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Vibrational spectra, force constants and conformations of molecules of trivalent tricoordinate phosphorus compounds

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Abstract. Data on the interpretation of the IR and Raman spectra based on normal coordinate analysis, on the force constants and on the conformations of the molecules of trivalent tricoordinate phosphorus compounds are summarised. The existing correlations between the spectra and molecular structures are refined and some new correlations are proposed. The bibliography includes 171 references.

I. Introduction

Vibrational spectroscopy is widely used in the chemistry of organophosphorus compounds for the identification of functional groups, determination of the molecular structure and studies on the molecular conformations, inter- and intramolecular interactions. Monographs by Thomas[1,2] and atlases by Shagidullin *et al.*[3–5] are devoted to the interpretation of IR spectra of organophosphorus compounds. Unfortunately, Raman spectroscopy has not become a routine method in phosphorus chemistry as yet, though the scope of possible application of this experimental technique in structural studies is as large as that of IR spectroscopy. This is to a great extent due to the lack of studies devoted to the generalisation of scarce information on the Raman spectra of different organophosphorus compounds. In this review, a comparative analysis is given of a continuously growing body of data on both the IR and Raman spectra of phosphorus-containing molecules. An attempt to summarise information on the 'fingerprints' of rotational isomerism in the molecules of tricoordinate phosphorus compounds as manifested in vibrational spectra is also undertaken.

A distinctive feature of the review is that here we consider only those molecules the spectra of which have been interpreted on the basis of normal coordinate analysis. A normal coordinate analysis makes it possible to calculate the eigenvectors of normal vibrations, *i.e.*, to assess the contribution of each valence bond and each bond angle to a particular molecular vibration.[6,7] This allows unambiguous assignment of the frequencies to the vibrations of particular structural fragments. Knowledge of the eigenvectors of normal vibrations is also necessary for the analysis of the interactions between vibrations of particular bonds in a molecule. It is known that effective coupling of vibrations of two molecular fragments is achieved if their individual frequencies are close ($\nu_1 \approx \nu_2$) and the fragments either share a number of atoms or are connected by a valence bond.[8] For the coupling of vibrations to occur, they should also be of the same symmetry.[9] As a result, coupling of two individual vibrations gives rise to two new coupled vibrations. Each fragment of the molecule makes a contribution to each of the new vibrations. Their frequencies (ν'_1 and ν'_2) can differ appreciably from the frequencies of the 'old' vibrations; as a rule, $\nu'_1 < \nu_1 \approx \nu_2 < \nu'_2$.

Thus in the molecule of methylphosphine (**1**), vibrations with a predominant contribution of the P–C bond occur at a frequency of about 670 cm^{-1}. Vibrations of two P–C bonds in the molecule of dimethylphosphine (**2**) give rise to two new vibrations, *viz.*, a symmetric stretch of both bonds at a frequency $\nu'_1 \approx 660$ cm^{-1} and an antisymmetric vibration at a frequency $\nu'_2 \approx 700$ cm^{-1}. These changes in the ν(P–C) frequencies on going from molecule **1** to the molecule **2** are mainly due to the coupling of two individual oscillators sharing the phosphorus atom.

Vibrations of the PCl_2 group in the molecule of methyl phosphorodichloridite, CH_3OPCl_2 (**3**), are characterised by strong IR absorption bands at ~ 460 and ~ 500 cm^{-1}. The frequencies of bending vibrations of the butyl group lie in the same spectral region. However, analysis of the molecular structure of butyl phosphorodichloridite, $C_4H_9OPCl_2$, shows that these two vibrations cannot interact, since the structural fragments under consideration share no atoms and are not connected by a covalent bond. Therefore, vibrations of the PCl_2 group have identical patterns in the IR spectra of both $C_4H_9OPCl_2$ and CH_3OPCl_2.

These examples show that, strictly speaking, the lack of information on the eigenvectors of some vibrations makes it impossible to conclude whether they will be characteristic on going from one molecule to another. Therefore, spectral – struc-

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tural correlations become much more reliable if they are based on theoretical interpretation of the spectra.

A normal coordinate analysis also makes it possible to calculate the force constants of chemical bonds and bond angles in molecules. The force constants are primarily of interest as transferable parameters, which are used for calculating the vibrational spectra of related molecules.[6] At the same time, they are also numerical characteristics of the potential surface of a molecule. It should be noted that for several reasons [6,10] the force constant values depend on the type of computational procedures employed, so that small differences between the estimates of the force fields obtained by different authors for the same molecule are virtually inevitable. Because of this, here we compared the force constants assessed using the same approximations for series of related compounds. This makes it possible to judge the changes in the electronic structure of the molecules if analysis of their force fields reveals large and systematic deviations. The notations are given according to monograph [6] and the values of force constants are given in 10^2 N m^{-1}.

Compounds of trivalent tricoordinate phosphorus were chosen to be the subject of this review primarily since they are most widely used in the syntheses of organophosphorus compounds. Additionally (probably, because of relatively low stability of tricoordinate phosphorus compounds), their vibrational spectra have been less studied than those of tetracoordinate phosphorus compounds. Virtually all results of normal coordinate analyses of vibrational spectra of organophosphorus compounds reported to date have been analysed. The exceptions are the results of studies on the simplest tetraatomic molecules of phosphine (PH_3) and its halogen derivatives (H_nPHal_{3-n}).

Spectral characteristics of all the compounds under discussion are listed in Tables. Each fundamental vibration was assigned a number as follows. The whole set of vibrations was divided into groups according to particular symmetry types of the vibrations. Within each symmetry type, the vibrations were numbered in descending order of their frequencies.

