			Calcd freq, cm^{-1}	Nearest obsd[a] freq, cm^{-1}	Approx form of vibration from PED
	D_{2h}	C_{2h} (z)	C_i			
1	A_g	A_g	A_g	1217	1200	C–N–P str
2				929	906 or 962	PF′ str
3				726	741	PF_2 str
4				504	564	Ring str
5				358	359	Ring distortion[b]
6				110	106	PF_2 bend
7	B_{1g}	A_g	A_g	855	840	Ring mode
8				629	627	PF_3 bend and ring mode
9				271	268	Skeletal
10				242	242	Skeletal
11	B_{2g}	B_g	A_g	479	477	Skeletal
12				163	. . .	Skeletal
13	B_{3g}	B_g	A_g	932	906 or 962	PF_2 str
14				271	268	PF_3 bend
15				163	. . .	PF_3 bend
16	A_u	A_u	A_u	99	99	PF_3 bend
17	B_{1u}	A_u	A_u	972	935	PF_2 str
18				743	765	Ring puckering and PF_3 bend
19				214	229	PF_3 bend
20				147	142	Skeletal
21				77	75	Ring puckering
22	B_{2u}	B_u	A_u	855	857	Ring str
23				807	806	PF′ str
24				745	806	PF_2 str
25				305	315	PF_2 bend
26				186	142?	Skeletal
27	B_{3u}	B_u	A_u	1257	1263	C—N–P str
28				555	535	Skeletal str
29				203	229	PF_3 bend
30				153	142	PF_3 bend

[a] Frequency no. 1–15 from Raman spectrum of liquid; frequency no. 16–30 from infrared spectrum of vapor. [b] Ring vibrations approximately perpendicular to the *z* axis are called ring distortions, and the parallel ones are called puckerings.

The diagonal terms in the factored *F* matrix were adjusted after several tests by inspection of the Jacobian matrix elements $J_{ij} = 1/\nu_i(\partial\nu_i/\partial F_j)$. In some of the symmetry species the observed frequencies could not be satisfactorily reproduced using diagonal elements only, which is to be expected. In such cases the off-diagonal elements which appeared to have the most sensitive J_{ij}'s were allowed to take nonzero values.

Unfortunately, several skeletal frequencies fall together in narrow regions and owing to the very low symmetry of the molecule interactions are likely to occur. This increases the difficulty of interpreting the vibrational spectrum, and permutations in the assignment of neighboring frequencies are possible within the precision of the present analysis. An agreement within 10% of the observed and calculated frequencies was regarded as satisfactory for the purpose of assigning the fundamental vibrations.

TABLE IV

CALCULATED FREQUENCIES OF SKELETAL MODES IN $(CH_3NPCl_3)_2$

Freq no.	Species			Calcd Freq, cm^{-1}	Nearest obsd[a] freq, cm^{-1}	Approx form of vibration from PED
	D_{2h}	C_{2h} (z)	C_i			
1	A_g	A_g	A_g	1204	. . .	C–N–P str
2				718	. . .	N–P–Cl′ str
3				435	458	Ring str and distortion[b]
4				353	352	PCl_2 str
5				263	268	Ring distortion and PCl′ str
6				71	. . .	PCl_2 bend
7	B_{1g}	A_g	A_g	855	. . .	Ring mode
8				535	544	Ring mode and PCl_3 bend
9				218	204	Skeletal
10				133	. . .	PCl_3 bend
11	B_{2g}	B_g	A_g	471	458	Skeletal
12				130	. . .	Skeletal
13	B_{3g}	B_g	A_g	658	. . .	PCl_2 str
14				201	204	PCl_3 bend
15				99	. . .	PCl_3 bend
16	A_u	A_u	A_u	62	62	PCl_3 bend
17	B_{1u}	A_u	A_u	743	700	Ring puckering and PCl_2 str
18				629	660	PCl_2 str
19				128	122	Skeletal
20				98	122?	PCl_3 bend
21				56	62	Ring puckering
22	B_{2u}	B_u	A_u	837	847	Ring str
23				444	429	PCl′ str
24				379	391	PCl_2 str
25				195	212	Skeletal
26				125	122	PCl_2 bend
27	B_{3u}	B_u	A_u	1204	1210	C—N–P str
28				577	576	Skeletal str
29				130	122	PCl_3 bend
30				74	62	PCl_3 bend

