bond (*cf.* Figure 4b). Although one cannot distinguish between a cyclopentadienyl group bonded in the allylic manner and one bonded as a six-electron donor,[20] it is entirely reasonable that the nitrogen in a pyrrolenyl ligand causes enough electron asymmetry to produce a distortion. It is noteworthy that the E mode of C≡O stretch is split by 11 cm^{-1} in PyMn(CO)$_3$. This reflects the electronic asymmetry at the Mn *via* the loss of the fivefold symmetry of the ring (*e.g.*, Cp$^-$ *vs.* Py$^-$). Moreover in substituted RCpMn(CO)$_3$[21] molecules where R equals C(O)CH$_3$, C(O)C$_6$H$_5$, etc., splittings of the same order of magnitude are observed. Whether or not the pyrrole slippage is real, the pyrrolenyl affects the Mn 3d orbitals by removing the degeneracy of the 3d$_{xz}$ and 3d$_{yz}$ orbitals.

The similarity in the properties, particularly the ν_x and ν_y's, of PyMn(CO)$_3$ and CpMn(CO)$_3$ as displayed in Table I, indicate that the direction of the field gradient tensor in the PyMn(CO)$_3$ is essentially the same as in CpMn(CO)$_3$. The major factor contributing to the asymmetry parameter, η, is therefore the population difference of the 3d$_{xz}$ and 3d$_{yz}$ orbitals. The difference can be calculated from η. In terms of a molecular orbital interpretation[22] of the field gradient an equation for η

$$\eta = \frac{{}^3/_2\,(\#3d_{xz} - \#3d_{yz})eq_{3d_{z^2}}Q}{eq_{zz}Q} \qquad (2)$$

can be derived where #3d$_{xz}$ and #3d$_{yz}$ are the orbital populations and $eq_{3d_{z^2}}Q$ and $eq_{zz}Q$ are the quadrupole coupling constants for one 3d$_{z^2}$ electron and for PyMn(CO)$_3$, respectively. Using eq 2 the difference #3d$_{xz}$ − #3d$_{yz}$ is 0.03 ± 0.01 electron.[23] This difference arises from the donation of pyrrolenyl π electrons to the manganese in predominantly ligand molecular orbitals since the metal molecular orbitals having 3d$_{xz}$ and 3d$_{yz}$ character would be empty.

In summary, the temperature-dependent ^{55}Mn nqr data are consistent with a slipped pyrrolenyl–manganese bond (*cf.* Figure 4b), although final confirmation of such a distortion must come from a crystallographic study of PyMn(CO)$_3$.

Acknowledgments.—M. D. F. acknowledges the NSF for an undergraduate fellowship. This work was supported by the Inorganic Materials Research Division, Lawrence Radiation Laboratory, under the auspices of the United States Atomic Energy Commission.

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(20) J. L. Calderon, F. A. Cotton, and P. Legzdins, *J. Am. Chem. Soc.*, **91**, 2528 (1969).

(21) J. Kozikowski, R. E. Maginn, and M. S. Klove, *ibid.*, **81**, 2995 (1959).

(22) F. A. Cotton and C. B. Harris, *Proc. Natl. Acad. Sci. U. S.*, **56**, 12 (1966).

(23) The error of ±0.01 electron is due to the 25% uncertainty in Q for ^{55}Mn.

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Vibrational Spectra and Structure of Organophosphorus Compounds. VIII. Tetramethylbiphosphine(1)

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The infrared spectra of gaseous, liquid, and solid tetramethylbiphosphine have been recorded from 4000 to 33 cm^{-1}. The Raman spectra of the liquid and the solid have also been recorded and depolarization values have been measured. A comparison of the Raman spectra of the liquid and the solid indicates that the liquid consists of a mixture of *trans* and *gauche* conformers with the *gauche* structure slightly predominant. A similar comparison of the infrared and Raman bands of solid tetramethylbiphosphine below 750 cm^{-1} shows the mutual exclusion principle is operative, and it is concluded from this alternate forbiddeness that the *trans*-P$_2$(CH$_3$)$_4$ isomer of C$_{2h}$ symmetry gives rise to these mutually exclusive bands. Assignments of the observed frequencies based on depolarization values, band positions, and relative intensities are presented for the molecule in both the C$_2$ and C$_{2h}$ configurations. It is also shown that the two isomers may differ little in energy in the liquid state.

Introduction

The symmetry of molecules which have the general formula X$_2$Y$_4$ has been the subject of several recent vibrational studies. The possible structures for X$_2$Y$_4$-type molecules include planar (D$_{2h}$ symmetry), staggered (D$_{2d}$), *trans* (C$_{2h}$), *gauche* (C$_2$), and *cis* (C$_{2v}$). It has been found that, for molecules in which the central pair of atoms is nitrogen or phosphorus, the structures determined have been either *trans* or *gauche*. These structures correspond to a pyramidal arrangement of neighboring atoms and nonbonded electron pairs about the central group V atoms. The relative amounts of the *trans* or *gauche* isomers will depend upon the interactions of the two nonbonded electronic clouds and the steric repulsions of the substituent atoms as

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(1) Part VII: J. R. Durig and J. S. DiYorio *J. Mol. Struct.*, **3**, 179 (1969).