The frequencies assigned to overtones and combination bonds are omitted. The notations of vibrations are ν for stretching, δ for bending, r for rocking, w for wagging, t for twisting and χ for torsional vibrations; γ denotes vibrations associated with the out-of-plane deviation of particular bonds. These notations describe the type of motion of particular structural fragments of molecules. In discussing any vibration of the entire molecule, that is, a simultaneous motion of several individual oscillators, the above-mentioned notations have a somewhat different meaning. For instance, the totally symmetrical fundamental vibration of the molecule **1** is composed of the contributions from not only the stretching vibrations ν(P−C) of the P−C bond, but also the wagging vibrations of the phosphino group, $w(PH_2)$. However, the major contribution to the energy of the resultant vibration is make by the P−C bond; therefore, such a vibration is denoted below as ν(P−C).

All frequencies are given in cm^{-1}. The intensities (I) and shapes of spectral bands, as well as the degree of depolarisation of the Raman lines (ρ), are qualitatively described using the following notations: w for weak, m for medium, s for strong, ms for medium strong, br for broad, v for very, sh for shoulder, p for polarised and dp for depolarised.

Spectral data listed in Tables are presented in the following order: the vibrational frequency (in cm^{-1}), a qualitative or quantitative description of the intensity (in the latter case, the intensity of a line with respect to that of the strongest Raman peak, taken as 100) and a qualitative or quantitative description of the degree of depolarisation.

II. Alkylphosphines

Vibrational spectra and conformations of primary alkylphosphines have been studied in most detail. Interpretation [11–13] of the IR spectra [11] and the Raman spectra [14] of methylphosphine (Table 1) and its D-isotopomers CH_3PD_2, CD_3PH_2 and CD_3PD_2 has been given and the force constants have been estimated. Vibrational spectra of ethylphosphine (**4**) have been investigated in a number of studies.[15–21] Using vibrational [15] and microwave [16,17] spectroscopy, the molecules of compound **4** were shown to exist in the liquid and gas phases in two rotameric forms, as *trans* (*T*) and *gauche* conformers (*G*) (Fig. 1; X = H, Y = CH_2, Z = CH_3). Crystals of this compound are built of the molecules of the *trans* conformer only, so that the spectra are simplified owing to the disappearance of the bands of the *gauche* isomer. Interpretation of the spectra of ethylphosphine was based on the results of normal coordinate analysis [22] performed simultaneously for both $C_2H_5PH_2$ and $C_2H_5PD_2$ molecules (Table 2). In studies of vibrational spectra of n-propylphosphine (**5**) [23] (Table 3) it has been shown that this compound exists in the liquid phase as a mixture of five conformers (Fig. 2; X = H, Y = CH_2). Vibrational and microwave spectra of isopropylphos-

Table 1. Interpretation of vibrational spectra of methylphosphine.

No.	Symmetry	Assignment	Raman (l)	IR (g)
11	A″	$\nu_{as}(PH_2)$	2297, vs, p	2309, vs
3	A′	$\nu_{s}(PH_2)$	2297, vs, p	2305, vs
12	A″	$\delta_{as}(CH_3)$	∼ 1440, w	1435, m
4	A′	$\delta_{as}(CH_3)$	∼ 1440, w	1429, m
5	A′	$\delta_{s}(CH_3)$	1288, m, p	1296, w
6	A′	$\delta(PH_2)$	1086, m, p	1092, s
13	A″	$r(CH_3)$, $t(PH_2)$		1017, m
7	A′	$r(CH_3)$, $w(PH_2)$, $\delta(PH_2)$	974, m, p	978, s
8	A′	$w(PH_2)$, $r(CH_3)$, ν(P−C)	740, s, p	730, w
14	A″	$t(PH_2)$, $r(CH_3)$		696, w [a]
9	A′	ν(P−C), $w(PH_2)$	673, s, p	676, s

Note. Hereafter, l stands for liquid and g for gas. Totally symmetric fundamental vibrations of the A′ type were labelled with figures from 1 to 9 and antisymmetric vibrations of the A″ type were labelled with figures from 10 to 15. Vibrations with the highest frequency and belonging to the A′ type (Nos 1 and 2) and A″ type (No. 10) and vibration No. 15 are not included, since they correspond to the C−H stretching vibrations of the bonds, which are insignificant for analytical purposes. For the same reason, some vibrations are also not included in Tables 2–25.

[a] Appears only in the spectrum of crystals.

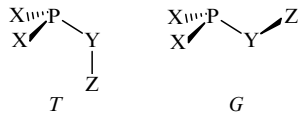


Figure 1. Conformers of molecules X_2PYZ: *trans* (*T*) and *gauche* (*G*).

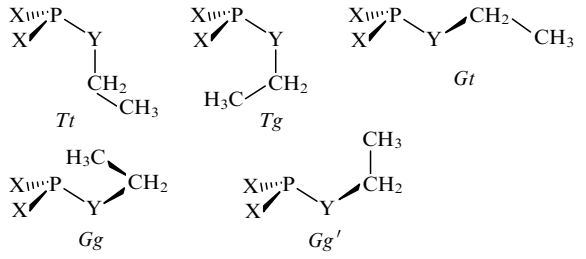


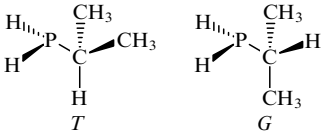
Figure 2. Conformers of molecules $X_2PYCH_2CH_3$: *trans*,*trans* (*Tt*), *trans*,*gauche* (*Tg*), *gauche*,*trans* (*Gt*), *gauche*,*gauche* (*Gg*) and *gauche*,*gauche′* (*Gg′*).

