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SPECTRA AND STRUCTURE OF ORGANOPHOSPHORUS COMPOUNDS XI.* INFRARED AND RAMAN SPECTRA OF $(CH_3)_2PCl$

J. R. DURIG and J. E. SAUNDERS**†

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208 (U.S.A.)

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ABSTRACT

The infrared spectra of gaseous and solid dimethylchlorophosphine have been recorded from 4000 to 33 cm^{-1}. The Raman spectra of the gas, liquid and solid have also been recorded and depolarization values have been measured for the liquid. Assignment of the fundamentals based on their gas phase contours, depolarization values and frequency is given and discussed. For the crystalline solid there were marked changes in both the infrared and Raman spectra below 1000 cm^{-1} and virtually all of the intramolecular fundamentals in this low-frequency region were doubled. The largest splitting was found for the P—Cl stretch which was found at 462 cm^{-1} in the liquid state but at 420 and 542 cm^{-1} in the solid state. Such a large difference in frequency cannot be ascribed to factor group splitting in the solid but it is attributed to a non-centrosymmetric dimer since mutual exclusion was not observed.

INTRODUCTION

We have been interested [1] in the substituent effects on the barriers to internal rotation of methyl rotors attached to atoms of the IVA and VA series. In these studies it has been found that the chlorine atom has the most pronounced effect on the barriers of the group IVA molecules and for the ethane series the effect was nearly additive with the addition of each successive chlorine atom. In a previous study [2] of methyldichlorophosphine, the torsional mode was assigned at 226 cm^{-1} and a barrier to internal rotation of 3.37 kcal mol^{-1} was calculated. This value was considerably higher than the value of 1.9 kcal mol^{-1} found [3] for methylphosphine which was taken to indicate that chlorine has a significant effect on the barriers of organophosphorus molecules. In order to examine further this concept, the vibrational spectrum of dimethylchlorophosphine was recorded. To our surprise the infrared and Raman spectra of the solid were drastically changed from those

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†Present address: Sylvania Lighting Center, Danvers, Massachusetts, U.S.A.

found for the fluid state and the interpretation of these observations are presented. There has been one cursory vibrational study [4] of chloromethylphosphines and chlorophenylphosphines in which some general assignments were presented. However, there has not been any extensive investigation of the vibrational spectrum of dimethylchlorophosphine.

EXPERIMENTAL

The infrared spectra in the 4000—200 cm^{-1} region were recorded on a Perkin—Elmer 621 spectrophotometer with extended source which was purged with dry air and calibrated with the frequencies of atmospheric water vapor [5] and standard gases [6]. For gas phase studies, the compound was condensed into a 25 cm glass cell equipped with CsI windows. For studies of the solid phase a vacuum cold cell similar to that described previously [7] with CsI outer windows and either a CsI or silicon substrate was used. The far infrared spectra (500—33 cm^{-1}) were studied with a Beckman IR-11 spectrophotometer which was flushed with dry nitrogen and calibrated with water vapor. Studies in the solid state were carried out with cells similar to that for the mid-infrared region except that the outer windows were high density polyethylene. Temperatures at the silicon substrate were measured with a copper—constantan thermocouple referenced to 0°C.

All Raman data were obtained with a Cary 82 Raman spectrophotometer [8] equipped with a Coherent Radiation Model 53A argon ion laser operated at 5145 Å. For liquid and solid studies, the power was typically 2 watts (CW) while, for gas phase studies, maximum power of ~4 watts (CW) was used. The instrument was calibrated with neon emission lines and frequently checked against the gas spectrum of air, especially the 60 cm^{-1} line. The solid phase studies were carried out with a cell similar to the one described by Miller and Harney [9]. The sealed capillary which was also used for the liquid phase studies, was inserted into a vacuum-jacketed tube and was cooled with dry, cold nitrogen. The nitrogen flow and, therefore, the temperature was controlled by the adjustment of the current through a nichrome resistor immersed in a liquid nitrogen Dewar. In all low-temperature Raman studies, the temperature was monitored with an iron—constantan thermocouple referenced to 0°C. The gas phase studies were carried out with the Cary multipass, gas-cell accessory. Samples were condensed via a vacuum system into multipass quartz cells approximately 2 inches in length which were equipped with paralleled Brewster-angle quartz windows. The laser beam typically makes a minimum of ten passes through the cell with critical adjustment sometimes permitting a considerably larger number. When too high a vapor pressure is present in the cell, an "aerosol effect" occurs which appears to condense the sample in a visible dispersion. The cell must then be pumped out and a lower pressure of sample introduced.

