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Vibrational Spectra and Structure of Tetrakis(trifluoromethyl)diphosphine in the Crystalline and Fluid States[1]

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The infrared spectra of gaseous and solid tetrakis(trifluoromethyl)diphosphine, $(CF_3)_2PP(CF_3)_2$, have been recorded from 1600 to 33 cm^{-1}. The Raman spectra of the gas, liquid, and solid have also been recorded and depolarization values have been measured. A comparison of the vibrational spectra in the solid and fluid states indicates that there are two conformers present in the fluid states. A similar comparison of the frequencies of the infrared and Raman bands in the solid state shows that the mutual exclusion principle is operative, and it is concluded that $P_2(CF_3)_4$ exists in only the trans (C_{2h}) structure in the solid. The liquid and gas are believed to be a mixture of trans and gauche conformers, with the trans predominating. A study of the temperature dependence of the intensities of the Raman spectrum of the liquid gives an energy difference of approximately 780 cal/mol between the two conformers. Assignments of the observed frequencies to the normal modes based on depolarization measurements, band positions, and relative intensities are presented for the molecule in the C_{2h} conformation. As an aid in making vibrational assignments for the $(CF_3)_2P$– portion of the molecule, the infrared and Raman spectra of bis(trifluoromethyl)phosphine, $(CF_3)_2PH$, have also been recorded and the data interpreted in detail.

Introduction

The symmetry of molecules having the general formula X_2Y_4 has been the subject of a number of recent investigations in this laboratory.[2-8] It has been found that when the central pair of atoms is a group Va element, only the trans (C_{2h}) or gauche (C_2) structures are present. These structures correspond to a pyramidal arrangement of neighboring atoms and nonbonded electron pairs about the central group V atoms. The relative amounts of trans or gauche isomers will depend upon the interactions of the two nonbonded electron clouds and steric repulsions of the substituent atoms, as well as other less important forces.[9]

Among the substituted diphosphines which have been previously investigated, there is a much greater tendency for the trans structure to predominate as compared with the substituted hydrazines. All of the halogen-substituted diphosphines have been shown to exist predominantly in the trans configuration. Tetramethyldiphosphine was shown[3] to be a 40–60% mixture of the trans–gauche isomers, respectively, in the liquid state. Only P_2H_4 exists completely in the gauche form. As a continuation of our studies of X_2Y_4 molecules and the effect of the trifluoromethyl group as a substituent, we have investigated the infrared and Raman spectrum of tetrakis(trifluoromethyl)diphosphine, $P_2(CF_3)_4$, in the fluid and solid states. In particular, we were interested in comparing the results for this molecule with those previously reported for the corresponding methyl compound. In addition, Su and Bartell[10] have reported that the $P_2(CF_3)_4$ molecule is predominantly trans in the gas phase (less than 10% gauche). Since we have shown that the presence of two X–X stretching modes is a convenient method for the detection of two isomers and the rule of mutual exclusion between the infrared and Raman frequencies is rather conclusive for the determination of the C_{2h} symmetry, we felt that the verification of the symmetry for the $P_2(CF_3)_4$ by another technique was quite desirable. Also, the symmetry of this molecule in the crystalline state had not been previously determined. Thus, we are reporting the results of our infrared and Raman spectral studies of this molecule. As an aid in determining the symmetry and normal vibrations of this molecule, we also report the vibrational spectrum of a simpler perfluoromethylphosphine molecule, $(CF_3)_2PH$.

Experimental Section

The samples of $(CF_3)_2PP(CF_3)_2$ used in this study were prepared by the method of Bennett, *et al.*[11] The method consists of treating red phosphorus with CF_3I in a stainless steel bomb at 200°. Among the several resulting products is $(CF_3)_2PI$ which is then allowed to react with Hg according to the reaction

$$2(CF_3)_2PI + Hg \rightarrow (CF_3)_2PP(CF_3)_2 + HgI_2$$

Two different samples were prepared by this method. One was donated by Dr. R. G. Cavell and Dr. A. J. Tomlinson of the University of Alberta, and another sample was prepared in our laboratory; both samples gave identical spectra. Bis(trifluoromethyl)phosphine, $(CF_3)_2PH$, was prepared by the method of Burg and Mahler.[12] For this molecule, a sample of $(CF_3)_2PI$ is shaken with Hg in the presence of trifluoroacetic acid; the resulting phosphine was then purified by trap-to-trap distillation.

The infrared spectra were recorded from 1600 to 250 cm^{-1} with a Perkin-Elmer Model 621 spectrophotometer. Atmospheric water vapor was removed from the spectrophotometer housing by flushing with dry air. In the higher region, the instrument was calibrated with standard gases.[13] The low-wave-number region was calibrated by using atmospheric water vapor and the frequencies reported by Hall and Dowling.[14] The spectrum was recorded with the gaseous sample contained in a 20-cm cell equipped with CsI windows. The spectrum of the solid was obtained by condensing the sample on a CsI plate maintained at −190° with boiling nitrogen. Mid-infrared survey spectra of $(CF_3)_2PP(CF_3)_2$ are shown in Figure 1. Infrared spectra of $(CF_3)_2PH$ are shown in Figure 2.