Table 2. Interpretation of vibrational spectra of ethylphosphine.

No.	Sym-metry	Assignment	Raman (g)	IR (g)
17	A″	$\nu_{as}(PH_2)$		2304, vs
4	A′	$\nu_s(PH_2)$ 2298, vs	2296, vs 2294, vs	
8	A′	$w(CH_2)$, $\nu_{as}(PCC)$, $\delta(CH_2)$	1271, vw	
19	A″	$t(CH_2)$	1247, m	1247, w
9	A′	$\delta(PH_2)$, $\nu(C-C)$, $w(PH_2)$	1086, w	1085, m
10	A′	$\nu(C-C)$, $\delta(PH_2)$	1065, m, sh	1067, m
20	A″	$r(CH_3)$, $r(CH_2)$, $t(PH_2)$	1056, m	1055, m
11	A′	$r(CH_3)$, $w(CH_2)$, $\delta(PCC)$	982, w	979, w
21	A″	$t(PH_2)$, $r(CH_3)$, $r(CH_2)$	835, w	833, m
12	A′	$w(PH_2)$, $w(CH_2)$, $\delta(CH_2)$, $\delta(PH_2)$	818, m	817, m
22	A″	$r(CH_2)$, $t[PH_2(G)]$	692, m	
		$r(CH_2)$, $t(PH_2)$	640, vs	643, w
13	A′	$\nu(P-C)$, $\delta(PCC)$	636, vs	634, w
14	A′	$\delta(PCC)$	307, m	
		$\delta[PCC(G)]$	288, w	
23	A″	$\chi(CH_3)$, $\chi(PH_2)$		245, w
24	A″	$\chi(PH_2)$, $\chi(CH_3)$		183, w
		$\chi[PH_2(G)]$	162, vw	

Note. The number of vibration, symmetry type and assignment are given for the *T* conformer (see Fig. 1). Lines of the *G* conformer were interpreted only if they did not coincide with the corresponding lines of the *T* conformer (their assignments are denoted by the character '*G*').

phine (**6**) and its D-isotopomer, iso-$C_3H_7PD_2$, have been studied.[24,25] It was shown that the *G* and *T* conformers of these molecules are stable in the liquid and gas phases.



T *G*

The calculated assignments[22] for isopropylphosphine **6** (see Table 4) are somewhat different from the empirical ones.[24]

Compared with the spectra of primary alkylphosphines, the interpretation of the spectra of secondary and tertiary alkylphosphines is more complicated because of the necessity to take into account the coupling of vibrations of adjacent alkyl groups at the phosphorus atom. Therefore, it is not surprising that the spectra of such simple representatives of organophosphorus compounds as dimethylphosphine and its isotopomers have been interpreted in different ways.[26–29] The problem of contradictory assignments was alleviated only after performing a normal coordinate analysis.[12,13,29] Different versions of empirical interpretation of the vibrational spectra of phosphirane $(CH_2)_2PH$ (**7**) and its deutero derivatives have also been suggested.[30,31] Calculations[32] made it possible to refine the vibrational assignments and to assess the force constants of the molecule, its thermodynamic functions and the barrier to inversion of the phosphirane ring.

Trimethylphosphine (**8**) is the first organophosphorus compound for which a normal coordinate analysis has been performed.[33] The data on both the eigenvectors of molecular vibrations of $(CH_3)_3P$ and $(CD_3)_3P$ and the force fields of the molecules have been repeatedly revised.[13,14,34–40] These molecules have a C_{3v} symmetry, therefore the A_2 modes are optically inactive and not observed in the spectra. Some of the modes were observed owing to the reduction of symmetry of the molecule as a result of crystallisation of the substance.[39] Nevertheless, a number of vibrational assignments had to be revised after the spectra of low-symmetric D-isotopomers, $(CH_3)_2CD_3P$ and $CH_3(CD_3)_2P$, had been reported.[41] The force constants of the molecule **8** have been re-calculated[42–44] using the results of *ab initio* quantum-chemical calculations; it should be mentioned that not only the spectra of deuterated specimens, but also those of ^{13}C-isotopomers of trimethylphosphine **8** have been analysed[43] and that vibrational anharmonicity has also been taken into account.

The molecule of triethylphosphine (**9**) can adopt four conformations;[45] however, it has been shown[45,46] that vibrational spectra of compound **9** in the liquid phase (see Refs 46, 47) can be interpreted assuming the existence of only three conformers shown below.

Table 3. Interpretation of vibrational spectra of n-propylphosphine.