Dimethylchlorophosphine was prepared by the reaction of $[(CH_3)_2PS]_2$ with phenyldichlorophosphine under a nitrogen atmosphere. After being heated to ~200°C, the yellow solution was distilled at reduced pressure. A small amount of yellow amorphous solid, not previously reported, was observed to distil with the clear liquid. Further purification by trap-to-trap distillation yielded a clear, colorless liquid whose boiling point, 76°C, and melting point, —1°C, agreed well with the literature values [10]. The tetramethyldiphosphinedisulfide was prepared by the reaction of the Grignard of methyl chloride with $PSCl_3$ in ethyl ether at 0°C. The product was washed with a 10% sulphuric acid solution in ice and dried at 60°C after washing with a small amount of ethanol. This material was recrystallized from a 3:1 toluene-ethanol mixture until long prisms (M.P. 227°C) were obtained.

RESULTS

The interpretation of both the infrared and Raman spectra of the gaseous and liquid states was relatively straightforward since the symmetry is expected expected to be C_s, with the plane bisecting the CPC angle and containing the P—Cl bond. The normal vibrations span the 13a′ + 11a″ representation. Only the interpretation of the low-frequency modes is difficult. However, when the sample is crystallized, the region below 1000 cm^{-1} undergoes drastic change. There are approximately twice the number of bands found in the infrared spectrum of the solid (see Fig. 1) in the region expected for the

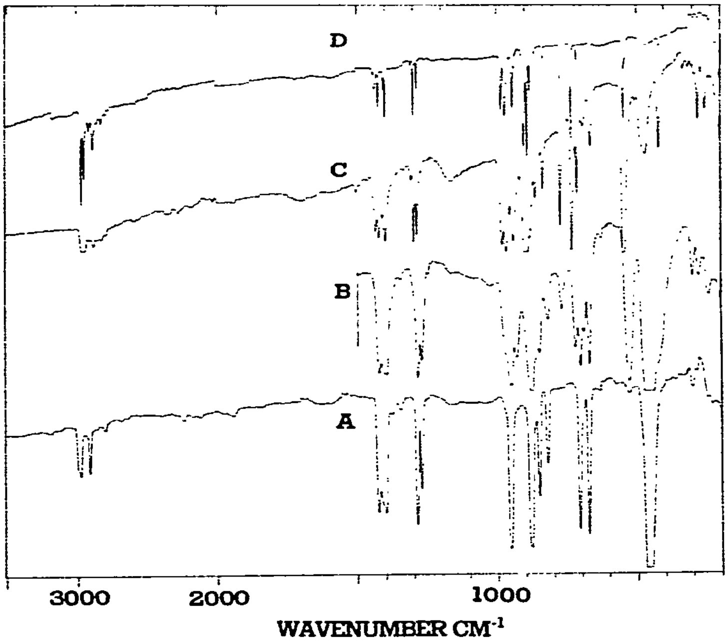

Fig. 1. Infrared spectrum of solid Me_2PCl, 3500—200 cm^{-1}: (A) initial deposit, glass phase, (B) partially annealed sample, (C) further annealing, (D) completely annealed sample. All spectra recorded at —190°C.

methyl rocking, carbon—phosphorus stretching and phosphorus—chlorine stretching modes.

The latter mode undergoes the most severe perturbation resulting in two bands each being approximately 60 cm^{-1} removed from the original band in the gaseous state. It is interesting to note that a considerable perturbation is also observed in the liquid state for this mode with the band being shifted to a frequency 20 cm^{-1} lower than that found in the spectrum of the gas. By itself, this would have not been so surprising; however, considered with the fact that there is evidence of interaction in the "glass" or non-crystalline solid phase, these observations indicate that relatively strong intermolecular association is occurring which is not totally dependent on the crystal structure. As seen in Table 1, the spectrum of the crystalline state has been interpreted in terms of an in-phase (I-P) and out-of-phase(O-P) vibration for those modes in which splitting is evident. Such an assignment requires that the molecules be oriented in a dimeric or higher polymeric form. Since the simplest model is preferable and can best explain the observed results, a dimeric structure has been proposed. There are several types of dimeric structures possible. If a center of symmetry were present, there should be mutual exclusion of the in-phase and out-of-phase vibrations of the dimer. However, it will be shown that all observed modes have corresponding frequencies in both the infrared and Raman spectra.

