Table IV. Transport Properties of CuP_2, NiP_2, and RhP_3

	CuP_2 (chemical vapor)	CuP_2 (tin flux)	NiP_2	RhP_3
ρ_{77K}, Ω cm	0.97	1.14	0.29	4.87×10^{-5}
ρ_{290K}, Ω cm	0.106	0.126	0.39	14.03×10^{-5}
No. of carriers (77 K)	1.0×10^{16}	0.6×10^{16}	7.3×10^{17}	0.37×10^{20}
No. of carriers (290 K)	6.6×10^{17}	4.3×10^{17}	8.7×10^{17}	0.6×10^{20}
Sign of carriers				
Hall	+	+	−	+
Seebeck	+	+	−	+
Seebeck coeff, $\mu V/°C$		692	392	32
Activation energy of impurity levels, eV	0.03	0.03	0.002	
Optical absorption edge, eV	1.55	1.51	0.73	

samples are listed in Table III. p-Type conduction was determined from Seebeck and Hall measurements.

Figure 7 shows that the resistivity of RhP_3 increases with increasing temperature over the whole temperature range studied (4–300 K).

Conclusion

From this study of single crystals grown from a tin flux, NiP_2 was ascertained to be a diamagnetic n-type semiconductor with a band gap of 0.7 eV. The observed diamagnetic behavior of NiP_2 is consistent with the presence of low-spin d^8 configuration for the nickel atom.

The magnetic, optical, and electrical properties of single crystals of CuP_2 grown from a tin flux were studied and found to be very similar to those of single crystals of CuP_2 grown by the chemical-vapor transport technique. This similarity indicates that the tin did not substitute chemically into the CuP_2 structure but rather occurred as inclusions, as observed experimentally on flux-grown crystals.

The negative and temperature-independent magnetic susceptibility of RhP_3 indicates the presence of low-spin state d^6 rhodium in this compound. Hall, Seebeck, and resistivity measurements indicate p-type metallic conduction.

Table IV summarizes the transport properties of the different phases investigated.

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Registry No. CuP_2, 12019-11-3; NiP_2, 12035-47-1; RhP_3, 12202-48-1.

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Contribution from the Departments of Chemistry, University of Missouri at Kansas City,
Kansas City, Missouri 64110, and University of South Carolina, Columbia, South Carolina 29208

An Infrared and Raman Study of 1,2-Dimethyldiphosphine

JAMES R. BARD,[1a,b] ANTONIO A. SANDOVAL,*[1b] CHARLES J. WURREY,[1b] and JAMES R. DURIG*[1c]

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The Raman spectra of 1,2-dimethyldiphosphine have been recorded in the liquid and solid phases to 4000 cm^{-1}. The infrared spectrum of the solid phase was also recorded from 4000 to 200 cm^{-1}. The spectra were consistent with the presence of both the trans and gauche meso conformers and presumably the gauche conformer of the *d,l* isomer in the liquid phase. The gauche meso conformer was absent from the solid phase. A tentative vibrational assignment is proposed for the molecule.

Introduction

The synthesis, reactions, and structure of diphosphine and certain of its tetrasubstituted derivatives have been the subject of continuing investigations in our laboratories.[2-9] Although there are a number of additional recent theoretical and experimental conformational studies on these types of compounds,[10-17] there are few such reported studies of the 1,2-disubstituted diphosphines.[18,19] No vibrational study has been reported for any 1,2-disubstituted diphosphine although the infrared spectrum of gaseous 1,2-bis(trifluoromethyl)diphosphine has been reported and fragmentary assignments were made.[20] However, no structural conclusions regarding conformers were made from the data.

The successful preparation of diphosphorus tetrachloride by electric discharge in mixtures of phosphorus trichloride and hydrogen[21] has stimulated the recent synthesis of 1,2-dimethyldiphosphine by low-pressure silent electric discharge.[22] For this molecule, which can exist in both the meso and *d,l* diastereomers, there are a number of possible conformers, which previous studies have shown may be most readily investigated by a study of its vibrational spectra.[4,6] These conformers exist in both the trans and gauche forms, and illustrations representative of each form for similarly substituted diphosphines may be found in the literature.[13,18,19] In this paper, we present results obtained from the infrared and Raman spectra on the structure of 1,2-dimethyldiphosphine.