No.	Sym-metry	Assignment	Raman (l)	IR (g)
5	A′	$\nu_s[PH_2(Tg,Gg')]$	2300, sh, p	2306, s [a]
		$\nu_s(PH_2)$	2289, sh, p	2298, vs
23	A″	$\nu_{as}(PH_2)$	2285, vs, p	2294, vs
11	A′	$w(CH_2P)$	1228, m, p	1233, sh [a]
26	A″	$t(CH_2P)$, $r(CH_3)$, $r(CH_2)$	1218, m, p	1221, w [a]
		$t[CH_2P(Gg,Gg')]$	1203, sh, p	1207, sh
12	A′	$\delta(PH_2)$	1097, m, p	1104, sh
		$\delta[PH_2(Gt, Gg')]$	1094, m, p	1096, w [a]
13	A′	$r(CH_3)$, $\nu_s(CCC)$	1075, m, p	1085, s
27	A″	$r(CH_3)$, $t(CH_2P)$, $t(PH_2)$, $t(CH_2)$	1061, w [b]	1073, m [a]
		$r(CH_3)$, $t[CH_2P(Gg, Gg')]$	1052, w [c]	1052, sh
14	A′	$\nu_{as}(CCC)$	1032, m, p	1037, sh
28	A″	$t(PH_2)$	907, vw, p	910, sh
		$t(PH_2)$, $r(CH_3)$, $\nu_s[CCC(Gt)]$	898, m, p	898, m
		$t(PH_2)$, $\nu_s[CCC(Gg')]$	880, m, p	883, sh
15	A′	$\nu_s(CCC)$, $r(CH_3)$, $t(PH_2)$	898, m, p	898, m
		$\nu_s(CCC)$, $w(PH_2)$, $\nu[P-C(Tg)]$	846, m [c]	845, m
		$\nu_s(CCC)$, $t(PH_2)$, $\nu[P-C(Gt)]$	812, vw, dp	812, sh
		$w(PH_2)$, $r(CH_3)$, $r(CH_2P)$, $\nu_s[CCC(Gt)]$	889, m, p	891, sh
		$w(PH_2)$, $\nu_s[CCC(Tg,Gg)]$	880, m, p	883, sh
16	A′	$w(PH_2)$, $\nu_s(CCC)$, $\nu(P-C)$	840, m, p	838, m [a]
29	A″	$r(CH_2)$, $r(CH_3)$, $t(PH_2)$	768, w, p	770, m
		$\nu[P-C(Gt)]$	704, s, p	700, vw [a]
17	A′	$\nu(P-C)$, $w(PH_2)$, $\delta(CCC)$	676, s, p	680, m
		$\nu[P-C(Gg')]$	636, sh, p	640, sh
		$\nu[P-C(Gg)]$	628, sh, p	
		$\nu[P-C(Tg)]$	624, s, p	625, m
30	A″	$r(CH_2P)$, $t(PH_2)$	648, w [c]	647, w [c]
18	A′	$\delta(CCC)$, $\nu(P-C)$, $\delta(PCC)$	357, s, p	355, s
		$\delta(CCC)$, $\nu(P-C)$, $\delta(PCC)$, $\nu_s[CCC(Gt)]$	348, m [b]	348, s
		$\chi(C-CH_3)$, $\chi(P-C)$, $\chi[C-C_2H_5(Tg,Gg')]$	284, w, p	285, w
		$\chi(C-CH_3)$, $\delta(PCC)$, $\chi[C-C_2H_5(Gg)]$	268, sh [b]	
31	A″	$\chi(C-CH_3)$		239, w
19	A′	$\delta(PCC)$, $\delta(CCC)$	230, w, p	227, sh
		$\delta(PCC)$, $\delta[CCC(Gt)]$	215, vw [b]	215, sh
32	A″	$\chi(P-C)$	214, vw [c]	185.4, s
		$\chi[P-C(Gt)]$		177, s
33	A″	$\chi(C-C_2H_5)$	126, vw [c]	105, m

Note. The number of vibration, symmetry type and assignment are given for the *Tt* conformer (see Fig. 2). Vibrations of other conformers (for notations of their frequencies, see Caption to Fig. 2) were interpreted only if their frequencies did not coincide with the corresponding lines of the *Tt* conformer.

[a] From the spectrum of n-propylphosphine solution in liquid krypton.

[b] From the gas-phase spectrum.

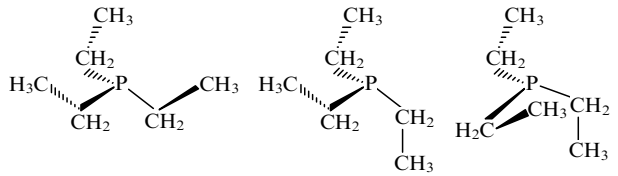
[c] From the low-temperature spectrum of solid n-propylphosphine.

Table 4. Interpretation of vibrational spectra of isopropylphosphine.

No.	Sym-metry	Assignment	Raman (g)	IR (g)
		$\nu_{as}[PH_2(G)]$	2299, vs	2299, vs
22	A″	$\nu_{as}(PH_2)$		2288, vs
		$\nu_s[PH_2(G)]$	2297, vs	2297, vs
5	A′	$\nu_s(PH_2)$	2286, vs	
9	A′	$\delta(CH)$, $w(PH_2)$	1255, m	1256, m
26	A″	$r(CH)$, $\nu_{as}(CC_2)$, $r(CH_3)$	1237, w	1234, w
		$r(CH)$, $\nu_{as}(CC_2)$, $r[CH_3(G)]$	1231, w	
27	A″	$\nu_{as}(CC_2)$, $r(CH)$	1164, vw	
10	A′	$r(CH_3)$, $\delta(CH)$, $\nu_s(CC_2)$	1114, m	
11	A′	$\delta(PH_2)$	1077, m	
12	A′	$r(CH_3)$, $\nu(P-C)$, $w(CC_2)$, $\delta(PH_2)$	1067, m	1066, s
28	A″	$r(CH_3)$	~ 970 [a]	~ 970 [a]
29	A″	$r(CH_3)$, $\delta(CH)$		924, vw
13	A′	$\nu_s(CC_2)$, $r(CH_3)$, $\delta(CH)$	892, m	892, w
		$w(PH_2)$, $\delta[CH(G)]$	813, m	813, s
14	A′	$w(PH_2)$, $\delta(CH)$	792, w	791, s
30	A″	$t(PH_2)$		809, m
		$\nu(P-C)$, $w(CC_2)$, $\delta[CC_2(G)]$	628, m, sh	626, vw
15	A′	$\nu(P-C)$, $w(CC_2)$, $\delta(CC_2)$	606, s	606, w
16	A′	$\delta(CC_2)$, $\chi(CH_3)$		388, w
17	*A′*	$w(CC_2)$, $\chi(CH_3)$	325, m	325, w
		$w(CC_2)$, $\chi[CH_3(G)]$	309, vw	
31	A″	$r(CC_2)$, $\chi(CH_3)$	322, w, sh	322, w
18	A′	$\chi(CH_3)$		287, w
32	A″	$\chi(CH_3)$		266, vw, br
33	A″	$\chi(P-C)$	163, vw	163, s

Note. The number of vibration, symmetry type and assignment are given for the *T* conformer. The lines of the *G* conformer (denoted by character '*G*') were interpreted only if their frequencies did not coincide with the corresponding lines of the *T* conformer.