Since the same normal mode is involved in both the in-phase and out-of-phase vibrations, the magnitude of the splitting gives an indication of how effectively the environment about the bond alters the potential energy of the mode. Therefore, it is expected that the splittings will be different for the various modes. As can be seen in Table 1, the carbon—hydrogen stretching and deformational modes show little evidence of in-phase and out-of-phase behavior, although there are noticeable frequency differences in the various physical states. This lack of splitting for the higher-frequency modes is not surprising, especially in view of the similarity of the molecular motions and accidental or "hidden" degeneracy which often occurs.

VIBRATIONAL ASSIGNMENT

CH Stretches

Just as in the case of dimethylphosphine [11], four antisymmetric and two symmetric CH_3 stretches are expected. The antisymmetric modes are considered to be the highest frequency fundamentals and are often found to be accidentally degenerate. The complex contour in the infrared spectrum of the gas between 2970 and 3000 cm^{-1} indicates two bands. This is verified in the other phases in both the infrared and Raman spectra. The fact that both bands are depolarized strengthens their assignment as antisymmetric modes. The higher-frequency band, 2959 cm^{-1} in the infrared spectrum of the polycrystalline solid, is thought to correspond to ν_{14} and ν_{15} of a$''$

TABLE 1

Infrared and Raman spectra of dimethylchlorophosphine

Infrared							Raman						Assignment
Gas (cm^{-1})	I[a]	Band type	Glass (cm^{-1})	I[a]	Crystal (cm^{-1})	I[a]	Gas (cm^{-1})	I[a]	Crystal (cm^{-1})	I[a]	Liquid (cm^{-1})	I[a]	Depol.[b] ratio	
2991 Q	s	?	2980	s	2969	vs	2995	wm	2960	vs	2982	m	dp	ν_{14}, ν_{15} CH_3 antisymmetric stretch
2982 R,P														
2972 Q	s	C	2964	s	2942	s	2978	wm	2947	ms	2966	m	dp	ν_1, ν_2 CH_3 antisymmetric stretch
2917 R					2905	w			2905	ms				
2911 Q	s	C	2900				2910	vs			2901	s	p	ν_3, ν_{16} CH_3 symmetric stretch
2905 P					2877	m			2882	ms				
2850	vw		2845	w	2850	vw	2864	w	2855	w	2852	w		$\nu_5 + \nu_{17}$
2829	vw						2830 br	w	2835	w				$\nu_{17} + \nu_{18}$
2817	w				2819	w					2815			$\nu_5 + \nu_{18}$
2808 Q?	w		2796	mw	2798	w	2806	w	2800	vw	2796		p	$2\nu_{18}$
2799 sh	w													
1440 sh	s				1442 sh	wm								
1432 Q	s				1435	m			1450	wm				ν_4 CH_3 antisymmetric deformation
1416 Q	s		1425	s	1424	s	1420 br	w	1427	wm	1415 br		dp	ν_5 CH_3 antisymmetric deformation
1411 R	s		1410 sh	s	1405	m								ν_{17} CH_3 antisymmetric deformation
1406 ctr		B	·1398	s	1399	s			1402	w				ν_{18} CH_3 antisymmetric deformation
1403 P	s													
1365	w		1376	w										$\nu_9 + \nu_{22}$
1357	w		1346	mw										$\nu_8 + \nu_{10}$
					1308	w								893 + 423 = 1316
1303 sh														
1293 Q	s	C	1286	s	1298	s	1295	w	1295	w	1291	wm	p	ν_6 CH_3 symmetric deformation
1285 R														
1279 ctr	s	B	1272	s	1287	ms			1277	w				ν_{19} CH_3 symmetric deformation
1276 P														
					1172 br									776 + 423 = 1199
									1124	wm				717 + 420 = 1137
					983	s			984	w				ν_7 (O-P)
					971	s			970 sh	vw				ν_7 (I-P)
957 R														
949 Q	s	B—C?	953	s			952	vvw			952	w	dp?	ν_7 CH_3 rock
940 P														
					944	s			946	w				ν_8 (O-P)
					903	s			902 sh	w				ν_8 (I-P)