Experimental Section

1,2-Dimethyldiphosphine was prepared by passing methylphosphine through a silent electric discharge using a Siemans-type discharge tube.[22] The methylphosphine was prepared by the reduction of dimethyl methylphosphonate with $LiAlH_4$ in monoglyme.[23] All sample preparations and manipulations were carried out using standard high-vacuum techniques due to the toxicity of these compounds in general, their ease of oxidation, and the thermal instability of 1,2-dimethyldiphosphine. This compound decomposes rapidly at room

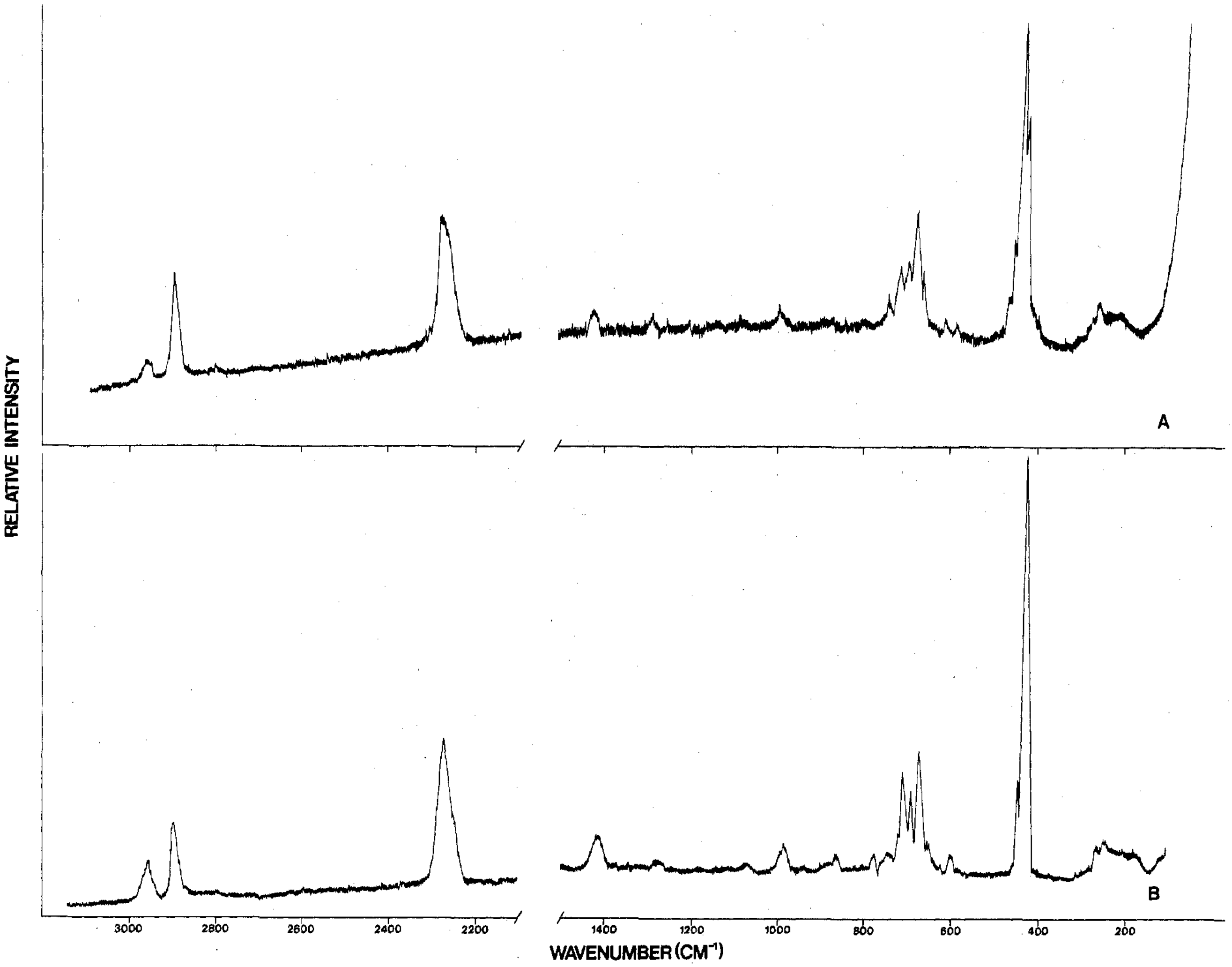

Figure 1. (A) Raman spectrum of liquid $CH_3HPPHCH_3$. (B) Raman spectrum of solid $CH_3HPPHCH_3$.