(2) Taken in part from the thesis submitted by J. S. DiYorio to the Department of Chemistry in partial fulfillment of the Ph.D. degree.

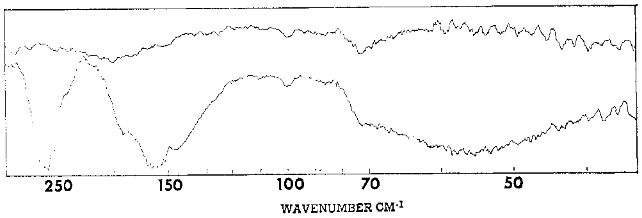

Figure 1.—Far-infrared spectrum of gaseous $(CH_3)_2PP(CH_3)_2$.

well as other less important forces.[3] Since the N–N and P–P bond distances are considerably different, there is no reason to believe these forces will be the same in the corresponding phosphorus and nitrogen compounds. Thus, one might expect grossly different concentrations of the two isomers between the corresponding phosphorus and nitrogen compounds as seems apparent from the available data on tetrafluorohydrazine[4–7] and tetrafluorobiphosphine.[8] Tetrafluorohydrazine is a 53–47% mixture of *trans* and *gauche* isomers, respectively, whereas tetrafluorobiphosphine appears to be all in the *trans* form.

The vibrational spectra of N_2H_4[9,10] and P_2H_4[11,12] in both the gaseous and liquid states have been interpreted in terms of only the *gauche* structure. However, the tetrahalobiphosphines have been found to exist only in the *trans* conformation. Frankiss and Miller[13] have examined the vibrational spectra of solid, liquid, and gaseous P_2Cl_4 and assigned the spectra on the basis of C_{2h} molecular symmetry in all phases. The vibrational spectra of P_2I_4[14] as a solid and in solution have also been recorded and C_{2h} symmetry was also found for the P_2I_4 molecule. Therefore all of the vibrational spectra of the substituted biphosphine molecules have been interpreted in terms of only the *trans* configuration. As a continuation of our spectral studies of organophosphorus compounds, we investigated the infrared and Raman spectra of tetramethylbiphosphine [$(CH_3)_2PP(CH_3)_2$] in order to determine the symmetry and normal vibrations of this molecule.

Experimental Section

The samples used in this study were obtained from a commercial source and were purified by trap-to-trap distillation. The main impurity was dimethylphosphine and we followed the purification progress by monitoring the relative intensity of the P–H stretching mode at 2290 cm^{-1}. The infrared spectra from 4000 to 250 cm^{-1} were recorded with a Perkin-Elmer Model 621 spectrophotometer whose housing was purged with dry air. The high-frequency region was calibrated with standard gases[15] whereas the low-frequency region was calibrated with atmospheric water vapor and the assignments of Randall, *et al.*[16] The spectra were recorded of the vapor contained in a 20-cm gas cell and of the solid contained in a low-temperature cell described previously.[5] The observed frequencies are listed in Table I. Infrared spectra below 250 cm^{-1} were recorded with a Beckman Model IR-11 spectrophotometer. The atmospheric water vapor was removed from the instrument housing by flushing with dry air. Water vapor with the assignments of Randall, *et al.*,[16] was used to calibrate the instrument. The observed bands are listed in Table I and typical spectra are shown in Figures 1 and 2. All infrared frequencies of sharp bands are believed to be accurate to ±2 cm^{-1}.

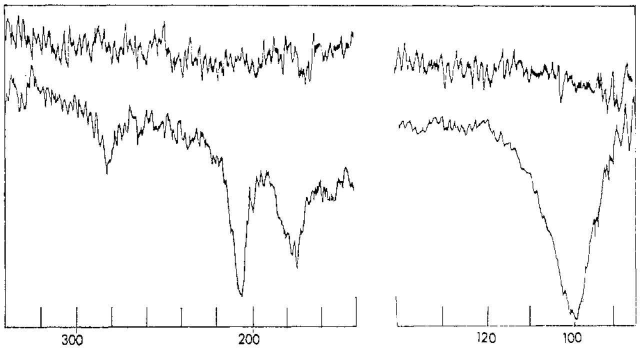

Figure 2.—Far-infrared spectrum of solid $(CH_3)_2PP(CH_3)_2$.

Raman spectra were recorded with a Cary Model 81 spectrophotometer equipped with an He–Ne laser source. The spectra of both the liquid and solid phases were obtained by using a cell previously described.[17] All Raman shifts are reported in Table I and are believed to be accurate to ±2 cm^{-1}.