TABLE 1 (continued)

Infrared							Raman							Assignment
Gas (cm^{-1})	I^a	Band type	Glass (cm^{-1})	I^a	Crystal (cm^{-1})	I^a	Gas (cm^{-1})	I^a	Crystal (cm^{-1})	I^a	Liquid (cm^{-1})	I^a	Depol.^{b} Ratio	
					893	s			896	w				ν_{20} (O-P)
889 R														
885 Q	s	B—C?	879	s			880	vvw			881	w	p	ν_8 CH_3 rock
881 Q														
873 P														
					883	m								ν_{20} (I-P)
					886	w								ν_{21} (O-P)
857														
852 ctr	ms	B	851	s			860	vvw			853	w	dp	ν_{20} CH_3 rock
848 P														
					837	wm			840	vw				ν_{21} (I-P)
824 R														
817 ctr	m	B	822	s							822	w	dp	ν_{21} CH_3 rock
814 P														
					776	m	777	w						ν_{22} (O-P)
					736	s			736	wm				ν_{22} (I-P)
717 Rsh	s													
					716	wm			717	wm				ν_9 (O-P)
703 Q	s	?	707	s			700 br	br			708	wm	dp	ν_{22} CP antisymmetric stretch
			695	w										460 + 248 = 708
681 R														
675 ctr	s	B	675	s			675	m			674	ms	p	ν_9 CP symmetric stretch
672 P														
					670 br	vw			670	wm				ν_9 (I-P)
			533 sh	mw	551	s			542	ms				ν_{10} (O-P)
481	vs		460	vs	470 br	vw	485	m			462	ms	p	ν_{10} PCl stretch
					423	wm			420	s				ν_{10} (I-P)
					333	w			330	wm				ν_{11} (O-P)
			306	m			299	wm			301	wm	p	ν_{11} CPC deformation
			301	w	296	w			291 sh	w				ν_{11} (I-P)
			282	m	282	m			282	wm				ν_{12} (O-P)
			248	wm	258	m			256	m				ν_{23} (O-P)
							243	w			247	m	p	ν_{12} PCl symmetric deformation
			235	wm			232	w	242	ms	233	wm		ν_{23} PCl antisymmetric deformation
							223 sh							ν_{13} ?
					193	m								ν_{12} (I-P) skeletal bend (dimer)
					167	m			165	m				ν_{23} (I-P) skeletal bend (dimer)

135	vs			lattice mode
104	vs			lattice mode
65	m	70	s	lattice mode
		54		lattice mode
		38		lattice mode

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[a] Relative intensity: w, weak; m, medium; s, strong; v, very; sh, shoulder; br, broad; ctr, center.

[b] Depolarization ratios for liquid state: p, polarized; dp, depolarized.

[c] Vibrations are numbered according to standard notation, i.e. in the order of decreasing frequency within a given symmetry block with the symmetry blocks ordered highest to lowest symmetry. Therefore, all the vibrations of the a' block are numbered, here 1 to 13, before any of the vibrations of the a'' block are assigned, here 14 to 24. When combination, difference and overtone bands occur in more than one phase, only the identity rather than the frequencies of the fundamentals involved are shown. To list the frequencies for each phase is unnecessarily complicated.

symmetry, whereas the band at 2942 cm^{-1} is probably ν_1 and ν_2 of a′ symmetry although these assignments could be reversed. The two remaining symmetric stretches, ν_3 and ν_{16}, are also probably degenerate. The fact that the very strong band at 2901 cm^{-1} in the Raman spectrum of the liquid is polarized indicates that the symmetry of the methyl group may be localized. This problem has recently been treated theoretically [12]. It has been shown that the vibrational spectrum of the localized modes is not determined by the spatial arrangement of the symmetry equivalent groups alone, but is fundamentally influenced by the nature of the interaction of the groups with each other and with the immediate environment. When the molecule is in the crystalline state, there appears to be a significant change in the potential field surrounding the methyl groups. The strength of the infrared band decreases markedly and shifts to 2905 cm^{-1}, whereas a stronger band is found at 2877 cm^{-1}. Bands of nearly equal relative intensity are found in the Raman spectrum. The higher-frequency band is tentatively assigned as the ν_3 mode on the basis that the totally symmetric mode is expected to be less intense in the infrared than in the Raman spectrum.