temperature to form methylphosphine and a viscous liquid.[22] The 1,2-dimethyldiphosphine was purified by a fractional condensation (trap-to-trap) method.[22]

The Raman spectra were recorded to 4000 cm^{-1} on a Cary Model 82 Raman spectrophotometer equipped with a Coherent Radiation Labs Model 53A krypton ion laser operating on the 6471-Å line. The spectrum of the liquid was recorded at −40 °C with the sample in a sealed glass capillary tube held in a cell previously described.[24] The cell was cooled with dry nitrogen obtained from the boil-off of liquid nitrogen and the temperature was monitored with an iron–constantan thermocouple. The spectrum of the solid was obtained by condensing the sample on a copper block maintained at ca. −190 °C by boiling nitrogen in a standard low-temperature cell. Polarization measurements for the liquid phase were made using the standard Cary accessories. Frequencies measured for sharp, resolvable lines are believed to be accurate to ±2 cm^{-1}.

The infrared spectrum of the solid was recorded from 4000 to 200 cm^{-1} using a Perkin-Elmer 621 spectrophotometer. The sample was condensed on a CsI plate maintained at ca. −190 °C by boiling nitrogen in a cell described previously.[25] The atmospheric water vapor was removed from the spectrometer housing by purging with dry nitrogen, and the instrument was calibrated as described in the literature.[26]

The melting point of the sample is below −150 °C and the condensed sample appeared to form a glass rather than a crystalline solid. Thus, a well-annealed solid was not obtained, and the usual sharpening and splitting of lines found in the spectra of the solid phase were not observed.

Results and Discussion

For 1,2-dimethyldiphosphine the probable conformations of the meso form are the trans (C_i) and gauche (C_1) and trans and gauche (both C_2) for the *d,l* isomer. All vibrations for the C_2 and C_1 conformers will be both infrared and Raman active, whereas for the C_i conformer half will be infrared active and half Raman active. Also, for the C_1 species, all vibrations are expected to be polarized in the Raman effect.

Original tracings of the Raman spectra for 1,2-dimethyldiphosphine in both the liquid and solid states are illustrated in Figure 1, and the infrared spectrum of this compound in the solid state is shown in Figure 2. The observed frequencies, approximate intensities, polarization information, and proposed assignments are given in Table I.

For convenience of discussion and interpretation, the 30 fundamentals have been divided into three types of vibrations: (1) hydrogen stretching modes, (2) hydrogen bending modes, and (3) the skeletal vibrations. In general, the assignments of most of the frequencies were straightforward and made by analogy with methylphosphine,[27-29] diphosphine,[9] and tetramethyldiphosphine.[4]

Hydrogen Stretching Vibrations. There are six CH_3 and two P–H stretching modes to be assigned. The assignments of these vibrations were straightforward since they each have characteristic group frequencies. The two P–H stretching fundamentals are certainly responsible for the strong band at 2280 cm^{-1} in both the infrared and Raman spectra. By analogy with methylphosphine and diphosphine, these two modes are nearly coincident as expected and give a rather broad band. Little, *if any, intermolecular* hydrogen bonding in this diphosphine is to be expected, and the slight shifts (Table I) of the frequencies due to the P–H stretching and bending modes in going from the liquid to the solid state