Results

Only the frequencies of the skeletal stretching and bending motions are expected to show significant variations with changes in molecular structure. All of the carbon–hydrogen motions except the methyl torsions fall above 800 cm^{-1} and the frequencies of the skeletal motions are all below 800 cm^{-1} and can easily be distinguished from the C–H vibrations. An inspection of the Raman spectrum of liquid tetramethylbiphosphine (see Figure 3) shows nine Raman lines below 500 cm^{-1}. However, the Raman spectrum of the solid is quite simple with only four lines in this spectral region. A comparison of the two spectra (see Figure 3) shows dramatically that the strongest Raman line in this spectral region is conspicuously absent from the spectrum of the solid. Since the 429-cm^{-1} Raman line which disappeared with solidification is considerably more intense than the 455-cm^{-1} line that remains, the two lines can be discounted as a Fermi doublet. Also, the most intense Raman line cannot be considered a difference tone but must arise from a different conformer of the tetramethylbiphosphine molecule.

Further evidence for the presence of a second isomer is found in the complex number of lines in the 200–300-cm^{-1} region. The relatively intense Raman lines at

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(3) W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.*, **2**, 492 (1934); *Trans. Faraday Soc.*, **30**, 898 (1934).

(4) C. B. Colburn, F. A. Johnson, and C. Haney, *ibid.*, **43**, 4526 (1965).

(5) J. R. Durig and J. W. Clark, *ibid.*, **48**, 3216 (1968).

(6) D. F. Koster and F. A. Miller, *Spectrochim. Acta*, **24A**, 1487 (1968).

(7) M. J. Cardillo and S. H. Bauer, private communication.

(8) R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3729 (1966).

(9) A. Yamayuchi, I. Ichishima, T. Shimanouchi, and S. Mizushima, *Spectrochim. Acta*, **16**, 1471 (1959).

(10) J. R. Durig, S. F. Bush, and E. E. Mercer, *J. Chem. Phys.*, **44**, 4238 (1966), and references cited therein.

(11) E. R. Nixon, *J. Phys. Chem.*, **60**, 1054 (1956).

(12) M. Baudler and L. Schmidt, *Angew. Chem.*, **68**, 378 (1956); *Z. Anorg. Allgem. Chem.*, **289**, 219 (1957); *Naturwissenschaften*, **44**, 488 (1957).

(13) S. G. Frankiss and F. A. Miller, *Spectrochim. Acta*, **21**, 1235 (1965).

(14) S. G. Frankiss, F. A. Miller, H. Stammreich, and Th. T. Sans, *ibid.*, **23A**, 543 (1967).

(15) "IUPAC Tables of Wavenumbers for the Calibration of Infrared Spectrometers," Butterworth Inc., Washington, D. C., 1961.

(16) H. M. Randall, D. M. Dennison, W. Ginsburg, and L. R. Weber, *Phys. Rev.*, **52**, 160 (1937).

(17) D. J. Antion and J. R. Durig, *Appl. Spectry.*, **22**, 675 (1968).

TABLE I[a]
INFRARED AND RAMAN SPECTRA OF TETRAMETHYLBIPHOSPHINE

Infrared				Raman					
Gas		Solid		Liquid			Solid		
freq, cm^{-1}	Intens	Freq, cm^{-1}	Intens	Freq, cm^{-1}	Rel intens	Polarizn	Freq, cm^{-1}	Rel intens	Assignment
2977	s	2965	m	2967	10				CH_3 antisym str
2966	s	2950	m	2955	11				CH_3 antisym str
		2914	w						
2909	s	2891	m	2899	52				CH_3 sym str
		2843	m						2 × 1429 = 2858
2817	m			2812	11				2 × 1409 = 2818
1432	s	1429	m	1425					CH_3 antisym def
		1409	m	1417					CH_3 antisym def
		1404	m, sh						CH_3 antisym def
		1385	w						
		1325	vw						
1296	m								
1290	m			1290	15				CH_3 sym def
1288	m								
1278	m	1277	m	1270	14				CH_3 sym def
		1274	m						
945	s	944	s	940	6				CH_3 antisym rock
				910	4				CH_3 antisym rock
				903	4				CH_3 antisym rock
892									
888 Q		890	w						CH_3 sym rock
876									
869 Q		872	s						CH_3 sym rock
853				855	1				CH_3 sym rock
		845	w	850	1				CH_3 sym rock
				817	1				?
709	s	709	s						PC_2 antisym str
				699	40	dp	698	50	PC_2 antisym str
				663	100	p	668	100	PC_2 sym str
663 R									
657 Q	m	668	m						PC_2 sym str
650 P									
				455	75	p	455	50	P–P str (*trans*)
				429	97	p			P–P str (*gauche*)
				301	52	p	314	50	PC_2 wag (*trans*)
				287	17	p			PC_2 wag (*gauche*)
266	m	280	w						PC_2 wag (*trans*)
260	m								PC_2 wag (*gauche*)
				258	35	dp	260	14	PC_2 twist (*trans*)
245	w			243	40	dp			PC_2 twist (*gauche*)
				226	58	p	231	22	PC_2 scissor (*trans*)
		205	m						PC_2 twist (*trans*)
186	m								
				190	1	?			PC_2 twist (*gauche*)
166	m	174	m						PC_2 scissor (*trans*)
147	w			158	4	?			PC_2 scissor (*gauche*)
58	s, b	100	s						Torsion

[a] Abbreviations used: s, m, w, v, b, p, and dp denote strong, medium, weak, very, broad, polarized, and depolarized, respectively.