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(14) R. T. Hall and J. M. Dowling, *J. Chem. Phys.*, 47, 2454 (1967); 52, 1161 (1970).

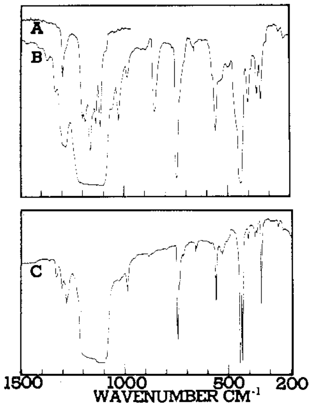

Figure 1. Mid-infrared spectra of $P_2(CF_3)_4$: A, gas phase less than 1 Torr; B, gas phase at 15 Torr; C, solid phase at −190°. Ordinate is in arbitrary units of absorption.

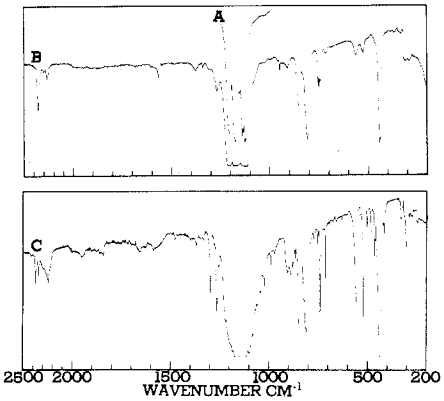

Figure 2. Mid-infrared spectra of $(CF_3)_2PH$: A, gas phase at 1 Torr; B, gas phase at 5 Torr; C, solid phase at −190°. Ordinate is in arbitrary units of absorption.

The Raman spectrophotometer used was a Cary Model 82 equipped with a Model 53A argon ion laser source.[15] The spectrum of the liquid at room temperature was recorded with the sample sealed in a capillary tube. The spectrum of the solid sample (−120°) was obtained by using a cell which was identical in design with that reported by Miller and Harney.[16] Depolarization measurements in the liquid phase were made by using the analyzer method.[17] Representative Raman spectra of $(CF_3)_2PH$ and $(CF_3)_2PP(CF_3)_2$ are shown in Figures 3 and 4.

The far-infrared spectrum of solid $(CF_3)_2PP(CH_3)_2$, shown in Figure 5, was recorded from 33 to 300 cm^{-1} on a Beckman IR-11 spectrophotometer. The low-temperature cell used for recording the spectrum at −190° has been previously described.[1] Frequencies for all observed infrared and Raman bands are expected to be accurate to ±2 cm^{-1}. The observed frequencies are listed in Tables I and II along with their relative intensities and proposed assignments.

Vibrational Assignment

As an aid in making the vibrational assignment for $(CF_3)_2$-$PP(CF_3)_2$, the infrared and Raman spectra of $(CF_3)_2PH$ have been recorded. An analysis of the vibrational spectra of this molecule is expected to be of considerable importance in assigning the $(CF_3)_2P$- group frequencies. Therefore, the vibrational analysis of $(CF_3)_2PH$ will be presented first in order to put our later assignments of $(CF_3)_2PP(CF_3)_2$ on firmer ground.

A. $(CF_3)_2PH$. Assuming C_s symmetry, the 24 fundamental vibrations of $(CF_3)_2PH$ are represented by 13 a′ + 11 a″. All vibrations are allowed in both the infrared and Raman spectra with polarized Raman bands expected for the a′ vibrations. The vibrational motions of $(CF_3)_2PH$ may be described in terms of eleven pairs of in-phase (a′) and out-of-phase (a″) motions, plus the P-H stretch and PC_2 skeletal deformation. It will be shown that many of these in-phase and out-of-phase motions are approximately degenerate.

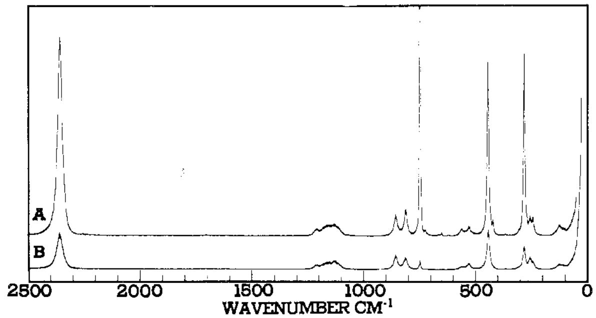

Figure 3. Raman spectra of liquid $(CF_3)_2PH$ at room temperature: A, parallel polarization; B, perpendicular polarization. Ordinate in arbitrary units of intensity. Laser excitation used was 5145 Å.