Table I. Infrared and Raman Spectra of 1,2-Dimethyldiphosphine

Raman					Infrared		
Solid Δ, cm^{-1}	Rel int[a]	Liquid Δ, cm^{-1}	Rel int	Polarizn[b]	Solid ν, cm^{-1}	Rel int	Assignment[c]
					3946	vw	$\nu_1 + \nu_{16}$ 2964 + 990 = 3954
					3885	vw	$\nu_5 + \nu_{16}$ 2903 + 990 = 3893
					3780	vw	$\nu_5 + \nu_{19}$ 2903 + 885 = 3785
					3260	vw	2964 + 303 = 3267
					3156	vw	
2963	m	2965	m	dp	2964	m	ν_1 CH_3 antisym stretch
2903	m	2904	m	p	2903	m	ν_5 CH_3 sym stretch
					2810	wm	$2 \times \nu_9$ 2 × 1415 = 2830
					2690	vw	1415 + 1279 = 2694
					2542	vw	2 × 1279 = 2558
2277	s	2280	s	p	2280	vs	ν_7 PH stretch
					2138	vw	2 × 1071 = 2142
					1928	vw	990 + 944 = 1934
1494	vw						
1420	m	1416	w		1415	s	ν_9 CH_3 antisym def
1280	w	1282	w		1279	m	ν_{13} CH_3 sym def
1165	w						
					1148	w	
1128	w						
					1109	w	
1071	w				1071	m	ν_{15} PH def
992	m	987	w		990	s	$\nu_{16,17}$ PH def
					958	w	CH_3 rock trans meso
942	w				944	w	ν_{18} CH_3 rock
					931	sh	CH_3 rock trans meso
922	vw						CH_3 rock trans meso
890	w				885	s	ν_{19} CH_3 sym rock
870	w						
					862	sh	ν_{20} CH_3 rock
783	w				781	m	ν_{21} PH def
748	w				747	m	ν_{22} CH_3 rock
		739	w	p			CH_3 rock gauche meso
					731	sh	
712	m	712	m	p?	708	m	ν_{23} PC antisym stretch
696	m	693	m	p	693	w	PC stretch?
678	m	673	m	p	678	m	ν_{24} PC sym stretch
653	w	659	w	p	650	m	
630	w						
604	wm	604	vw		603	m	PC stretch
585	w	583	vw				
560	vw						
533	vw						
		461?	w	dp?			
451	wm	447	m	p			PP stretch trans meso
435	s	434	s	p	437	m	ν_{25} PP stretch *d,l* isomer
		427	sh	p			PP stretch gauche meso
					303	w	PC wag trans meso
285	vw						PC wag gauche
267	w	267?	vw	p	269	w	PC wag
252	w	253	w	p			
230	vw						
209	vw						CH_3 torsion?
177	vw						PP torsion?

[a] Relative intensity: w, weak; m, medium; s, strong; v, very; sh, shoulder. [b] Polarization 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.

indicate little evidence for intermolecular hydrogen bonding. In contrast, extensive hydrogen bonding is found in 1,2-dimethylhydrazine as indicated by the relatively large shifts in frequency for the N–H stretching and bending modes in going from the liquid to the solid state.[30]

The four antisymmetric C–H stretching vibrations and the two symmetric C–H stretching modes are assigned to the infrared and Raman lines of medium intensity at 2964 and 2903 cm^{-1}, respectively. It is expected that the antisymmetric modes will be of higher frequency than the symmetric modes, and the polarization data for these lines are in agreement with this assignment.

Hydrogen Bending Vibrations. Two of the P–H bending vibrations were assigned to the lines at 1071 and 783 cm^{-1} in