CH_3 Deformations

As is usually found with these vibrations, the antisymmetric modes result in a series of overlapping band contours in the gas phase. All four of the vibrations, two a′ and two a″, are assigned to bands betweeen ~1400 and 1450 cm^{-1}. The only recognizable band contour is the B-type centered at 1406 cm^{-1}. This corresponds to strong bands in the infrared spectra of the "glass" and polycrystalline states and a relatively weak band in the Raman spectrum of the latter state. Thus, it is assigned as an a″ mode. Only two distinct bands remain in the Raman spectrum of the solid in this region. Appearing at 1450 and 1427 cm^{-1}, they are assigned as ν_4 and ν_5, respectively. A difficult problem now arises since only the 1427 cm^{-1} Raman band has a corresponding infrared band. This would leave two infrared bands of significant intensity at 1437 and 1406 cm^{-1} with only one fundamental, ν_{17}, left to be assigned. The probability of in-phase and out-of-phase components and of possible overtones of the phosphorus—carbon stretching modes makes this a relatively insoluble problem. Tentatively the remaining a″ mode, ν_{17}, is assigned to the 1405 cm^{-1} band. The 1435 cm^{-1} band may be associated with ν_4 even though the frequency split is large.

The symmetric deformations are assigned with more certainty. Again, overlapping gas-phase contours are observed in the infrared spectrum of the gas. However, the higher-frequency C-type band with a Q branch at 1293 cm^{-1} and the B-type band centered at 1279 cm^{-1} are clearly recognizable. Since the Raman band at 1291 cm^{-1} is definitely polarized, this clearly indicates that the higher-frequency band is the ν_6, a′ mode. The a″ mode, ν_{19}, is expected to be weaker than the a′ mode in the Raman spectrum and, in fact, is found only in the crystalline phase. Beyond this, neither of these modes seems affected by conversion to the postulated dimeric structure, although there is some frequency shift upon the change in physical state. The frequencies assigned to these deformations are virtually identical with those assigned to the same modes in dimethylphosphine [11].

CH_3 Rocks

The rocking modes are the methyl vibrations that are expected to be the most sensitive to a change in environment about the methyl groups since these motions usually mix with the heavy atom skeletal modes. The infrared spectrum of the gas phase is almost a classic of simplicity with B—C type hybrid bands with Q branches at 949 and 881 cm^{-1} and B-type bands centered at 852 and 817 cm^{-1}. These correspond to lines at 952, 881, 853 and 882 cm^{-1}, respectively, in the Raman spectrum of the liquid. Whereas the line at 881 cm^{-1} is definitely polarized, the 952 cm^{-1} appears depolarized. This latter fact, however, does not forbid the assignment of both of these bands to a′ modes, ν_8 and ν_7, respectively. The bands at 853 and 822 cm^{-1} are associated with the a″ modes, ν_{20} and ν_{21}, respectively. The order of the vibrations, i.e. both higher-frequency modes assigned to the a′ vibrations, is again consistent with the assignments for the corresponding motions in the dimethylphosphine assignment [11].

The assignment becomes complex when the molecules are annealed to the crystalline state. Initial experimental data in the mid-infrared region, for example, scans similar to Fig. 1B, were thought to indicate decompositon or some irreversible polymerization. However, when the samples were sealed in capillaries and studied in the Raman effect as crystalline solids, drastic changes in the spectra were also observed (see Fig. 2). When the samples were returned to 25°C, the spectrum was unchanged from that recorded previous to the crystallization. Further study of the infrared spectrum made it evident that the frequency shifts were not artifacts but were caused by changes in the potential forces with crystallization.