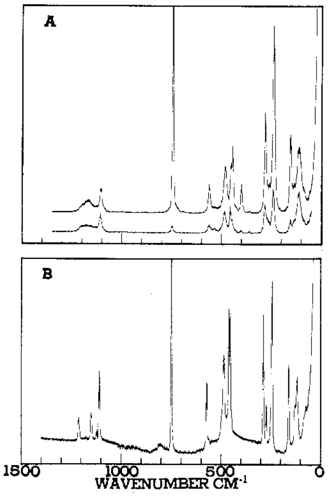

Figure 4. Raman spectra of $P_2(CF_3)_4$: A, liquid-phase spectrum taken at room temperature; upper trace represents parallel polarization, while the lower trace represents perpendicular polarization; B, solid-phase spectrum at −130°. Ordinate in arbitrary units of intensity. Laser excitation used was 5145 Å.

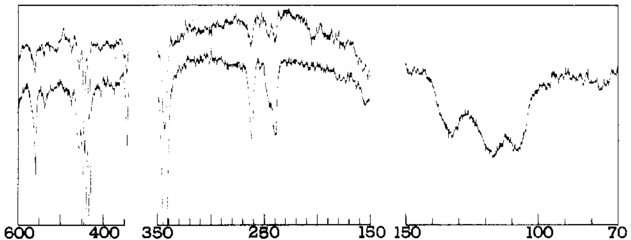

Figure 5. Far-infrared spectrum of solid $P_2(CF_3)_4$ at various thicknesses at −190°. Ordinate is in arbitrary units of absorption.

The highest frequency fundamental in this molecule is the P-H stretch, ν_1. This mode appears as a very strong Raman band at 2358 cm^{-1}, approximately 70 cm^{-1} higher than in the analogous methyl derivative, $(CH_3)_2PH$.[18] In the infrared spectrum of the solid phase, the band splits into a doublet, 2372 and 2342 cm^{-1}. This splitting is indicative of the presence of more than one molecule per unit cell. The two P-H bending modes, ν_5 and ν_{17}, appear strongly in the infrared spectrum at 808 and 854 cm^{-1}, respectively. The

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[15] The Raman spectrophotometer was purchased with funds from National Science Foundation Grant GP-28068.

[16] F. A. Miller and B. M. Harney, *Appl. Spectrosc.*, 24, 291 (1970).

[17] J. R. Scherer and G. F. Bailey, *Appl. Spectrosc.*, 24, 259 (1970).

[18] H. C. Beachell and B. Katlafsky, *J. Chem. Phys.*, 27, 182 (1957).

Table I. Infrared and Raman Spectra of $(CF_3)_2PH^a$

Infrared, ν, cm^{-1}		Raman			
Gas	Solid	$\Delta\nu$, cm^{-1} Liquid	Polarizn	Rel intens	Assignment
	2372 m	2358	p	90	
2354 m	2342 m				ν_1, P–H str
2298 w					
	∿2225 m				
2261 w					
	1300 m				
	1268 s				
1207 vs		1212		3	
1175 vs	1176 vs				
		1155		4	$\left.\begin{matrix}\nu_2, \nu_3, \nu_4, \\ \nu_{14}, \nu_{15}, \nu_{16}\end{matrix}\right\}$ CF_3 str
1142 vs					
	1149 vs	1130		4	
1136 vs					
1126 vs					
	1122 vs	1118		4	
1121 vs					
	1098 vs				
854 m	851 s	856	dp	10	ν_{17}, P–H out-of-plane bend
808 s	815 s	813	p	13	ν_5, P–H in-plane bend
		747	p	100	ν_6, CF_3 sym def
747 Q m	743 s				ν_{18}, CF_3 sym def
	714 m				combination
561 w	561 s	562	p	3	ν_7 and ν_8, CF_3 antisym def
525 w	524 s	528	dp	4	ν_{19} and ν_{20}, CF_3 antisym def
		444	p	80	ν_9, PC_2 sym str
442 s	444 s				ν_{21}, PC_2 antisym str
		308	p	3	ν_{10}, CF_3 rock
	280 w	282	p	83	ν_{11}, CF_3 rock
	253 w	256	dp	4	ν_{22}, CF_3 rock
	235 w	244	dp	4	ν_{23}, CF_3 rock
		124	p	5	ν_{12}, PC_2 sym def

[a] Abbreviations used: w, weak; m, medium; s, strong; vs, very strong; p, polarized; dp, depolarized; R, Q, P, vibration rotation.

higher frequency band appears to be depolarized in the Raman spectrum.