[a] The frequency was suggested after normal coordinate analysis [22] (was not observed experimentally).



The *GGG* and *TG′G* conformers are present simultaneously in the crystalline phase.[45,46] Theoretical interpretation of the spectra [46,47] of triethylphosphine **9** was based on the results of normal coordinate analysis [45] performed using the force constants for molecules **8** and **4**.

Comparison of the spectra of primary alkylphosphines reveals three vibrations, *viz*., the $\nu_{as}(PH_2)$, $\nu_s(PH_2)$ and $\delta(PH_2)$ ones, which seem to be the most characteristic vibrations of these compounds. The first two vibrations appear as two very strong bands with similar frequencies near ~ 2300 cm^{-1} in the gas-phase spectra. On going from gases to liquids, these bands usually coalesce into one band observed in the frequency range 2275–2300 cm^{-1} (see, *e.g*, Refs 15, 18–20, 23, 24, 48, 49). A normal coordinate analysis shows that the vibrations $\nu_{as}(PH_2)$ and $\nu_s(PH_2)$ are the characteristic vibrations, *i.e*., that the frequencies and intensities of the corresponding spectral peaks are determined solely by the properties of the P–H bonds.

Scissoring vibrations of the phosphino group, $\delta(PH_2)$, can mix to a certain degree with vibrations of the alkyl radical (see, *e.g*., Table 2), which affects mainly the intensities of corresponding bands. At the same time, the frequency of the $\delta(PH_2)$ vibration depends only slightly on the vibration of the alkyl fragment of the molecule and lies in a relatively narrow frequency range between 1073 and 1097 cm^{-1} (for liquids).[15,18–20,23,24,48,49] Mixing of the scissoring deformation vibration $\delta(PH_2)$ with the wagging vibration $w(PH_2)$ also occurs (see Table 2). Probably, that is why the former vibration has been interpreted [20] as $w(PH_2)$.

The structure of the alkyl fragments of the molecules of primary alkylphosphines strongly affects the frequency of vibration with predominant contribution of the P–C bond (Tables 1–5). For instance, the frequency of the vibration

Table 5. Stretching vibrations of P–C bonds in the spectra of alkylphosphines and their substituted derivatives.

Molecule	Assignment	Raman	IR
CH_3PH_2	$\nu(P-C)$, $w(PH_2)$	673, w, p (l)	676, s (g)
CH_3PCl_2	$\nu(P-C)$, $\delta_s(CH_3)$	691, w, p (l)	690, s (cr)
CH_3PF_2	$\nu(P-C)$, $w(PF_2)$, $\delta_{as}(CH_3)$	709, w, p (l)	727, w (cr), 711, m (cr)
$C_2H_5PH_2$	$\nu(P-C)$, $\delta(PCC)$	636, vs (g)	634, w (g)
$C_2H_5PCl_2$	$\nu(P-C)$, $\delta[CCP(G)]$	663, m, p (l)	666, s (g)
	$\nu(P-C)$, $\delta[CCP(T)]$	631, m, p (l)	632, m (g)
$C_2H_5PF_2$	$\nu[P-C(G)]$	682, m, p (g)	680, s (g)
	$\nu(P-C)$, $\delta(CCP)$, $w[CH_2(T)]$	655, s, p (g)	651, m (g)
n-$C_3H_7PH_2$	$\nu[P-C(Gt)]$	704, w, p (l)	700, w (s)
	$\nu(P-C)$, $w(PH_2)$, $\delta[CCC(Tt)]$	676, w, p (l)	680, m (g)
	$\nu[P-C(Gg')]$	636, sh, p (l)	640, sh (g)
	$\nu[P-C(Gg)]$	628, sh, p (l)	
	$\nu[P-C(Tg)]$	624, w, p (l)	625, m (g)
n-$C_3H_7PCl_2$	$\nu[P-C(Gt)]$	736, w, p (l)	738, w (g)
	$\nu(P-C)$, $\delta(CCC)$, $\delta[CCP(Tt)]$	687, w, p (l)	690, w (g)
	$\nu(P-C)$, $r[CH_2(Gg')]$	650, w, p (l)	650, w (g)
iso-$C_3H_7PH_2$	$\nu(P-C)$, $w(CC_2)$, $\delta[CC_2(G)]$	628, m, sh (g)	626, vw (g)
	$\nu(P-C)$, $w(CC_2)$, $\delta[CC_2(T)]$	606, s (g)	606, w (g)
$(CH_3)_2PH$	$\nu_{as}(PC_2)$	704, (g)	704.5, s (g)
	$\nu_s(PC_2)$	660, m, p (g)	667, w (g) 660, w (g)
$(CH_2)_2PH$	$w(CH_2)$, ring 'breating',[a] $r(PH)$, symmetric deformation [b]	1056, s, p (g)	1058, vs (g)
	$t(CH_2)$, $r(CH_2)$, non-symmetric deformation [c] $r(PH)$	650, m, dp (g)	657, s (g)
$(CH_3)_2PCl$	$\nu_{as}(PC_2)$	708, m, dp (l)	707, s (l)
	$\nu_s(PC_2)$	674, w, p (l)	675, s (l)
$(CH_3)_3P$	$\nu_{as}(PC_3)$	708, m, dp (g)	716, m (g) 709, m (g) 706, m (g)
	$\nu_s(PC_3)$	653, vs, p (g)	
$(C_2H_5)_3P$	$\nu_{as}(PC_3)$, $\delta[PCC(TGG')]$ [d]	697, m (l)	690, s (l)
	$\nu_{as}(PC_3)$, $\delta[PCC(GGG,TGG)]$	669, s (l)	670, m (l)
	$\nu_{as}(PC_3)$ [e]		659, m (l)
	$\nu_s(PC_3)$, $\delta[PCC(GGG)]$		625, m (l)
	$\nu_s(PC_3)$, $\delta[PCC(TGG')]$	619, vs (l)	619, m (l)
	$\nu_s(PC_3)$, $\delta[PCC(TGG)]$		600 m (l)