287 and 243 cm^{-1} in the spectra of the liquids have no corresponding lines in the Raman spectrum of the solid. Similarly, the infrared spectrum of the solid is quite simple below 300 cm^{-1} and a comparison of the infrared frequenices in this region with the observed Raman lines in the same frequency range shows a definite mutual exclusion. This alternate forbiddeness then provides conclusive evidence that solid tetramethylbiphosphine exists as the *trans* isomer. Similarly one is forced on the *basis of the Raman spectrum* alone to conclude that a second isomer is present in the liquid, and steric considerations favor the *gauche* isomer over the *cis* isomer.

Vibrational Assignment for the *trans* Isomer.—No vibrational assignment has previously been presented for the $P_2(CH_3)_4$ molecule but with depolarization values of the Raman lines along with the alternate forbiddeness between the infrared and Raman spectra of the solid such an assignment is relatively straightforward. There are 48 fundamental vibrations for the tetramethylbiphosphine molecule and 36 of these are motions of the methyl group and 12 are skeletal vibrations. The skeletal motions are represented by $4\ A_g + 3\ A_u + 2\ B_g + 3\ B_u$ species for the *trans* structure with the A_g and B_g vibrations being Raman active. Further, the four vibrations of the A_g symmetry species should give rise to polarized Raman lines whereas the two vibrations of the B_g symmetry species should give depolarized lines. From earlier work on organophosphorus compounds[18–21] one can be relatively certain that all of the skeletal modes fall below 800 cm^{-1}. Therefore the Raman lines at 231, 260, 314, and 455 cm^{-1} which have no counterparts in the infrared spectrum of the solid can be ascribed to the *trans* isomer. The two Raman lines at 698 and 668 cm^{-1} for the solid must also be skeletal modes of the *trans* conformer. Also, four of these Raman lines—231, 314, 455, and 668 cm^{-1}—have been shown to lead to polarized lines in the liquid phase. Except the 301-cm^{-1} band, none of the Raman lines showed any appreciable shift when the sample solidified. Thus, the correspondence between the lines for the liquid and solid phases is readily apparent.

We have shown[18–20] the phosphorus–carbon stretching modes fall in the 600–750-cm^{-1} range and give rise to strong Raman lines. Therefore, the very strong polarized Raman line at 663 cm^{-1} is assigned the PC_2 symmetric stretching mode and the relatively strong depolarized line at 699 cm^{-1} is assigned to the antisymmetric PC_2 stretching mode of symmetry species B_g. Because of the intensity of the two Raman lines in the 400-cm^{-1} region there can be little doubt that they originate from motions of the P–P bond. Therefore the polarized Raman line at 455 cm^{-1} is assigned to the P–P stretching mode. The polarized Raman lines at 301 and 226 cm^{-1} are assigned to the PC_2 wagging and scissoring motions, respectively. The scissoring motion is derived from the PC_3 antisymmetrical deformation and is expected to fall at a lower frequency than the wagging motion whose frequency should be compared to the symmetrical deformation.[22] It also should be mentioned that the XY_2 wagging frequencies are usually 100 cm^{-1} higher than the scissoring frequencies for most atoms except hydrogen or deuterium. Thus, the assignment of the higher frequency to the wagging motion is consistent with previous data on XY_2 bending motions. The depolarized Raman line at 258 cm^{-1} is then confidently assigned to the PC_2 twisting mode. Therefore, the Raman-active skeletal modes can be assigned straightforwardly and are summarized in Table II.

The fact that two of the three PC_2 bending modes are polarized rules out the coplanar D_{2h} structure. For such a structure the PC_2 wagging mode is not totally symmetric and there should then be only one polarized Raman line in the PC_2 bending region. Therefore, from this datum we conclude that the molecule is in the C_{2h} *trans* configuration in the solid state and reject the coplanar structure.