The antisymmetric CF_3 stretching modes, ν_3, ν_4 and ν_{15}, ν_{16}, as well as the symmetric CF_3 stretches, ν_2, ν_{14}, occur between 1207 and 1100 cm^{-1}. These vibrations appear as very intense infrared bands centered at 1207, 1175, 1139, and 1123 cm^{-1}. Due to the breadth and weakness of the bands in the Raman spectrum, accurate depolarization measurements were not possible. The in-phase and out-of-phase symmetric CF_3 deformations, ν_6 and ν_{18}, are accidently degenerate at 747 cm^{-1}. The a″ component appears with a type A contour in the infrared spectrum (in $(CF_3)_2PH$, a″ vibrations occur along the smallest principal inertial axis), whereas the a′ component appears as the most intense Raman band. The intensity and narrow frequency range of the symmetric CF_3 deformation in CF_3-P-containing compounds (see Table III) makes this vibration an excellent choice for a characteristic group frequency. There are four antisymmetric CF_3 deformations in $(CF_3)_2PH$. The two a′ vibrations are assigned to a polarized Raman band at 562 cm^{-1}, whereas the two a″ vibrations are assigned to a depolarized Raman band at 528 cm^{-1}. In the gas-phase infrared spectrum, these vibrations appear very weakly, although both bands assume a much greater intensity in the infrared spectrum of the solid. There are also four CF_3 rocking vibrations in $(CF_3)_2PH$. In the Raman spectrum, a very intense polarized band at 282 cm^{-1} may be assigned as one of the a′ rocks with a weak polarized shoulder at 308 cm^{-1} assignable as the other. Two weak depolarized bands at 256 and 244 cm^{-1} are assigned as the a″ components. No evidence was observed for either of the CF_3 torsional modes, although they are expected to occur below 50 cm^{-1}.

The remaining three vibrations to be discussed are the skeletal stretching and bending modes. The in-phase C-P stretch gives rise to a strong, polarized Raman band at 444 cm^{-1}, whereas the out-of-phase C-P stretch appears as a strong infrared band at 442 cm^{-1}. The near degeneracy of these vibrations is important in assigning the similar vibrations of $(CF_3)_2PP(CF_3)_2$ in which there are four C-P stretches. The C-P stretch appears to occur over a limited frequency range as shown in Table III. The PC_2 skeletal deformation is expected to be quite low, and it is assigned to a weak polarized Raman band at 124 cm^{-1}. This large difference in frequency between the PC_2 deformation and CF_3 rocking motions will aid in the assignments of $(CF_3)_2PP(CF_3)_2$ where there are several additional skeletal deformations to be considered. A summary of the assignments for $(CF_3)_2PH$ is presented in Table IV.

B. $(CF_3)_2PP(CF_3)_2$. There are 48 fundamental vibrations for $P_2(CF_3)_4$, and 36 of these are motions due to the CF_3 groups. The trifluoromethyl group, CF_3, has a set of more or less well-defined group frequencies. As a result of accidental degeneracies caused by the presence of four CF_3 groups, only some general assignments of the CF_3 vibrations will be attempted. The remaining twelve skeletal vibrations are represented under C_{2h} symmetry by $4\ a_g + 3\ a_u + 2\ b_g + 3\ b_u$. The a_g and b_g modes are Raman active only, with the a_g modes giving rise to polarized Raman bands.

The twelve stretching vibrations of the CF_3 groups are expected to occur between 1100 and 1200 cm^{-1}. These vibrational modes produce extremely intense infrared bands and rather weak, broad Raman bands. The only sharp Raman band occurs at 1108 cm^{-1} and it is depolarized.

The CF_3P linkage gives rise to several very characteristic bands, both with regard to frequency and intensity. One of these bands occurs at 747 cm^{-1} in $(CF_3)_2PP(CF_3)_2$ and is

Table II. Infrared and Raman Spectra of $P_2(CF_3)_4$[a]

Infrared, ν, cm^{-1}		Raman						
		$\Delta\nu$, cm^{-1}			Rel intens		Rel intens	
Gas	Solid	Gas	Liquid	Polarizn	(liquid)	$\Delta\nu$, cm^{-1} solid	(solid)	Assignment
1374								
1332	1333 w							
	1328 w							
1297	1304 w							
1284	1283 w							
	1210 w					1210	12	CF_3 str
1204	1201		1201		3			
1190								
1165			1170		6			
	1160 vvs, b							
1138						1148	15	
1117						1122	8	
			1108	dp	11	1108	37	
1027								
987	988 w							
850								
746	747 s	748	747	p	100	747	100	CF_3 sym def
	744 s							
666	655 vw							
			566	p	14	569	35	CF_3 antisym def
560	561 m					560	4	
						545	3	
	538 w		537	dp	1			
534	530 w					530	2	
		488	486	p	22	484	43	P–P str (trans)
		∿460	458	dp	24	459	67	PC_2 antisym str
		∿450	450	p	32	452	65	PC_2 sym str
	447 s							PC_2 antisym str
440								
	434 s							PC_2 sym str
404	406 w	406	404	p	14			P–P str (gauche)
	374 w							
362	364 w							
344	344 m							
		282	284	p	48	286	69	CF_3 rocks
			272		1	273	22	
	263 w		263					
	246 vvw							
	240 w	∿240	241	p	90	243	88	
		154	157	p	36	160	43	PC_2 wag
			140	dp	4			PC_2 bend (gauche)
	133 w							PC_2 wag
						128	20	PC_2 twist
	117 vw							PC_2 twist
		115	116	p	29	117	33	PC_2 def
			∿100 sh		1			PC_2 bend (gauche)
	108 vw							
			∿60		2	76	6	CF_3 torsion

[a] Abbreviations used: vvw, very very weak; vw, very weak; w, weak; m, medium; s, strong; vvs, very very strong; b, broad; sh, shoulder; p, polarized; dp, depolarized.