In the region between 800 and 1000 cm^{-1} where there are four strong bands in the infrared spectrum of the glass, eight pronounced bands are clearly discernible in the infrared spectrum of the crystalline material. The easiest way to assign these eight bands is to assume that each of the four rocking modes is split in the crystalline material by the proposed dimerization (see Table 1). Such an assignment requires a significant increase in the frequency of each of these normal modes with crystallization. For example, ν_7, which is found at 953 cm^{-1} in the spectrum of the "glass" (952 cm^{-1} in the Raman spectrum of the liquid) would have its out-of-phase and in-phase components at 983 and 971 cm^{-1}, respectively. Similarly, ν_8 which is found at 879 cm^{-1} in the "glass" would have its two components in the crystalline solid at 944 and 903 cm^{-1} which represents a considerable shift plus a large splitting between the in-phase and out-of-phase motions. An alternative assignment could be given where the two components of ν_8 were assigned to

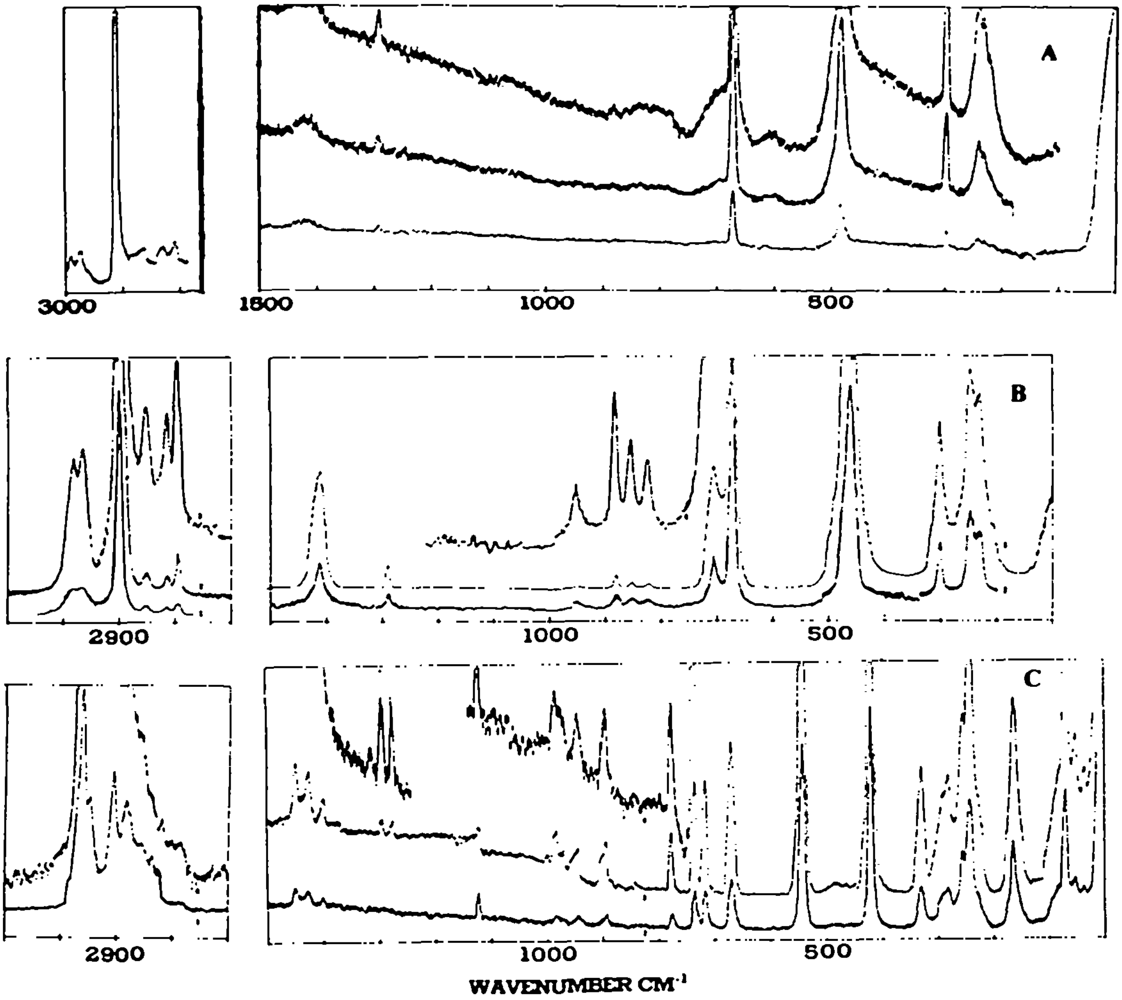

Fig. 2. (A) Raman spectrum of gaseous Me_2PCL, 3000—10 cm^{-1}, at various sensitivities. No bands were observed in regions not shown. (B) Raman spectrum of liquid Me_2PCl, 25°C. The numbered scans indicate increased sensitivities for comparison of relative intensities. (C) Raman spectrum of polycrystalline Me_2PCl, —150°C. The numbered scans indicate increased sensitivities.

the 903 and 893 cm^{-1} bands and one of the three higher-frequency bands of 983, 971 and 944 would be assigned as a combination band in Fermi resonance with ν_7. This latter assignment would also necessitate that ν_{21} has only one component in the solid phase at 837 cm^{-1} unless the next lower-frequency band at 776 cm^{-1} is considered a rocking mode. There is no way of distinguishing among the various alternatives for the assignment of the CH_3 rocking modes in the solid but it is clear that there is some splitting for some of the modes. Although one or two components might be reassigned, it is felt that there is sufficient evidence to warrant assignment as in-phase and out-of-phase components of a dimer which does not have a center of symmetry or a dimer with a symmetry center but occupying a site of C_2, C_s or C_1 symmetry.

CP Stretches