[a] Frequency no. 1–15 from Raman spectrum of CS_2 or benzene solutions; frequency no. 16–30 from infrared spectrum of CS_2–CCl_4 solutions. [b] See footnote *b* of Table III.

The *F* elements which make up the *F* matrices for the various vibrational species are given in Table VI. These values are of limited significance because the force constant set is greatly underdetermined.

We believe, however, that the fundamental frequencies have been identified and we propose an approximate description for most of the vibrations. This was based on potential energy distribution (PED), computed in the usual way.[12] Several comments on the assignments given in Tables III and IV may be made.

(1) Assignment of the CH_3 group vibrations is given by analogy to those reported for other molecules containing the group $P–N–CH_3$.[13] The fundamentals are broadly describable as C–H stretching, CH_3 deformation, and CH_3 rocking vibrations. The presence of a

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(12) J. H. Schachtschneider, Technical Report No. 263-62, Shell Development Co., Emeryville, Calif.

(13) A. B. Burg and J. Heners, *J. Am. Chem. Soc.*, **87**, 3092 (1965).

TABLE V

SYMMETRY COORDINATES FOR $(CH_3NPX_3)_2$ (X = F or Cl) (D_{2h} SYMMETRY)[a,b]

A_g

$S_1 = \Delta(R_1 + R_3 + R_3 + R_4)$
$S_2 = \Delta(D_1 + D_2)$
$S_3 = \Delta(\omega_1 + \omega_2)$
$S_4 = \Delta(\beta_1 + \beta_2)$
$S_5 = \Delta(r_1 + r_3 + r_4 + r_6)$
$S_6 = \Delta(r_2 + r_5)$
$S_7 = \Delta(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6 + \phi_7 + \phi_8)$

B_{1g}

$S_8 = \Delta(R_1 - R_2 + R_3 - R_4)$
$S_9 = \Delta(\alpha_1 + \alpha_2)$
$S_{10} = \Delta(\epsilon_1 + \epsilon_2)$
$S_{11} = \Delta(\phi_1 - \phi_2 - \phi_3 + \phi_4 + \phi_5 - \phi_6 - \phi_7 + \phi_8)$

B_{2g}

$S_{12} = \Delta(\tau_1 - \tau_2 - \tau_3 + \tau_4) \equiv 0$
$S_{13} = \Delta(\delta_1 - \delta_2)$
$S_{14} = \Delta(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6 + \phi_7 - \phi_8)$

B_{3g}

$S_{15} = \Delta(\tau_1 + \tau_2 - \tau_3 - \tau_4) \equiv 0$
$S_{16} = \Delta(r_1 - r_3 + r_4 - r_6)$
$S_{17} = \Delta(\theta_1 - \theta_2)$
$S_{18} = \Delta(\phi_1 + \phi_2 - \phi_3 - \phi_4 + \phi_5 + \phi_6 - \phi_7 - \phi_8)$

A_u

$S_{19} = \Delta(\tau_1 + \tau_2 + \tau_3 + \tau_4) = 0$
$S_{20} = \Delta(\phi_1 - \phi_2 + \phi_3 - \phi_4 - \phi_5)$

B_{1u}

$S_{21} = \Delta(\tau_1 - \tau_2 + \tau_3 - \tau_4)$
$S_{22} = \Delta(\delta_1 + \delta_2)$
$S_{23} = \Delta(r_1 - r_3 - r_4 + r_6)$
$S_{24} = \Delta(\theta_1 + \theta_2)$
$S_{25} = \Delta(\phi_1 + \phi_2 - \phi_3 - \phi_4 - \phi_5 - \phi_6 + \phi_7 + \phi_8)$