Note. Notations: cr stands for crystal and s for solution (in Kr).

[a] Ring 'breating' vibration accompanied by synchronous changes in the P–C and C–C bond lengths.

[b] Symmetric ring deformation accompanied by synchronous lengthening of two P–C bonds and shortening of the C–C bond.

[c] Non-symmetric ring deformation associated with $\nu_{as}(PC_2)$.

[d] Vibrations of the A′ symmetry type.

[e] Vibrations of the A″ symmetry type.

ν(P–C) decreases by $\sim 70\ cm^{-1}$ on going from the molecule **1** to the molecule **6** (see Tables 1 and 4). According to calculations, this is due to not only the 'weighting' of the alkyl group, but also a decrease in the force constant K_{P-C}.

The ν(P–C) vibration can mix with deformation vibrations of the phosphino group and alkyl radical. Because of the changes in the contributions of particular groups to the vibrations, the intensities of the corresponding bands in the IR spectra can vary over a wide range on going from one alkylphosphine to another, which severely hampers their assignment. It is much easier to use the Raman spectra for identification of the vibration ν(P–C), since the corresponding lines in the spectra of compounds in question always are the most intense and polarised in the frequency range $550-705\ cm^{-1}$. Thus, it is the Raman spectra that should be used for easy discrimination between different primary alkylphosphines.

When assigning the ν(P–C) vibration, it should be remembered that the corresponding frequency can be 'sensitive' to molecular conformations. Therefore, a number of 'extra' peaks is often observed in the vibrational spectra of compounds, whose molecules can adopt several conformations (see, *e.g.*, Tables 2 and 5). Some of the 'extra' peaks disappear as a result of crystallisation of the specimens.

Like the ν(P–H) vibrations of primary alkylphosphines, those of the secondary alkylphosphines are observed in nearly the same spectral region $2270-2298\ cm^{-1}$. On the other hand, lines corresponding to two (rather than one) stretching vibrations of the P–C bonds are observed in the spectra of secondary phosphines (see Table 5). An intense, strongly polarised Raman line observed in the region $550-670\ cm^{-1}$ is associated with symmetric $\nu_s(PC_2)$ vibrations, while a somewhat weaker and weakly polarised line in the region $600-710\ cm^{-1}$ is attributed to antisymmetric $\nu_{as}(PC_2)$ vibrations. In the IR spectra, the latter band is usually stronger than the former. As for the primary phosphines, the ν(P–C) frequencies are, as a rule, 'conformationally sensitive' and decrease substantially as the chain length of alkyl radicals increases. All the aforesaid refers to acyclic dialkylphosphines and unstrained cyclic systems. Closure of three-, four- and five-membered strained rings leads to an increase in the $\nu_s(PC_2)$ frequencies, so that they become higher than the $\nu_{as}(PC_2)$ frequencies and lie beyond the upper bounds of the corresponding spectral regions.

The $\nu_s(PC_3)$ and $\nu_{as}(PC_3)$ stretching vibrations of the P–C bonds in the molecules of tertiary phosphines have spectral features similar to those mentioned above (see Table 5). Since the lines corresponding to some characteristic vibrations such as ν(P–H) or $\delta(PH_2)$ are absent in this case, identification of the spectra of tertiary phosphines should be performed using both the $\nu_s(PC_3)$ and $\nu_{as}(PC_3)$ lines and the alkyl group bands. The frequencies of some vibrations of the methyl or ethyl radicals at the phosphorus atom are sufficiently characteristic, which makes it possible to use them in the spectral analysis. For instance, the bands associated with symmetrical $\delta_s(CH_3P)$ and antisymmetrical $\delta_{as}(CH_3P)$ deformation vibrations are observed in the IR spectra of any liquid alkylphosphines in the regions $\sim 1280-1295$ and $\sim 1410-1445\ cm^{-1}$, respectively. The $r(CH_3P)$ rocking vibrations mix with vibrations of other groups at the phosphorus atom (see Table 1). Changes in the environment around the P atom lead to substantial changes in the frequency and eigenvector of the resultant complex vibration. Therefore, the corresponding bands in the IR spectra of liquid alkylphosphines are observed in a rather wide region between 940 and $985\ cm^{-1}$ and their intensities can vary from weak to strong. In the Raman spectra of alkylphosphines, the lines attributed to all the three vibrations are usually of weak or medium intensity.