The two carbon—phosphorus stretching modes are found very close to the frequencies assigned for the corresponding modes in dimethylphosphine [11]. The antisymmetric mode, ν_{22}, is found at ~700 cm^{-1} with a Q branch at 703 cm^{-1} in the infrared spectrum of the gas phase. Upon crystallization, a strong band at 736 cm^{-1} and a weaker band at 776 cm^{-1} are observed in the infrared spectrum while bands of comparable intensity were found in the Raman spectrum. These are assigned as the out-of-phase and in-phase components of the a″ mode. The symmetric mode is found as a relatively strong band at 675 cm^{-1} in the non-crystalline states. When the compound is crystallized, there is a decrease in its intensity relative to the antisymmetric mode and the two components are assigned at 716 and 670 cm^{-1}.

PCl Stretch

The most dramatic change in the entire spectrum is the virtual disappearance of the strongest band in the infrared spectrum of the gas and "glass" states when the sample is crystallized. The same result is observed in the Raman spectrum. The P—Cl stretching mode is initially found at 481 cm^{-1} in the infrared spectrum, and 485 cm^{-1} in the Raman spectrum in good agreement with earlier assignments [4]. In the Raman spectrum of the liquid phase, the band is shifted ~20 cm^{-1} lower in frequency. Upon crystallization, two bands are observed which in the infrared spectrum are at 551 and 423 cm^{-1} and in the Raman are at 542 and 420 cm^{-1}. The higher-frequency band is stronger in the infrared spectrum whereas the lower-frequency one is slightly stronger in the Raman spectrum. It should be pointed out that both Raman bands are quite strong. Only a vestige of the original band is found in either spectrum. In accordance with the assignment of the rocking modes, the bands are assigned to the out-of-phase and in-phase components of the P—Cl stretching mode.

Low-Frequency Modes

There are five remaining fundamental modes to be assigned. These are the two R—Cl bending modes, ν_{12} and ν_{23}, the CPC symmetric deformation, ν_{11}, and the two torsional modes, ν_{13} and ν_{24}. Since all these modes are expected to be of similar energy with the torsions being the lowest frequency, the problem of mixing of the vibrations is expected to be quite severe. In fact, the designation of the bending modes as one or another motion is only to indicate the probable major contribution to the vibration. Thus, the P—Cl bending modes will have large contributions from the R—C deformation and vice versa. It is simplest to consider first the Raman spectra of the gaseous