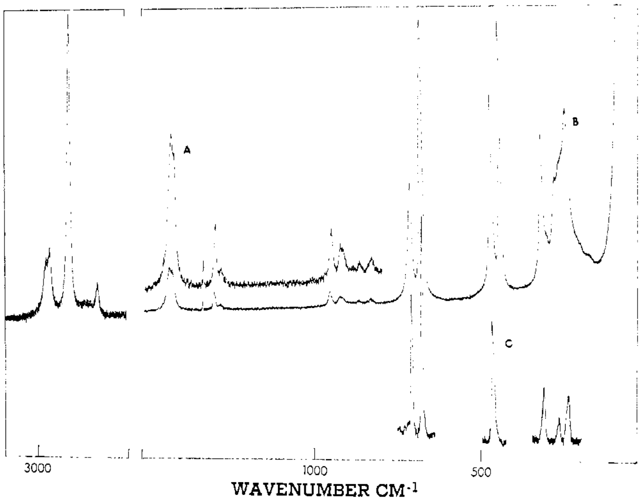

Figure 3.—Raman spectra of $(CH_3)_2PP(CH_3)_2$: (A) liquid phase, 6328-Å excitation, slits double 1 cm^{-1} × 5 cm, sensitivity 600, period 2; (B) liquid phase, sensitivity 110, period 2; (C) solid phase.

TABLE II

SUMMARY OF THE SKELETAL FUNDAMENTAL VIBRATIONS OF THE *trans*-TETRAMETHYLBIPHOSPHINE MOLECULE

Vib no.[a]	Sym species and approx description of the normal modes	Spectra, cm^{-1}	
		Raman (liquid)	Ir (solid)
	A_g		
9	PC_2 str	663	
10	P–P str	455	
11	PC_2 wag	301	
12	PC_2 def	226	
	A_u		
22	PC_2 str		668
23	PC_2 twist		205
25	Torsion		100
	B_g		
34	PC_2 str	699	
35	PC_2 twist	258	
	B_u		
45	PC_2 str		709
46	PC_2 wag		280
47	PC_2 def		174

[a] Each symmetry species will have three CH_3 stretching, three CH_3 deformation, two CH_3 rocking, and one CH_3 torsional modes; for example the first eight vibrations of symmetry species A_g correspond to the CH_3 stretching, deformational, and rocking modes.

The assignment of the infrared-active modes follows directly from the assignment of the Raman modes. The PC_2 antisymmetric mode is found at 709 cm^{-1} and the corresponding symmetric motion falls at 668 cm^{-1} (657 cm^{-1} for the gas). The PC_2 wagging mode is at 280 cm^{-1} with the PC_2 twisting and PC_2 scissoring motions falling at 205 and 174 cm^{-1}, respectively. The only skeletal vibration remaining to be assigned is the skeletal torsion. The 100-cm^{-1} band (see Figure 4) is too low in frequency to be assigned to PC_2 bending modes and it appears to be rather high for a lattice mode. The frequency of the 100-cm^{-1} band was studied as a function of temperature and it was found to be practically constant over the temperature range −170 to −75° (see Figure 4). Such behavior casts doubt on the assignment of the band to a lattice mode;

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(18) J. R. Durig, F. Block, and I. W. Levin, *Spectrochim. Acta*, **21**, 1105 (1965).

(19) J. R. Durig, B. R. Mitchell, J. S. DiYorio, and F. Block, *J. Phys. Chem.*, **70**, 3190 (1966).

(20) J. R. Durig, D. W. Wertz, B. R. Mitchell, F. Block, and J. M. Greene, *ibid.*, **71**, 3815 (1967).

(21) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1957.

(22) A. B. Harvey and M. K. Wilson, *J. Chem. Phys.*, **44**, 3535 (1966).

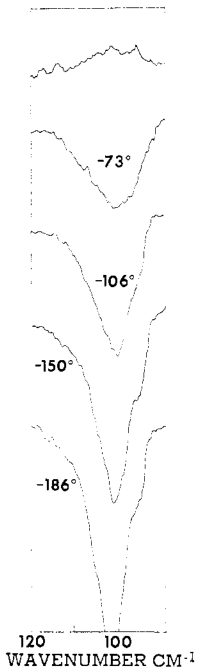

Figure 4.—Effect of temperature on the 100-cm^{-1} infrared band of $(CH_3)_2PP(CH_3)_2$.

therefore we assign this band to the skeletal torsion. The band becomes quite broad as the temperature is raised and it is expected that this anharmonicity along with the presence of the second isomer leads to just generalized absorption in this frequency region for the liquid. It should be pointed out that the assignment of this 100-cm^{-1} band has no bearing on the conclusions concerning the presence of the isomers and the structures of these species.

Further evidence that the 100-cm^{-1} band in the infrared spectrum of the solid is an intramolecular fundamental and not an intermolecular mode is found in the far-infrared spectrum of the gaseous material. The rather broad, strong infrared absorption centered at 58 cm^{-1} is too high in frequency to be the center of the "pure rotational spectrum" of such a heavy molecule. Thus, this infrared band must be an intramolecular fundamental and only the skeletal and methyl torsions are expected in this low-frequency region. We have found in our studies on neopentane, *t*-butyl bromide, and *t*-butyl chloride as well as other similar molecules that the frequency of the methyl torsions did not appreciably differ between those found for the gaseous and solid phases. A shift from 58 to 100 cm^{-1} for a methyl torsion is improbable and we conclude that the 58-cm^{-1} band is the skeletal torsion. A large shift for this intramolecular fundamental is not surprising when one considers the constraints placed on this torsional motion within the crystal. However, it may well be that the gaseous sample is predominantly the *gauche* isomer and the 58-cm^{-1} band would then be the torsional frequency for the *gauche* isomer.