Table III. Some Group Frequencies for Molecules Containing the CF_3–P Group

	Assignment		
Molecule	Sym CF_3 def	Sym P–C str	CF_3 rock
CF_3PCl_2[a]	743	487	?
$(CF_3)_2PH$[b]	747	444	282
$(CF_3)_2PPF_2$[c]	744	453	282
$N[P(CF_3)_2]_3$[d]	750	438	288
$(CF_3)_2PP(CF_3)_2$[e]	747	448	281, 272
CF_3PH_2[f]	740	423	231, 206

[a] J. E. Griffiths, *Spectrochim. Acta*, **21**, 1135 (1965). [b] This work. [c] H. W. Schiller and R. W. Rudolph, *Inorg. Chem.*, **10**, 2500 (1971). [d] P. J. Hendra, R. A. Johns, C. T. S. Miles, and C. J. Vear, *Spectrochim. Acta, Part A*, **26**, 2169 (1970). [e] This work. [f] F. Block, private communication.

assigned as the CF_3 symmetric deformation. The in-phase component gives rise to a very strong, polarized Raman band, while the out-of-phase component gives rise to a strong infrared band. Some other molecules containing the CF_3P group are shown in Table III, where it can be seen that the frequency range of this vibration is very small. The intensity of this band in both the infrared and Raman spectra is always at least medium and is often quite strong, and it is, therefore, a very reliable group frequency. The CF_3 antisymmetric deformations are generally very weak in the Raman effect but somewhat stronger in the infrared spectrum. In $P_2(CF_3)_4$, these vibrations appear at 569 and 561 cm^{-1} in the Raman and the infrared spectra, respectively. Two weaker bands appear between 530 and 540 cm^{-1}.

The next lowest frequency motion of the CF_3 group is the rocking mode. When CF_3 is bonded to a phosphorus atom, a strong Raman band is usually observed near 270–280 cm^{-1}. In Table III are listed the assignments for this vibration in a number of CF_3P-containing molecules. In $(CF_3)_2PP(CF_3)_2$, a strong polarized band is observed at 284 cm^{-1} with a

Table IV. Summary of Fundamental Frequencies ν_i (cm^{-1}) of (CF$_3$)$_2$PH

i	Freq	Approx description
		Species a′
1	2354	P–H str
2	1207	CF$_3$ sym str
3	1175	CF$_3$ antisym str
4	1139	CF$_3$ antisym str
5	808	P–H in-plane bend
6	747	CF$_3$ sym def
7	561	CF$_3$ antisym def
8	561	CF$_3$ antisym def
9	444	PC$_2$ sym str
10	308	CF$_3$ rock
11	282	CF$_3$ rock
12	124	PC$_2$ sym bend
13		CF$_3$ torsion
		Species a″
14	1207	CF$_3$ sym str
15	1175	CF$_3$ antisym str
16	1139	CF$_3$ antisym str
17	854	P–H out-of-plane bend
18	747	CF$_3$ sym def
19	525	CF$_3$ antisym def
20	525	CF$_3$ antisym def
21	442	PC$_2$ antisym str
22	256	CF$_3$ rock
23	244	CF$_3$ rock
24		CF$_3$ torsion

weaker shoulder at 272 cm^{-1}. In the infrared spectrum, weak bands at 263 and 246 cm^{-1} are observed. A medium-intensity band at 344 cm^{-1} in the infrared spectrum of the solid is also assigned as an out-of-phase CF$_3$ rock. The strongest Raman band in this region appearing at 241 cm^{-1} is also thought to be due to a CF$_3$ rock. There are four torsional motions due to the four CF$_3$ groups. No definite evidence for these vibrations was observed, although some weak Raman scattering at approximately 60 cm^{-1} was observed.

The assignment of the twelve skeletal vibrations of (CF$_3$)$_2$-PP(CF$_3$)$_2$ will now be presented. First we consider the stretching vibrations. Based on a survey of CF$_3$P-containing molecules shown in Table III, we would expect to find the CP stretching vibrations around 450 cm^{-1}. In the region between 400 and 500 cm^{-1}, there are four Raman bands of significant intensity. These bands appear at 404 (p), 450 (p), 458 (dp), and 486 (p) cm^{-1} in the liquid state. Upon solidification, the 404-cm^{-1} band disappears completely. In (CF$_3$)$_2$PH, the in-phase and out-of-phase CP stretches are approximately degenerate. One would expect a similar situation for (CF$_3$)$_2$PP(CF$_3$)$_2$, and the bands at 452 and 459 cm^{-1} in the Raman spectrum of the solid are assigned as the a_g and b_g modes, respectively. Two strong infrared bands in the solid at 447 and 434 cm^{-1} are assigned as the a_u and b_u motions. This lack of coincidence of the four CP stretches for the solid provides strong evidence for the trans conformation in this physical state.