(Fig. 2A) and liquid (Fig. 2B) states. In each case, bands at ~300, ~245 and ~233 cm^{-1} are found. The two-higher-frequency bands are found to be polarized. Therefore, these two bands must be considered as symmetric modes. This also does not leave any alternative but to assign the higher P—Cl bending vibration as the symmetric mode since only the lowest band is not polarized. This is the reverse of what is usually found for low-frequency bending modes. In methyldichlorophosphine, bands at 202, 243 and 288 cm^{-1} have been assigned [13, 14] to the PCl_2 deformational, twisting and wagging motions, respectively. To decide between the 300 and 245 cm^{-1} bands for assignment to the CPC and PCl symmetric deformations is much more difficult. The CPC bending was found at 267 cm^{-1} in the Raman spectrum of liquid dimethylphosphine [11]. It is possible that, in the isolated molecule, the chlorine will interact repulsively with the carbons more than the hydrogen does, thus raising the energy necessary to deform the CPC bond. By this reasoning, the CPC deformation is assigned to the higher frequency band at ~300 cm^{-1}. The P—Cl symmetric deformation must be assigned at ~245 cm^{-1} whereas the antisymmetric mode is at 233 cm^{-1}. No evidence of the torsional modes is found in either the spectra of the gas or liquid. The shoulder at 223 cm^{-1} could be the in-phase methyl torsion, ν_{13}.

The spectra are much more complicated in the crystalline state. To interpret either the Raman or infrared spectrum would be more difficult than to explain both simultaneously. Both spectra contain a relatively sharp band at 282 cm^{-1} with a broad band at approximately 293 cm^{-1} along with a pronounced band at 333 cm^{-1}. It is most likely that two of these features correspond to the CPC bending mode and are related as out-of-phase and in-phase components and we have chosen the two higher-frequency bands. It is possible that the broad band, 293 cm^{-1}, is associated with the non-bonded interaction between the phosphorus and chlorine or with some other motion of the skeletal bend of the postulated dimer.

The C—P—Cl bending modes, although found as two bands at 248 and 235 cm^{-1} in the infrared spectrum of the "glass", are present as only a broad, single band at 258 cm^{-1} in the infrared spectrum of the crystalline state, unless one assumes that the 282 cm^{-1} band is associated with these motions. In the Raman spectrum of the crystalline solid, bands at 248 and 256 along with the 282 cm^{-1} band are found with the lowest-frequency one being the strongest. It is therefore probable that in the crystalline state that the skeletal bending modes of the dimer are sufficiently different from the C—P—Cl bending modes in the monomer that out-of-phase and in-phase motions are not good descriptions of the actual motions. One would expect the low-frequency skeletal motions to show some of the largest effects with dimerization.

Aside from the low-frequency lattice modes, only the torsional modes remain to be assigned. In the Raman spectrum of the solid, a band is found at 165 cm^{-1} whose frequency appears to be insensitive to temperature changes. In the infrared spectrum two bands are found, 167 and 193 cm^{-1}, which shift only 1 to 2 cm^{-1} when the crystal is warmed. Therefore, it appears that these two bands are not high-frequency lattice modes but molecular vibrations of the dimer. In dimethylphosphine, only a single frequency of 182 cm^{-1} was observed [11] in this spectral region and it was assigned as the methyl torsion. If one assumes that the two bands at 167 and 193 cm^{-1} are methyl torsions, then a periodic barrier [1] of 2.08 kcal mol^{-1} is calculated. This barrier value appears to be too low compared with the corresponding value of 2.15 kcal mol^{-1} for dimethylphosphine [11] in the solid state since it has been found that the methyl barriers increase with the replacement of a hydrogen atom by a chlorine atom [1]. Also, these two bands appear to be too strong for methyl torsional modes. Thus, we have chosen an alternative assignment of these modes being in-phase motions of the C—P—Cl bending modes or more appropriately just skeletal bending modes of the dimer. It is quite probable that the methyl torsions are obscured by the skeletal bending modes in the 200—250 cm^{-1} region.

CONCLUSIONS

The analysis of the vibrational spectrum leads to the conclusion that the molecule is a non-centrosymmetric dimer in the crystalline state or a centrosymmetric dimer occupying C_2, C_s or C_i sites. The rocking modes, phosphorus—carbon and the phosphorus—chlorine stretching modes show the greatest effect with in-phase and out-of-phase components assigned. Additionally, the three low-frequency bending modes are no longer discernible in the solid state but instead seven well-pronounced bands are found in the similar region of the spectrum of the crystalline solid. It is clear that an X-ray diffraction of this crystal would be most interesting.

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