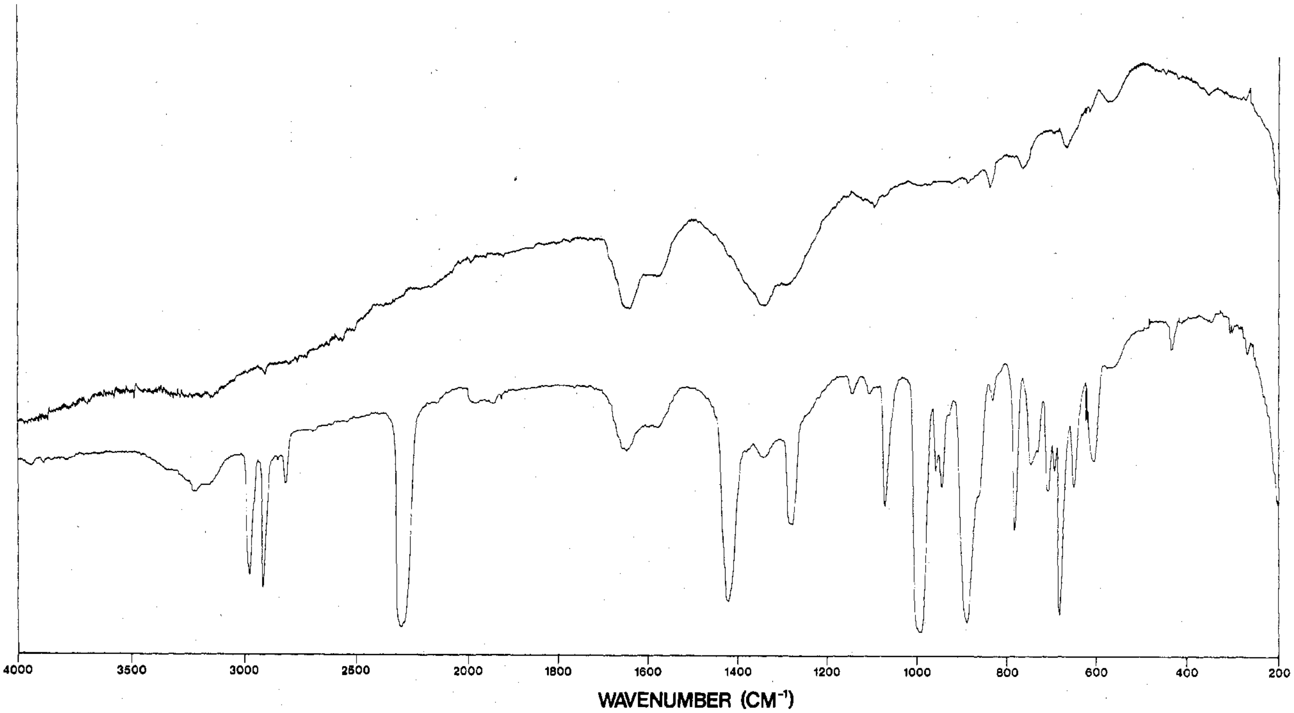

Figure 2. Infrared spectrum of solid $CH_3HPPHCH_3$ (bottom) and cell background (top).

the Raman and infrared spectra. The two remaining P–H bending modes are attributed to the line at approximately 990 cm^{-1} in both the infrared and Raman spectra. For the latter mode, as discussed above, the frequency in the Raman spectrum shows a slight shift to higher frequency in going from the liquid to the solid phase.

The strong line at 1415 cm^{-1} in the infrared spectrum and the corresponding weak line at 1416 cm^{-1} in the Raman spectrum of the liquid are attributed to the antisymmetric CH_3 deformations. It appears to be depolarized. This mode occurs at 1420 cm^{-1} in the Raman spectrum of the solid. The CH_3 symmetric deformations occur at 1279, 1280, and 1282 cm^{-1} in the infrared spectrum of the solid, the Raman spectrum of the solid, and the Raman spectrum of the liquid, respectively. The infrared absorption is of medium intensity whereas the Raman lines are weak as expected.

As with tetramethyldiphosphine,[4] the CH_3 rocking modes show different frequencies for the gauche (both isomers) and the trans meso structures. This difference is apparent when comparing the infrared and Raman spectra of the solid since the principle of mutual exclusion will apply for the trans meso conformer. The two CH_3 rocking modes (or one rock and one wag) of the trans meso conformer that are infrared active are found at 958 and 931 cm^{-1}. Only one of these two modes that are Raman active is found and is tentatively assigned at 922 cm^{-1}. All of the remaining conformers have all four of the rocking modes both infrared and Raman active, and these are tentatively assigned to the 944, 885, 862, and 747 cm^{-1} bands in the infrared spectrum and to the lines at 942, 890, 870, and 748 cm^{-1} in the Raman spectrum. The line at 739 cm^{-1} in the Raman spectrum of the liquid disappears with solidification and may be attributed to one of the CH_3 rocking modes of the gauche meso conformer.

Skeletal Vibrations. The skeletal vibrations of 1,2-dimethyldiphosphine consist of two P–C stretches, one P–P stretch, two P–C bends, two P–C torsions, and one P–P torsion.

The P–P stretching mode occurs in the 400–450-cm^{-1} region and is of greatest interest since the existence of different conformers is most readily confirmed by the presence of more than one P–P stretching vibration. It has been shown in other substituted diphosphines that the P–P stretching vibration typically gives rise to only weak bands in the infrared spectrum, if observed at all. However, it is the Raman spectra of the liquid and solid states that show the existence of different conformers most drastically. Although more than one conformer may exist in the liquid state, in general, only the most stable conformer(s) will be present in the solid; thus Raman lines in the liquid that disappear with solidification can be attributed to an additional conformer(s) in the liquid phase.