One would normally expect the P–P stretch to give rise to one of the most intense Raman bands. This was found to be the case in N$_2$(CF$_3$)$_4$,[8] as well as P$_2$(CH$_3$)$_4$[3] and P$_2$F$_4$.[19] However, the band assigned to the P–P stretch in the 400–500-cm^{-1} range in the solid state is the 484-cm^{-1} Raman line which is of medium intensity. This assignment of the 484-cm^{-1} Raman band as the P–P stretch is based primarily on an analogy with (CF$_3$)$_2$PPF$_2$ in which the strongest Raman band[20] in this region occurs at 486 cm^{-1}. It should be noted that in P$_2$Cl$_4$ the P–P stretch is rather weak,[7] so that the unexpectedly low intensity of the 484-cm^{-1} band in (CF$_3$)$_2$PP(CF$_3$)$_2$ is not without precedent. This band has no infrared counterpart consistent with C_{2h} symmetry. The 484-cm^{-1} assignment may be compared with 455 cm^{-1} in P$_2$(CH$_3$)$_4$ and 541 cm^{-1} in P$_2$F$_4$ which corresponds to the assignments given for the P–P stretch in these molecules.

An uncertainty in this analysis is the 404-cm^{-1} band in the Raman spectrum of the liquid. This band disappears completely on solidification, although a weak infrared counterpart persists. In previous studies of some X$_2$Y$_4$ molecules, the disappearance of a band upon solidification indicated the presence of an additional isomer. For example, if it resulted from a difference band it should persist in the solid and be only a function of temperature. However, the difference in frequency between the stretching modes for the two isomers for a given vibrational motion was always relatively small. For example, in P$_2$(CH$_3$)$_4$ where both trans and gauche isomers were detected, the P–P stretch was assigned at 455 and 429 cm^{-1}, respectively, a difference of 36 cm^{-1}. In N$_2$F$_4$, the N–N stretches of the trans and gauche isomers were assigned at 600 and 588 cm^{-1}, respectively. The assignment of the 404-cm^{-1} band to the P–P stretch of a second isomer requires a separation of approximately 80 cm^{-1} between the frequency for the P–P stretch for the trans and this second isomer. This separation seemed too large so we considered other alternatives for the origin of this band. Careful purification of both samples on a low-temperature distillation column did not remove the band from the spectrum, and its presence has been noted by at least one other investigator.[21] Therefore, the possibility of an impurity is rejected. Assignment of the band as a difference frequency is not consistent with its disappearance upon solidification of the sample. Since no alternative assignment can be given for this band, it is concluded that it arises from the presence of a second isomer in the gas and liquid states. Therefore, a study of the relative intensity as a function of temperature of this band in the Raman spectrum of the liquid was undertaken. The results of this study are shown in Figure 6. It is quite clear that the intensity of this band was strongly temperature dependent and the results were consistent with the presence of a second isomer which is assumed to be the gauche conformer and appears to have a relative abundance of near 30% at room temperature.

Additional evidence for the existence of a second isomer is found in the Raman spectrum of the liquid where bands at 263 and 140 cm^{-1} disappear with solidification. Also a shoulder near 100 cm^{-1} in the spectrum of the liquid is not present in the spectrum of the solid. It has been previously pointed out that only the X–X stretch and the XY$_2$ bending modes have appreciably different frequencies for the trans and gauche isomers of these X$_2$Y$_4$ molecules. Thus, it is not surprising that the frequencies for the CF$_3$ motions seem to be the same for the two isomers and that differences are only found for the PC$_2$ bending motions and the P–P stretch.

There are seven remaining skeletal deformations to be assigned. The data obtained for (CF$_3$)$_2$PH is particularly useful here because the PC$_2$ symmetric deformation was located at 124 cm^{-1}. In (CF$_3$)$_2$PP(CF$_3$)$_2$, there is a broad, weakly polarized band centered at 116 cm^{-1}. In the solid,

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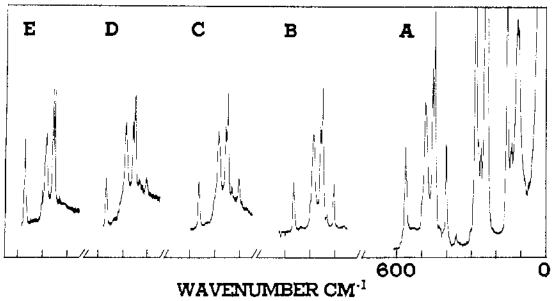

Figure 6. Relative intensity of the two bands assigned as P–P stretch as a function of temperature: A, room-temperature liquid; B, C and D, successive lower temperatures of the liquid phase; E, spectrum of the solid phase at −130°.