If the ethyl radical is bound to the phosphorus atom, the $\delta(CH_2)$ bending and $t(CH_2)$ twisting vibrations of the methylene group can be considered characteristic. The corresponding peaks in vibrational spectra are usually of medium intensity and observed in the spectral regions $\sim 1410-1430$ and $\sim 1230-1250\ cm^{-1}$, respectively. A complex vibration with predominant contribution of the wagging motion, $w(CH_2)$, is characterised by a slightly higher frequency ($\sim 1240-1280\ cm^{-1}$). Since this vibration is strongly coupled, the intensity of the corresponding peak can vary from very weak to medium. On the contrary, vibrations of the C–C bond are characteristic and associated with rather strong peaks in the region $\sim 1020-1065\ cm^{-1}$. Rocking and wagging vibrations of the methylene group mix with the motions of other atoms constituting the alkylphosphine molecule and usually give rise to several peaks in the spectral region $\sim 690-820\ cm^{-1}$. At least one of the peaks is of rather high intensity.

It should be noted that the above-mentioned frequencies are specific to not only alkylphosphines, but also other organophosphorus compounds,[1–5] the molecules of which contain the CH_3P or C_2H_5P fragments. This specificity is due to both the mass of the phosphorus atom and the peculiarities of the electronic structure of these fragments, which affect the force constant values. Bands corresponding to the bending and twisting vibrations of the methylene group at the phosphorus atom of an arbitrary coordination are observed in the spectral regions $\sim 1430-1380$ and $\sim 1190-1220\ cm^{-1}$, respectively, and can be used for the identification of non-branched alkylphosphorus groups. It is more convenient to use the Raman spectra for identification of twisting vibrations, since the corresponding bands in the IR spectra are often weak.

The above-mentioned frequency ranges for the 'fingerprint' bands are given for the liquid-phase spectra, since they are most widely used in routine studies. However, these spectral regions are only slightly shifted on going to the spectra of gases and crystals. For alkylphosphines, the shifts of spectral peaks due to the change in the state of aggregation usually do not exceed $10-15\ cm^{-1}$. The band intensities also vary only slightly, which indicates the absence of strong intermolecular interactions in the condensed phases. It should be taken into account that crystallisation of alkylphosphines, whose molecules can adopt several conformations, can lead to disappearance of some spectral bands.

III. Alkyl(halogeno)phosphines

Almost no interactions between the vibrations involving relatively heavy halogen atoms and light hydrogen atoms occurs in the molecules of alkyl(halogeno)phosphines. Therefore, skeletal vibrations in these compounds are much less 'sensitive' to substitution of deuterium atoms for hydrogen atoms, so that deuteration, which often facilitates the interpretation of the spectra, appears to be ineffective. Strengthening of intermolecular interactions due to the presence of halogen atoms in the molecules is yet another objectionable circumstance. This can cause shifts of spectral peaks comparable in magnitudes with those caused by structural rearrangement, which precludes the interpretation of experimental results.

Comparison of the spectral characteristics of the P–F stretching vibrations for different states of aggregation of difluoro(methyl)phosphine (**10**)[50,51] makes it possible to assess the effect of intermolecular interactions on these vibrations (Table 6). Vibrational spectra of compound **10** and dichloro(methyl)phosphine (**11**)[52–56] have been interpreted.[51,56,57] The results obtained in the two last-mentioned studies differ mainly in the assignment of the ν_8 and ν_9 frequencies. In Ref. 57, they were assigned to the vibrations $\delta(PCl_2)$ and $w(PCl_2)$, respectively, while the opposite assignment has been given in Ref. 56. The latter attribution is in better agreement with the vibrational assignments for the molecule $C_2H_5PCl_2$ (**12**) based on the results of *ab initio* quantum-chemical calculations.[58]

Difluoro(ethyl)phosphine (**13**) and dichloro(ethyl)phosphine exist in the gas and liquid phases as mixtures of the *T* and *G* conformers[21,56,58–60] (see Fig. 1; X = F, Cl; Y = CH_2; Z = CH_3). Vibrational spectra of the former substance and its deuterio derivative have been interpreted[60] and it was shown that

Table 6. Characteristic frequencies of the stretching vibrations of PF_2 bonds in the spectra of several organophosphorus compounds.

Molecule	Assignment	Raman	IR
CH_3PF_2	$\nu_s(PF_2)$, $r(CH_3)$	812, w, p (g)	
		795, w, p (l)	
		789, w (cr)	798, s (cr)
	$\nu_{as}(PF_2)$, $r(CH_3)$	800, w, dp (g)	
		769, w, dp (l)	
		755, w (cr)	767, s (cr)
$C_2H_5PF_2$	$\nu_s(PF_2)$	819, m, p (g)	830, vs (g)
	$\nu_{as}(PF_2)$, $r(CH_2)$	796, w, dp (g)	819, vs (g)
$ClCH_2PF_2$	$\nu_s(PF_2)$, ν(CCl), ν(P−C)	849, m, p (l)	859, vs (g)
	$\nu_s(PF_2)$, ν(CCl), ν[P−C(*G*)]	790, m, p (l)	826, vs (g)
	$\nu_{as}(PF_2)$, $r(CH_2)$	813, sh (l)	799, s (g)
CF_3PF_2	$\nu_s(PF_2)$	861, m, p (g)	864, s (g)
	$\nu_{as}(PF_2)$	850, m, dp (g)	848, sh, w (g)

crystallisation of the specimens leads to the 'freezing out' of the *gauche* conformers. Unlike difluoro(ethyl)phosphine, both conformers of dichloro(ethyl)phosphine exist in the crystalline state.[21, 56] Vibrational spectra of $C_2H_5PCl_2$ (see Refs 21, 56) and $C_2D_5PCl_2$ (see Ref. 21) have been analysed repeatedly.[21, 56, 58] It is believed that comparison of the results obtained in the *ab initio* calculations [58] of the vibrations of heavy atoms of molecule $C_2H_5PCl_2$ with assignments [21] of the vibrations with predominant contribution of hydrogen atoms provides a version of the interpretation of the spectra of compounds **12**, which does not contradict experimental results [21, 56, 58] (Table 7).