The assignment of the carbon–hydrogen motions can readily be given by using group frequencies from previously studied organophosphorus molecules which contained the $P(CH_3)_2$ moiety. The eight CH_3 antisymmetric stretching modes are assigned to the Raman lines at 2967 and 2955 cm^{-1} and the four symmetric stretchings are assigned to the strong Raman line at 2899 cm^{-1}. The antisymmetric deformations are found at 1425 and 1417 cm^{-1} and the symmetric deformations at 1290 and 1270 cm^{-1}. Only the CH_3 rocking modes show different frequencies for the *gauche* and *trans* structures. CH_3 rocking modes are found at 940, 910, 855, and 850 cm^{-1} in the Raman spectrum of the *trans* compound. In previous studies the highest frequency lines have been found to be polarized and we have arbitrarily assigned the lines of higher frequency to the symmetric motion for this molecule.

Vibrational Assignment for *gauche*-$P_2(CH_3)_4$.—The assignment of the normal vibrations for the *gauche* isomer is highly speculative for most modes. The vibrations for the methyl groups are the same for both isomers except for the CH_3 rocking modes. The 903-cm^{-1} Raman line of the liquid disappears with solidification and is attributed to the *gauche* isomer. The PC_2 stretching motions are also the same for the two conformers. The P–P stretching mode is readily assigned to the Raman line at 429 cm^{-1}. This Raman line is stronger than the line arising from the corresponding motion in the *trans* isomer. Since the polarizability is expected to be greater for the motion in the symmetric molecule, one can surmise that the *gauche* isomer is of considerably higher concentration in the liquid. The 287- and 243-cm^{-1} Raman lines disappear with solidification and must arise from motions of the *gauche* isomer and are assigned as PC_2 wagging and twisting motions on the basis of the assignments given for the corresponding motion for the *trans* isomer.

Similarly the rather weak Raman lines at 190 and 158 cm^{-1} which have counterparts in the infrared spectrum of the gas at 186 and 147 cm^{-1} were not observed in the Raman spectrum of the solid. On the basis of the frequencies of the infrared-active PC_2 twisting and PC_2 deformational motions of the *trans* isomer we assign these bands to the corresponding motions of the *gauche* conformer. The other PC_2 deformation is assigned to the 226-cm^{-1} Raman line. The intensity of the 226-cm^{-1} band relative to that of the 301-cm^{-1} line is higher in the liquid than in the solid and indicates that a mode of the *gauche* isomer may be coincident with the PC_2 deformation of the *trans* conformer. The other PC_2 bending mode (PC_2 wagging of B symmetry species) is assigned to the infrared band at 260 cm^{-1} in the spectrum of the vapors. These assignments are summarized in Table III.

The breadth of the 58-cm^{-1} infrared band for the gaseous sample suggests that the skeletal P–P torsion is in the same general frequency region as that found for the corresponding motion in the *trans* isomer. Because of the low frequency several excited torsional levels should be populated and because of the general

TABLE III
SUMMARY OF THE SKELETAL FUNDAMENTAL VIBRATIONS OF THE *gauche*-TETRAMETHYLBIPHOSPHINE MOLECULE

Vib no.[a]	Sym species and approx description of normal modes	Spectra, cm^{-1}	
		Raman (liquid)	Ir (gas)
	A		
17	PC_2 antisym str		709
18	PC_2 sym str	663	
19	P–P str	429	. . .
20	PC_2 wag	287	. . .
21	PC_2 twist	243	245
22	PC_2 def	226	. . .
25	Torsion	. . .	58
	B		
42	PC_2 sym str	699	
43	PC_2 sym str		657
44	PC_2 wag	258	260
45	PC_2 twist	190	186
46	PC_2 def	158	147

[a] Each symmetry species will have six CH_3 stretching, six CH_3 deformation, four CH_3 rocking, and two CH_3 torsional modes; for example, the first sixteen vibrations of symmetry species A correspond to the CH_3 stretching, deformational, and rocking modes.

anharmonicity associated with this motion, the breadth of this intramolecular fundamental should be extremely large. The absorption due to the skeletal torsion of N_2F_4 extended over about 40 cm^{-1}. Thus, the 58-cm^{-1} band compared to the band arising from the similar motion in tetrafluorohydrazine is not unusual.

Discussion

Since two isomers were found in the liquid phase, a temperature study of Raman lines attributed to different rotamers was attempted. The relative intensities of the Raman lines at 429 and 455 cm^{-1} remained essentially the same with the change in temperature. However, the temperature range (40°) was too small to conclude that there was no energy difference between the two forms.