B_{2u}

$S_{26} = \Delta(R_1 - R_2 - R_3 + R_4)$
$S_{27} = \Delta(\beta_1 - \beta_2)$
$S_{28} = \Delta(\alpha_1 - \alpha_2)$
$S_{29} = \Delta(r_1 + r_3 - r_4 - r_6)$
$S_{30} = \Delta(r_2 - r_5)$
$S_{31} = \Delta(\phi_1 + \phi_2 + \phi_3 + \phi_4 - \phi_5 - \phi_6 - \phi_7 - \phi_8$

B_{3u}

$S_{32} = \Delta(R_1 + R_2 - R_3 - R_4)$
$S_{33} = \Delta(D_1 - D_2)$
$S_{34} = \Delta(\omega_1 - \omega_2)$
$S_{35} = \Delta(\epsilon_1 - \epsilon_2)$
$S_{36} = \Delta(\phi_1 - \phi_2 - \phi_3 + \phi_4 - \phi_5 + \phi_6 + \phi_7 - \phi_8)$

[a] Definition of symbols used in Table V (see also Figure 3): $\Delta\{R_1, R_2, R_3, R_4, D_1, D_2, d_1, d_2, d_3, d_4, d_5, d_6\}$ (bond stretching): $\Delta\{r(2, 1), r(3, 2), r(4, 3), r(1,4), r(2, 6), r(5, 4), r(3, 7), r(3, 8), r(3, 9), r(10, 1), r(11, 1), r(12, 1)\}$; $\Delta\{\omega_1, \omega_2, \beta_1, \beta_2, \phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \phi_6, \phi_7, \phi_8\}$ (valence angle bond): $\Delta\{<(3, 2, 1), <(1, 4, 3), <(2, 1, 4), <(4, 3, 2), <(7, 3, 2), <(4, 3, 7), <(9, 3, 4), <(9, 3, 2), <(10, 1, 4), <(10, 1, 2), <(12, 1, 2), <(12, 1, 4)\}$; $\Delta\{\alpha_1, \alpha_2, \epsilon_1, \epsilon_2\}$ (in-plane wagging): $\Delta\{<(6, 2, 3, 1), <(5, 4, 1, 3), <(8, 3, 4, 2), <(11, 1, 2, 4)\}$; $\Delta\{\delta_1, \delta_2, \theta_1, \theta_2\}$ (out-of-plane wagging): $\Delta\{<(6, 2, 3, 1), <(5, 4, 1, 3), <(8, 3, 4, 2), <(11, 1, 2, 4)\}$; $\Delta\{\tau_1, \tau_2, \tau_3, \tau_4\}$ (torsion): $\Delta\{<(3, 2, 1, 4), <(4, 3, 2, 1), <(1, 4, 3, 2), <(2, 1, 4, 3)\}$.

[b] The set of symmetry coordinates includes six redundancies which arise from the ring structure. They fall in species A_g, B_{2g}, B_{3g}, A_u, B_{2u}, and B_{3u}.

band in the 2760–2820-cm^{-1} region has been reported to be a characteristic frequency of the $>NCH_3$ group, provided that the nitrogen atom retains its lone pair of electrons.[14] This band was further correlated with structural modifications involving the lone pair of electrons on the N atom. On this basis, it was suggested that delocalization of the lone pair of electrons on the nitrogen into the $(PN)_2$ ring in $(CH_3NPF_3)_2$ is not significant.[4] The presence of the band at 2849 cm^{-1} in the gas-phase spectrum of $(CH_3NPF_3)_2$ and at 2830 cm^{-1} in CCl_4 solution of $(CH_3NPCl_3)_2$ confirms the usefulness of this fundamental for identification of $>NCH_3$.

(2) The strong infrared bands at 1257 cm^{-1} in the fluorine compound and at 1210 cm^{-1} in the chlorine compound were assigned to C–N stretching vibrations.