As in the case of tetramethyldiphosphine,[4] it is readily apparent from an inspection of the 450-cm^{-1} region of the Raman spectra of both the liquid and solid phases that more than one conformational isomer is present in 1,2-dimethyldiphosphine. The Raman spectrum of liquid 1,2-dimethyldiphosphine shows three lines in this region, whereas the Raman spectrum of the solid shows only two lines in the same region. A comparison of the two spectra shows that while the intense Raman line at 435 cm^{-1} and the weak Raman line at 451 cm^{-1} are unchanged, the line of medium intensity at 427 cm^{-1} in the liquid state (shoulder) is no longer present in the spectrum of the solid. Further evidence that the 427-cm^{-1} line is missing in the Raman spectrum of the solid is that a noticeable sharpening of the low-frequency side of the base of the strong line at 435 cm^{-1} is also quite evident in the Raman spectrum of the solid, whereas, in the Raman spectrum of the liquid this region is much broader due to the presence of the 427-cm^{-1} line.

When the infrared and Raman spectra of the solid are compared, the weak Raman line at 451 cm^{-1} is seen to be absent in the infrared spectrum which shows only the 435-cm^{-1} absorption peak. On the basis of this mutual exclusion of the 451-cm^{-1} line, there is little doubt that there exists one conformer that is centrosymmetric. Thus the 427-cm^{-1} line is attributed to the gauche meso conformer, the 435-cm^{-1} line to the conformers of the *d,l* isomers, and the 451-cm^{-1} line to the trans meso conformer.

Assuming that the ratio of intensities is an accurate measure of the ratio of conformer concentrations,[31] the relative intensities of the lines at 451 and 427 cm^{-1} indicate that in the liquid phase at −40 °C the conformers in the meso isomer exist as 70% gauche and 30% trans. The validity of this assumption has been questioned,[10] since the peak intensity is a function of the polarizability change, and the assumption that this change is equal for all conformers may not necessarily be valid.

However, a 70% gauche form for the meso isomer of 1,2-dimethyldiphosphine seems reasonable compared to similar measurements on liquid tetramethyldiphosphine (60% gauche, 40% trans).[4] As evidenced by this ratio of gauche to trans conformers in tetramethyldiphosphine, and in the diphosphorus tetrahalides (~100% trans), it appears that a decrease in electronegativity of the substituent on phosphorus favors the gauche conformer.[4] However, the slightly lower electronegativity of the hydrogen atom (2.28) compared to a methyl group (2.3)[32] is probably not sufficient to account for diphosphine existing as ~100% gauche[9] and tetramethyldiphosphine being only 60% gauche.[4] The observed structure also depends on the distance between interacting groups,[33] with shorter P–P bond lengths favoring the gauche conformer. But diphosphine has a relatively long P–P bond length (2.219 Å) compared to tetramethyldiphosphine (2.192 Å). As discussed elsewhere,[9] this apparent anomaly may be resolved if the hydrogen atoms in diphosphine are too far apart to influence the structure and it is the effect of the lone pairs that determines the structure of diphosphine. For 1,2-dimethyldiphosphine, it would be reasonable to assume that the P–P bond length is somewhere intermediate between that of tetramethyldiphosphine and diphosphine thereby allowing for more influence on structure by the substituents on phosphorus and resulting in a concentration of the gauche form of the meso isomer between 60 and 100%. The observed 70% gauche form for this isomer is consistent with this assumption.

Furthermore, the relative intensity of the line at 435 cm^{-1} compared to the sum of the lines at 451 and 427 cm^{-1} indicates that 1,2-dimethyldiphosphine exists as 50% *d,l* and 50% meso isomers in the liquid phase, which is not unexpected when one considers, among other things, the method of synthesis. In this electric discharge synthesis the products are those resulting from bond cleavage and recombination of the resulting fragments. Phosphorus-containing fragments resulting from a single hydrogen atom being removed from methylphosphine may combine with equal facility in either of two orientations to form equal quantities of both possible diastereomers.