this band splits into two components at 117 and 128 cm^{-1}. The high depolarization ratio of approximately 0.66 is thought to result from the overlapping of a polarized and depolarized band. The more intense component at 117 cm^{-1} is assigned as the PC_2 symmetric deformation, whereas the 128-cm^{-1} component (considered to be depolarized in the liquid) is assigned as the PC_2 twist. From previous studies,[22] it is known that XY_2 wagging motions occur as much as 100 cm^{-1} higher than the symmetric deformations. Therefore, the strongly polarized Raman band at 157 cm^{-1} (160 cm^{-1} in the solid) is assigned as the PC_2 wag. The three infrared-active PC_2 bending motions–PC_2 wag, PC_2 twist, and PC_2 deformation–are assigned to bands at 133, 117, and 108 cm^{-1}, respectively. There is one accidental coincidence at 117 cm^{-1}. No evidence was observed for the skeletal torsion. A summary of the assignments for the skeletal vibrations of $(CF_3)_2PP(CF_3)_2$ is presented in Table V.

Discussion

Since two isomers were found in the liquid phase, a temperature study of the relative intensity of the Raman lines at 404 and 486 cm^{-1} was used to obtain a rough estimate of the relative energy difference. Assuming that the ratio of the intensities[23] is an accurate measure of the ratio of the concentrations, we calculate $\Delta H = 780$ cal/mol for the trans to gauche equilibrium. The relative intensities of these lines indicated that at room temperature $P_2(CF_3)_4$ exists in 70% trans and 30% gauche forms in the liquid state. It was not possible to determine the importance of the solvation effect on the concentrations of the two isomers, but the Raman spectrum of the gas at room temperature indicated that the relative concentration of the two isomers was nearly the same as that for the liquid at the same temperature.

The fact that a second isomer was not detected in the electron diffraction study is not particularly surprising. For example, in the initial electron diffraction study[24] of N_2F_4 the trans isomer, which is more than 50% abundant at room temperature, was not detected. Similarly in a recent study[25] of $P_2(CH_3)_4$ by the same technique no evidence was found for a second isomer, although the gauche isomer has an abundance[3,26] of about 60% at ambient temperature. Thus it is felt that the 30% gauche isomer of $P_2(CF_3)_4$ could have easily escaped detection in the electron diffraction study.

As pointed out in an earlier paper,[8] the factors which are expected to be the most important in determining the conformations of the X_2Y_4 molecules are the X–X bond length and the electronegativity of the Y group. Previous work has shown that an increased X–X bond length favors a greater percentage of the trans form. This result can be rationalized on the basis of exchange forces which have very high power dependence ($1/r^6$) on the X–X bond length, whereas the steric forces are expected to have relatively small ($1/r^2$) power dependence on this distance. Similarly, from a study of several substituted hydrazines as well as the study of $P_2(CH_3)_4$ and P_2Cl_4 it has been possible to show that a decreased electronegativity of the substituent favors the gauche isomer. On the basis of these two effects it is possible to rationalize the presence of the gauche isomer in $P_2(CF_3)_4$.

Table V. Summary of the Skeletal Vibrations (cm^{-1}) of *trans*-$(CF_3)_2PP(CF_3)_2$

Species	Approx description	Raman solid	Infrared solid
a_g	P–P str	484	
	PC_2 str	452	
	PC_2 wag	160	
	PC_2 def	117	
a_u	PC_2 str		447
	PC_2 twist		117
	Torsion		
b_g	PC_2 str	459	
	PC_2 twist	128	
b_u	PC_2 str		434
	PC_2 wag		133
	PC_2 def		108

In comparing the conformers of $P_2(CF_3)_4$ with P_2F_4 the electronegativity of the CF_3 group is somewhat less (~3.2) than that of the fluorine atom (4.0) which would favor the gauche conformer. In addition, the short P–P bond length[10] of 2.16 ± 0.01 Å in $P_2(CF_3)_4$ relative to the P–P bond length[27] of 2.281 ± 0.003 in P_2F_4 favors the gauche isomer. Thus, one can rationalize the 30% gauche conformer for $P_2(CF_3)_4$ compared to none for the P_2F_4 on the basis of the electronegativity and the X–X bond lengths. Even though the CF_3 group is quite large and expected to lead to a large steric interaction, the exchange forces dominate in the $P_2(CF_3)_4$ molecule because of the short P–P bond length. This result is consistent with the "gauche effect" which is a tendency to adopt the structure which has the maximum number of gauche interactions between the adjacent electron pairs as predicted by *ab initio* molecular orbital calculations.[28] Also, it has been shown both experimentally and theoretically that the gauche effect becomes less as the distance between the interacting ligands and electron pairs increases.[28]

Similarly, in comparing the conformers of $P_2(CF_3)_4$ with $P_2(CH_3)_4$, the electronegativity of the CF_3 group is considerably higher than the electronegativity of the methyl group (∿2.0) which would favor the trans isomer. However, the shorter P–P bond length in the perfluoro compound compared to the 2.192 ± 0.009 Å distance[25] for the similar bond in $P_2(CF_3)_4$ should mitigate the electronegativity effect, and the 30% gauche isomer for $P_2(CF_3)_4$ compared to the 60% abundance for the similar isomer of $P_2(CH_3)_4$ is consistent with the dominance of the electronegativity effect.