TABLE VI

ELEMENTS OF THE *F* MATRIX[a,b]

A_g: $F_{1,1} = 4.30\ (3.50)$, $F_{2,2} = 4.20\ (4.60)$, $F_{3,3} = 1.20\ (1.00)$, $F_{4,4} = 1.20\ (1.00)$, $F_{5,5} = 5.90\ (2.60)$, $F_{6,6} = 4.90\ (2.90)$, $F_{7,7} = 0.30\ (0.40)$
B_{1g}: $F_{8,8} = 2.90\ (2.60)$, $F_{9,9} = 1.70\ (2.00)$, $F_{10,10} = 2.00\ (2.20)$, $F_{11,11} = 2.00$
B_{2g}: $F_{13,13} = 0.40$, $F_{14,14} = 0.80$, $F_{13,14} = -0.10$
B_{3g}: $F_{16,16} = 4.00\ (2.00)$, $F_{17,17} = 0.65\ (1.00)$, $F_{18,18} = 0.65\ (1.00)$
A_u: $F_{20,20} = 0.32\ (0.60)$
B_{1u}: $F_{21,21} = 0.30\ (0.45)$, $F_{22,22} = 0.40\ (0.50)$, $F_{23,23} = 4.50\ (2.90)$, $F_{24,24} = 1.20\ (1.00)$, $F_{25,25} = 0.75\ (0.80)$, $F_{22,23} = 0.80\ (0.70)$, $F_{21,22} = 0.00\ (-0.20)$
B_{2u}: $F_{26,26} = 2.90\ (2.30)$, $F_{27,27} = 0.75$, $F_{28,28} = 0.75$, $F_{29,29} = 6.20\ (3.00)$, $F_{30,30} = 5.00\ (2.20)$, $F_{31,31} = 1.30\ (0.75)$, $F_{26,30} = -1.30\ (0.00)$
B_{3u}: $F_{32,32} = 3.00$, $F_{33,33} = 4.70\ (4.90)$, $F_{34,34} = 1.00$, $F_{35,35} = 0.65\ (0.75)$, $F_{36,36} = 0.80\ (0.75)$, $F_{32,33} = -0.60\ (0.00)$

[a] The units for the *F* elements are millidynes per angstrom for bond stretching constants and for cross-terms connecting two stretching motions, millidyne-angstroms for bending force constants and bending cross-terms, and millidynes for cross-terms connecting bending and stretching motions. [b] When two values are given for an element the values in parentheses refer to the chlorine compound.

These assignments as pure C–N stretching modes are crude approximations, since probably they are strongly coupled with the CH_3 deformation modes lying in this region.

(3) The frequency of the P–N single-bond stretching vibration in acyclic molecules has been assigned in the range 680–750 cm^{-1}.[15] In a recent paper the absorption frequencies of P–N bonds were discussed in detail and it was concluded that the P–N stretching vibration should be assigned in the range 873–1053 cm^{-1}.[16] Burg and Heners[13] assigned the P–N antisymmetric vibration of the P–N–P group of three phosphinoamines to the region 895–925 cm^{-1} and the symmetric P–N–P vibration to the region 647–808 cm^{-1}. The infrared spectra measured for a variety of organophosphorus compounds containing the $\overline{\mathrm{N{-}P{-}N{-}P}}$ ring showed an absorption band of fairly strong intensity near 850 cm^{-1}.[17] The infrared data for $(CH_3NPF_3)_2$ and $(CH_3NPCl_3)_2$, Tables I and II, also indicate the presence of two strong peaks at 857 and 847 cm^{-1}, respectively. The results of our normal-coordinate treatment show that these two vibrations actually involve a principal contribution from the P–N symmetry coordinate and thus may be described as ring stretching modes. The other fundamentals involving the P–N groups also contain contributions from other skeletal motions, as shown by the potential energy distributions.