Our observation of a 1:1 ratio of *d,l* to meso isomers in 1,2-dimethyldiphosphine is supported by a recent study of the importance of gauche steric interactions between alkyl groups in determining the ratio of *d,l* to meso isomers. Intensity measurements from an NMR study of several analogues of 1,2-dimethyldiphosphine having alkyl groups instead of hydrogen atoms bonded to the phosphorus atoms provide interesting data on the relative concentrations of *d,l* and meso isomers present in each diphosphine. For such diphosphines having ethyl, isopropyl, and *tert*-butyl groups instead of hydrogen atoms, the ratio of *d,l* to meso isomers is 1.17:1, 2:1, and all *d,l*, respectively.[13] These data show a definite trend for alkyl-substituted 1,2-dimethyldiphosphines in which an increasingly larger alkyl group favors a greater concentration of the *d,l* isomer and provide additional support for our observation of a 1:1 ratio for *d,l* to meso isomers in 1,2-dimethyldiphosphine.

The two lines at 712 and 678 cm^{-1} in the Raman spectra of both phases are assigned as the P–C antisymmetric and P–C symmetric stretching modes, respectively. In the infrared spectrum these same absorptions occur at 708 and 678 cm^{-1}, respectively. The P–C skeletal bending vibrations were observed in the 150–300 cm^{-1} range for tetramethyldiphosphine[4] and suggest a similar region for the two P–C bends in 1,2-dimethyldiphosphine. Although the infrared spectrum extends only to 200 cm^{-1}, there are two weak peaks at 303 and 269 cm^{-1}. The absorption at 303 cm^{-1} is not found in the Raman spectrum and is thus tentatively assigned as the A_u P–C wag for the trans meso conformer. The peak at 269 cm^{-1} occurs in both the infrared and Raman spectra and may be attributed to a P–C wag of a gauche conformer. In addition to the 269-cm^{-1} line, the Raman spectrum of the solid shows lines at 285, 252, 230, 209, and 177 cm^{-1}, all of weak intensity. Although these lines may arise from motions involving the P–C bonds in the various conformers possible, any attempt at specific assignments would be highly speculative. However, the methyl torsional mode has previously been reported to occur at 207 cm^{-1} in methylphosphine.[34] The 209-cm^{-1} line may be tentatively assigned to this mode, although the methyl torsion is usually quite weak in the infrared and is seldom observed in the Raman effect. The P–P torsion for the conformers of C_1 and C_2 symmetry is Raman active, and the weak line at 177 cm^{-1} does fall in the range between the values assigned for the P–P torsion in diphosphine (217 cm^{-1})[9] and tetramethyldiphosphine (58 cm^{-1}).[4] However, we believe that this torsional vibration cannot be assigned with great confidence.

Table II. Summary of the Skeletal Fundamental Vibrations (cm^{-1}) of 1,2-Dimethyldiphosphine and 1,2-Dimethylhydrazine[a]

Approx description	$P_2H_2(CH_3)_2$[b]		$N_2H_2(CH_3)_2$[c]	
	Raman	Infrared	Raman	Infrared
A				
Skeleton stretch	678	678		1034
Skeleton stretch	435	437	806	807
Skeleton bend	267	269		366
CH_3 torsion	209			241
Skeleton torsion	177			164
B				
Skeleton stretch	712	708		1192
Skeleton bend	285		480	468
CH_3 torsion	209			241

[a] The frequencies given are for the compounds in the solid state and for the conformer(s) assumed to have C_2 symmetry. [b] This work. [c] Taken from ref 30.

From the data presented in Table II it is seen that, with the exception of the skeletal torsional mode, each of the skeletal vibrations occurs at a higher frequency in the 1,2-dimethylhydrazine than in 1,2-dimethyldiphosphine. This is as one would expect on the basis of phosphorus having a greater mass than nitrogen. In addition, the skeletal vibrations are ordered in the same fashion; i.e., the stretching modes are higher in frequency than the bending modes, whereas the torsional modes are lowest in frequency. Thus, there is almost a 1:1 correspondence in the way the frequencies are ordered. Such trends may be considered a further corroboration of the band assignments for the diphosphine.

Conclusions

We conclude from the infrared and Raman spectra of 1,2-dimethyldiphosphine that in the liquid phase the molecule exists in both the trans and gauche conformations of the meso isomer and the *d,l* isomer for which the conformers cannot be distinguished but may be assumed to be predominantly in the gauche form. In the solid phase the gauche meso conformer is absent.