If one assumes a negligible energy difference between the rotational isomers, the equilibrium mixture would consist of a statistical distribution of the rotamers: two *gauche* molecules for one *trans* molecule, since there are two equally probable isomers for the *gauche* conformation. Indeed, the intensity of the Raman line at 429 cm^{-1} assigned to the *gauche* isomer is greater than that of the *trans* isomer. It was not possible to determine the importance of the solvation effect on the concentrations of the two isomers. The evidence in the infrared spectrum of the gaseous molecule which would indicate the presence of two isomers is marginal. The low-frequency bands are broad and ill defined but the gross features could easily be explained on the basis of "hot" bands arising from the skeletal torsional mode or other low-frequency bending modes. If one neglects the asymmetry on the low-frequency side of each of the infrared bands, one could come up with three bands at 266, 190, and 168 cm^{-1} for the three bending modes. The CH_3 torsional modes could then be used to explain the general breadth of the two low-wave-number bands. Thus, the infrared spectrum of the gaseous sample could adequately be explained on the basis of only the *trans* isomer. However, there seems to be little justification for neglecting this asymmetry, and if only one isomer were present in the gaseous state, then the data are most consistent with the *gauche* conformation. If the *gauche* isomer were indeed the predominant species in the vapor state, then it would not be necessary to postulate such a large frequency difference between the torsional mode in the solid and vapor. Similar comments could be made for some of the other bending modes. However, it is quite clear from the data on the liquid and solid states that both the *gauche* and *trans* isomers are present in the liquid and only the *trans* conformer is found in the solid. The data taken on the vapor really provide no conclusive evidence on the structure of the molecules in the gaseous state.

From this study and our earlier work on N_2F_4[5] it appears that the frequencies of the X–Y stretching modes are not very sensitive to the conformations of the X_2Y_4 molecules and the most sensitive probes appear to be the doubling of the X–X stretching vibration or the splitting of the X–Y bending modes. Thus, a Raman study of gaseous tetramethylbiphosphine in the wave-number region of the P–P stretching vibration should readily show the presence of the *gauche* isomer for this physical state.

There is an abundance of experimental evidence which indicates that all of the biphosphine molecules exist as the *trans* isomers in the solid state.[2,5,11,23] In several cases the evidence is not sufficiently definitive to determine the molecular symmetries of these molecules in the gaseous or liquid states and the importance of investigating both the infrared and Raman spectra of the materials in all three physical states should be exphasized.

Table IV lists the structures determined for various physical states of X_2Y_4 molecules. Tetramethylbi-

TABLE IV
STRUCTURES OF X_2Y_4 MOLECULES OF GROUP Va

Compound	Physical state			Technique
	Gas	Liquid	Solid	
N_2H_4	*gauche*[a]	*gauche*[b]	*gauche*[c]	Microwave, ir, and Raman
$N_2(CH_3)_4$	*gauche*[d]	*gauche*[d]	*gauche*[d]	Ir
N_2F_4	50% *gauche*[e] 50% *trans*	50% *gauche*[f] 50% *trans*	. . .	Microwave, nmr, ir, and Raman
P_2H_4	*gauche*[g]	. . .	*trans*[h]	Ir and Raman
$P_2(CH_3)_4$	. . .	~60% *gauche*[i] ~40% *trans*	*trans*[i]	Ir and Raman
P_2I_4	. . .	*trans*[j]	*trans*[k]	Ir, Raman, and X-ray
P_2Cl_4	. . .	*trans*[l]	*trans*[l]	Ir and Raman
P_2F_4	*trans*[m]	*trans*[m]	. . .	Ir and Raman

[a] T. Kojima, H. Hirakawa, and T. Oka, *J. Phys. Soc. Japan*, **13,** 321 (1958). [b] See ref 9 and 10. [c] F. G. Baglin, S. F. Bush, and J. R. Durig, *J. Chem. Phys.*, **47,** 2104 (1967). [d] D. C. McKean, *Spectrochim. Acta*, **10,** 161 (1958). [e] D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **31,** 1129 (1959). [f] See ref 4 and 5. [g] See ref 11. [h] See ref 23. [i] This work. [j] See ref 14. [k] Y. C. Yeung and J. Waser, *J. Phys. Chem.*, **60,** 539 (1956). [l] See ref 13. [m] See ref 8.

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(23) S. G. Frankiss, *Inorg. Chem.*, **7,** 1931 (1968).

phosphine appears to be unique in that it is the only biphosphine to be shown to have both the *gauche* and *trans* structures in the liquid phase. It is difficult to give a reasonable explanation for this behavior since sterically chloride- and methyl-substituted compounds should be similar. It may be the "normal" behavior for the substituted biphosphines and we plan to determine the symmetries of several additional substituted biphosphines in the liquid state in order to find a possible trend in their behaviors. Recently Gimarc has been able to predict the structures of X_2Y_2 molecules by simple molecular orbital theory.[24] It would seem a similar study of X_2Y_4 molecules could also lead to reasonable explanations for the structures of this group of molecules.