(4) The descriptions given in Tables III and IV for the different P–X stretching vibrations (X = F, Cl) are somewhat arbitrary since they refer to assumed D_{2h} symmetry. Because axial P–F stretching frequencies

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are usually lower than equatorial frequencies,[18] it would seem reasonable to assign the higher frequencies 962, 906 (Raman), and 937 cm^{-1} (infrared) to the equatorial P–F vibrations and 741 (Raman) and 795 cm^{-1} (infrared) to the axial vibrations. The ring vibrations involving axial and equatorial P–N bonds may well follow a similar pattern. The very strong peak at 937 cm^{-1} in $(CH_3NPF_3)_2$ occurs as a doublet, both in the vapor phase at low pressure with maxima at 933 and 937 cm^{-1} (Figure 1) and in CS_2 solution with maxima at 930 and 920 cm^{-1} (Figure 2). The doublet could plausibly arise from Fermi resonance with one of the combination bands which may appear in this region, *e.g.*, $\nu_8 + \nu_{25}$ (627 + 315), or by mixing with another fundamental mode (skeletal or associated with the CH_3 vibrations). The calculation shows that the P–F and even more the P–Cl stretching vibrations are mixed with other skeletal motions.

(5) The low-frequency skeletal modes involving the various angular motions are more difficult to identify with certainty. These fundamentals fall in the same region and it is apparent from the PED parameters obtained that they are strongly coupled. When several groups were involved in a vibration the rather broad description "skeletal" is given in Tables III and IV. The lower frequencies observed in the infrared spectra of the fluorine and chlorine compounds at 75 and 62 cm^{-1}, respectively, were assigned to the ring torsional modes. The PED parameters for these two frequencies showed that they were almost pure torsional bends with contributions of only a few per cent from the other symmetry coordinates. No evidence was found of a band in the far-infrared spectrum of either compound that could be confidently associated with the torsional vibration of the methyl group. This vibration is likely to occur at a very low frequency since for $(CH_3NPF_3)_2$ and $(CH_3NPCl_3)_2$ a sixfold potential function is expected, for which the potential barriers are usually small.[19]

(6) A few weak infrared bands and Raman lines below 1000 cm^{-1} that have not been assigned to fundamental frequencies were satisfactorily interpreted as overtones or combinations of the fundamentals (see Tables I and II). All the bands observed above 1500 cm^{-1}, which must be overtones except for the hydrogen stretching vibrations, have been omitted from the tables.

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Hydrazinium(+2) Hexafluorometalates(IV) and -(V) in the 4d and 5d Transition Series[1,2]

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The reactions of hydrazinium(+2) fluoride with some transition metal hexafluorides in hydrogen fluoride were studied at room temperature. Complex fluorides of the type $N_2H_6(MF_6)_2$ and $N_2H_6MF_6$, where M = Mo, Tc, Re, or Os, were obtained depending on which reactant was used in excess. No reaction occurs with tungsten hexafluoride. Infrared absorption frequencies and magnetic susceptibilities of these solid compounds are given. The $N_2H_6MF_6$ (M = Mo, Tc, Re) complexes are of body-centered cubic symmetry with a_0 = 10.55, 10.48, and 10.49 A, respectively. The other compounds are of lower symmetry. The end products of the thermal decompositions of these materials are the metals. For the tetravalent compounds, reduction is quantitative, while for the pentavalent compounds only partial recovery of the metals was observed owing to the volatilization of unknown intermediate products.

Introduction

Hydrazinium(+2) fluoride represents with its reducing properties and ability to form a bivalent cation an interesting substance to treat with hexafluorides. For example, reactions with uranium hexafluoride yield different complexes of lower oxidation number depending on the reaction conditions used.[4,5] The high dielectric constant, wide liquid range, and relative inertness of anhydrous hydrogen fluoride make this solvent a particularly suitable medium for these reactions. The transition metal hexafluorides do not ionize appreci-

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[2] Part of this paper was presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

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