The existence of more than one isomer is in agreement with the results based on NMR data reported for other 1,2-disubstituted diphosphines,[18,19] and tetrasubstituted diphosphines having two different substituents on the same phosphorus atom.[13,35,36] If it is assumed that the vicinal steric repulsions decrease in the order CH_3–CH_3 > CH_3–H > H–H, then the trans form of the meso isomer will be favored over the gauche at the temperature of the solid. Similarly, and using a rationalization based on the "gauche effect",[33] for the *d,l* isomer the gauche outer (relative to the methyl groups) conformer will be the most stable form since the methyl groups are again in the trans position, the lone pairs on phosphorus are in a gauche relationship, and the number of gauche interactions between lone pairs and the polar P–C bonds is at a maximum.

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Registry No. $CH_3HPPHCH_3$, 53684-00-7.

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Contribution from the Institute of General and Inorganic Chemistry
of the University of Rome, 00185 Roma, Italy

Ultraviolet Photoionization Spectra of the Valence Shell of (Difluorodithiophosphato)metal Complexes

M. V. ANDREOCCI, P. DRAGONI, A. FLAMINI, and C. FURLANI*

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The He I photoelectron spectra of HS_2PF_2, $M^{II}(S_2PF_2)_2$ (M^{II} = Mn, Co, Ni, Zn), and $Cr(S_2PF_2)_3$ are reported. Absence of interfering ionization bands by substituent groups outside the chelate rings allows correlation of all relevant PE bands throughout the series and identification, besides d-ionization bands in the case of the Mn(II), Cr(III), Co(II), and Ni(II) complexes, of a series of six main bands, corresponding to all p-based σ and π molecular orbitals of the metal chelate rings.

Metal complexes of the ligand $F_2PS_2^-$, discovered and extensively investigated by Muetterties and co-workers[1,2] as well as by other authors,[3,4] appear particularly suitable for the investigation of their electronic structure by UPS (photoelectron spectroscopy with far-ultraviolet excitation) not only because of their high volatility but also because of the simplicity of their molecular structure, since the substituent groups outside the chelate ring do not exhibit low-energy ionization processes and hence do not interfere with the spectral PE patterns of the chelate ring orbitals. The UPS spectra of Cr(III), Mn(II), Co(II), Ni(II), and Zn(II) difluorodithiophosphates are indeed rich in well-resolved bands so that extensive empirical correlations are possible; we propose an assignment which accounts for all σ and π orbitals in the metal chelate rings, except those based mainly on atomic s-valence orbitals. Considerable insight into the electronic structure of the complexes can thus be gained, the partly filled d shell constituting the levels of highest orbital energy (except for the Zn(II) compound), followed by the ligand orbitals of coordinative π character, whose energies are quantitatively identified, and by the σ_{MS} and σ_{PS} orbitals. A comparison along the investigated series yields evidence for the trend of falling d-orbital energy with increasing atomic number.

Experimental Section

HS_2PF_2, $Cr(S_2PF_2)_3$, $Mn(S_2PF_2)_2$, $Co(S_2PF_2)_2$, $Ni(S_2PF_2)_2$, and $Zn(S_2PF_2)_2$ were synthesized according to known literature methods[1,2] and the metal compounds purified by sublimation. UPS were taken on a Perkin-Elmer PS-18 instrument equipped with a He I source (21.22 eV) and calibrated by the argon 3p and xenon or iodine (in CH_3I) 5p doublets. The metal complexes were introduced into the spectrometer chamber as solid samples, and HS_2PF_2 was introduced as a volatile liquid sample. Particular care was required in handling $Co(S_2PF_2)_2$ because of easy oxidation and HS_2PF_2 because of its high reactivity leading to rapid attack of spectrometer walls and photomultiplier surfaces. Calculations on the free ligand were carried out by the CNDO/2 method.[5]

Results and Discussion

He I UPS spectra of the above mentioned compounds are reported in Figure 1 and Table I. Three regions of ionization energy can be identified, in order of increasing orbital energies.

Region i. Between ca. 16 and 20 eV IE, three band groups are observed at about 16.2, 17.8, and 19.0 eV and are related to σ and π ionization of fluorine-based orbitals. Such ionizations are observed in the same energy region for all P–F

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