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[24] B. M. Gimarc, private communication.

Notes

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Nuclear Magnetic Resonance Spectra of Several Trimethylamine–Boron Trihalide Complexes[1]

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Despite the continuing interest in Lewis acid–base complexes and the usefulness of nuclear magnetic resonance as a method of studying the molecular properties of these compounds, the number of nmr data available relating to typical donor–acceptor atoms are rather few. Little has been done in attempting to interpret results in terms of the electron distribution in the dative bond, a situation due, at least in part, to the scarcity of data. As part of another investigation, proton and boron-11 nmr spectra have been obtained for a number of trimethylamine adducts of boron halides and the results are reported here to corroborate and extend existing data.

At present, proton nmr spectra are available for trimethylamine complexes of BF_3, BCl_3, and BBr_3,[2–5] but no data have been published for the BI_3 complex. Since the literature results were obtained from samples prepared from natural boron, some ambiguity exists in the interpretation of the spectra due to complications introduced by the presence of two boron isotopes.

Boron-11 nmr spectra for these adducts have also been published[5–7] but, again, not on isotopically enriched compounds. Splittings due to coupling with nitrogen-14 have not been observed and no boron-11 spectra of nitrogen-15-enriched compounds have been reported. The B–N coupling constant is of some interest since it is directly related to the dative bond.

Experimental Section

Materials.—The complexes $(CH_3)_3N^{11}BX_3$ or $(CH_3)_3{}^{15}N^{11}BX_3$ were prepared by standard methods as described in ref 1. The fluoro, chloro, and bromo compounds were purified by sublimation and the iodo adduct was freshly crystallized from chloroform just before examination.

Apparatus and Method.—All spectra were taken at room temperature on a Varian HR-100 nuclear magnetic resonance spectrometer. The ^{11}B spectra were obtained using the instrument operating at 32.1 Mc with $B(CH_3)_3$ as the external standard. Calibration was by means of the known frequency separation of the side band and center band and the displacement of the center band from the external reference signal. The compounds were dissolved in $CDCl_3$ for the proton nmr studies and in acetone or acetonitrile for the boron-11. Chemical shifts in the proton spectra are estimated accurate to 0.002 ppm, and the coupling constants are estimated to 0.1 cps. In the boron-11 spectra, chemical shifts are estimated to 0.3 ppm and coupling constants are estimated to 1 cps.

Results and Discussion

Proton nmr spectra of boron-11-enriched $(CH_3)_3NBX_3$ complexes and also the boron-10-enriched chloro adduct are shown in Figure 1 and the chemical shifts and spin–spin coupling constants are listed in Table I. In $(CH_3)_3N^{11}BCl_3$, $\text{-}^{11}BBr_3$, and $\text{-}^{11}BI_3$, the methyl proton signal is split by the ^{11}B nucleus (spin $^3/_2$) into

TABLE I
PROTON CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR SOME TRIMETHYLAMINE–BORON TRIHALIDE COMPLEXES

Compound	δ, ppm[a]	J_{BH}, cps
$(CH_3)_3N^{11}BF_3$[b]	-2.612	. . .
$(CH_3)_3N^{11}BCl_3$[b]	-3.005	2.6
$(CH_3)_3N^{11}BBr_3$[b]	-3.160	2.9
$(CH_3)_3NBI_3$[c]	-3.369	3.4
$(CH_3)_3N^{10}BCl_3$	-3.002	0.85

[a] Downfield from tetramethylsilane standard. [b] Chemical shift and coupling constant values obtained for these three compounds agree satisfactorily with values previously published.[2,3] [c] The boron-11 enriched adduct was impure and gave a more complex nmr spectrum than the compound prepared with natural BI_3.

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[1] Taken from a Ph.D. dissertation submitted by P. H. Clippard to the Horace H. Rackham School of Graduate Studies of The University of Michigan, Jan 1969.

[2] J. M. Miller and M. Onyszchuk, *Can. J. Chem.*, **42**, 1518 (1964).

[3] A. Derek, H. Clague, and A. Danti, *Spectrochim. Acta*, **23A**, 2359 (1967).

[4] O. Ohashi, Y. Kurita, T. Totani, H. Watanabe, T. Nakagawa, and M. Kubo, *Bull. Chem. Soc. Japan*, **35**, 1317 (1962).

[5] C. W. Heitsch, *Inorg. Chem.*, **4**, 1019 (1965).

[6] H. Noth and H. Vahrenkamp, *Chem. Ber.*, **99**, 1049 (1966).

[7] D. E. Young, G. E. McAchran, and S. G. Shore, *J. Am. Chem. Soc.*, **88**, 4390 (1966).