The explanation for the large variation in the two frequencies for the P–P stretching modes is not readily

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apparent. A significant difference between the two P–P bond distances would probably have been detected in the electron diffraction study.[10] Coupling between this motion and the P–C symmetric modes seems to provide a reasonable alternative. The effect of such coupling was illustrated[29] in a study of the frequencies for the P–X and P=S modes in some organophosphorus compounds. If the X substituent is a methyl group, it is found that the P–C stretch and P=S stretch interact very strongly with a "repulsion" of the two energy levels. Thus, the symmetric P–C stretch was found to be shifted by as much as 135 cm^{-1} by this type of interaction. Assuming the P–P stretch for the trans isomer is slightly higher than the 448 cm^{-1} observed for the symmetric PC_2 stretch, the interaction could shift the frequency 10 or 20 cm^{-1} resulting in the 486-cm^{-1} band which should be compared with the 455-cm^{-1} frequency observed for the P–P stretch for the *trans*-$P_2(CH_3)_4$. Similarly, the gauche isomer is expected to have a P–P stretching frequency somewhat lower than the PC_2 stretch (this mode was observed at 429 cm^{-1} in *gauche*-$P_2(CH_3)_4$) so the shift would be expected to be in the opposite direction by 10 or 20 cm^{-1} which is consistent with the observed frequency of 404 cm^{-1}. In addition, there is a shoulder on the high-frequency side of the PC_2 antisymmetric stretching mode which disappears with solidification which can be attributed to the PC_2 stretch of the *gauche* isomer. Thus the 80-cm^{-1} difference in the two P-P stretching modes may be the result from a small coupling with the phosphorus–carbon stretches.

This study reiterates the necessity of recording the vibrational spectrum in the solid state[2–8] if the presence or absence of conformers is to be determined by this technique for this type of molecule. The failure to observe a second isomer in the vibrational studies of H_2PPF_2 and $(CF_3)_2PPF_2$ seems surprising when one considers the P-P bond distance.[30] Both molecules had Raman bands near 404 cm^{-1} which were attributed to PF_2I impurity; infrared and Raman studies of the solids should be carried out to verify the presence of a single conformer for these molecules in the fluid states. Since two of the energy levels for the molecular orbitals of the X_2Y_4 molecules are highly dependent upon the molecular symmetry,[31] it may turn out that all of the unsymmetrical biphosphines will exist in only the trans conformation. Since both $P_2(CF_3)_4$ and $P_2(CH_3)_4$ were found to have appreciable concentrations of the gauche isomers, a study of the conformations of $(CH_3)_2PP(CF_3)_2$ should indicate the importance of the symmetry in the stabilization of the gauche isomer. Such studies are currently being undertaken in our laboratory.

Registry No. $(CF_3)_2PP(CF_3)_2$, 2714-60-5; $(CF_3)_2PH$, 460-96-8.

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Proton Magnetic Resonance Studies on Pentaalkyldialuminum Alkali Metal Oxides and Related Complexes[1]

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The nmr spectra of R_5Al_2ZM in aromatic hydrocarbon solutions can be explained by the structure of donor–acceptor type binuclear complexes of the type $[R_2AlZM][AlR_3]$ with nonequivalent Al atoms for R = Et, *i*-Bu; Z = O; M = Na, K, at the temperatures studied. This structure is also predominant for R = Et, Z = O, NPh, M = Li; R = Et, Z = S, M = Na; R = Et, Z = O, M = Cs; R = *i*-Bu, Z = O, M = Cs. However, at higher temperatures in benzene, intramolecular alkyl exchange through a cyclic intermediate is important for R = Et, Z = O, NPh, M = Li. The alkyl-exchange reaction is highly predominant for R = *i*-Bu, Z = O, NPh, M = Li. The complexes containing Cs seem to have a cyclic ionic structure. One of the factors determining the structure appears to be a combination effect of ionization energy and ionic radii of the alkali metals. The complex has weak interaction with toluene, predominantly at the Al atom of the R_2AlZM moiety. A tetrahydrofuran molecule can preferentially coordinate on the same aluminum atom.

Introduction

Recent works have shown that the reaction products of trialkylaluminums with alkali metal hydroxides[2–4] and N-substituted lithium amides[2b,3,5] in a molar ratio of 1:0.5 can be used as active catalysts for the highly stereospecific polymerization of acetaldehyde. Information about the catalyst structure in solution for the purified organoaluminum compounds obtained from the catalyst system is required in order to elucidate the stereocontrolling factor of the polymerization reaction. Synthetic studies[6] have indicated that the series of organoaluminum products can be rationalized as donor-ac-

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