The molecule of dichloro(propyl)phosphine, n-$C_3H_7PCl_2$ (**14**), can adopt five stable conformations (see Fig. 2; X = Cl, Y = CH_2). Analysis of the vibrational spectra of compound **14** showed [61] that the *Tt*, *Gt* and *Gg′* conformers exist in the liquid phase. The interpretation of the spectra of dichloro(propyl)phosphine was based on the results of *ab initio* quantum-chemical calculations.[61]

Table 7. Interpretation of vibrational spectra of dichloro(ethyl)phosphine.

No.	Symmetry	Assignment	Raman (l) [a]	IR (g) [a]
8	A′	ν(CC)	1038, w, p	1040, m
		ν[CC(*G*)]	1022, w, p	1026, m
9 [b]	A′	$r(CH_3)$, δ(CCP)	990, vw, p	994, w
19 [b]	A″	$r(CH_3)$, $r(CH_2)$	975, vw, dp	976, vw
		$r(CH_2)$, r[CH_3(*G*)]	750, vw, p	752, s
20	A″	$r(CH_2)$, $r(CH_3)$	727, vw, dp	728, m
		ν(P−C), δ[CCP(*G*)]	663, m, p	666, s
10	A′	ν(P−C), δ(CCP)	631, m, p	632, m
11	A′	$\nu_s(PCl_2)$, δ(CCP)	499, vs, p	506, vs
21	A″	$\nu_{as}(PCl_2)$	478, s, p	498, vs
12	A′	δ(CCP), $\nu_s(PCl_2)$	400, m, p	403, s
		δ[PCl_2(*G*)]	320, m, p	321, m
13	A′	$\delta(PCl_2)$	213, m, p	213, m
22	A″	$t(PCl_2)$	191, m, dp	185, s
		t[PCl_2(*G*)]	165, w, p	156, w
		w[PCl_2(*G*)]	286, m, p	287, s
14	A′	$w(PCl_2)$	178, w, p	175, s, sh
23	A″	$\chi(CH_3)$		184, w
		χ[CH_3(*G*)]		180, w
24	A″	$\chi(PCl_2)$	113, w	
			83, vw [c]	

[a] Vibrations with frequencies higher than 1200 cm^{-1} are not listed.
[b] The reverse assignment of the ν_9 and ν_{19} vibrations has also been reported.[18]
[c] From the gas-phase spectrum.

Table 8. Interpretation of vibrational spectra of dichloro(chloromethyl)-phosphine.

No.	Symmetry	Assignment	Raman (l)	IR (g)
		$r(CH_2)$, t[CH_2(*G*)]	812, w	816, m
12	A″	$r(CH_2)$	776, vw, p	774, sh
4	A′	ν(CCl), δ(PCCl), ν[P−C(*G*)]	746, w	757, m
		ν(P−C), δ(PCCl), $\delta(CH_2)$, δ[PCl_2(*G*)]	683, s, p	688, s
5	A′	ν(P−C)	620, vw, p	623, vw
13	A″	$\nu_{as}(PCl_2)$, ν_s[PCl_2(*G*)]	494, vs	508, vs
6	A′	$\nu_s(PCl_2)$, ν_{as}[PCl_2(*G*)]	494, vs, p	498, vs
7	A′	δ(PCCl)	364, vw	365, w
		δ(PCCl), $\delta(PCl_2)$, $w(CH_2)$, t[PCl_2(*G*)]	274, w	274, vs
		$w(PCl_2)$, $\delta(PCl_2)$, ν_s[PCl_2(*G*)]	256, vs, p	256, vs
8	A′	$w(PCl_2)$	228, vw	
14	A″	$\delta(PCl_2)$	203, w, p	
		$t(PCl_2)$, δ(PCCl), w[CH_2(*G*)]	143, w	136, s
9	A′	$\delta(PCl_2)$, ν(P−C), δ(PCCl), w[CH_2(*G*)]	187, s	187, s
15	A″	χ(P−C)	90, vw	85, w

Note. The number of vibration, symmetry species and tentative vibrational assignments are given for the *T* conformer only. Detailed assignment is given for the *G* conformer only.

The molecules of (chloromethyl)difluorophosphine $ClCH_2PF_2$ (**15**) and (chloromethyl)dichlorophosphine $ClCH_2PCl_2$ (**16**) exist [62–65] both in the liquid and gas phases as mixtures of the *T* and *G* conformers (see Fig. 1; X = F, Cl; Y = CH_2; Z = Cl). Crystallisation of these substances leads to the 'freezing out' of one isomeric form, so that the crystals of compound **16** comprise the molecules of only the *gauche* conformer,[64] while the molecules of compound **15** comprise the *trans* conformer.[63] The spectra of both compounds were interpreted using the force fields obtained from normal coordinate analysis for the corresponding deuterio derivatives.[63, 64] The assignments suggested [64] for compound **16** (Table 8) differ from those given earlier,[56, 66] which is likely due to impurities present in the specimens studied.[56, 66]

In studying the vibrational spectra of $(CH_3)_2PCl$ (**17**) it has been shown [49, 67] that the molecules of this compound form asymmetrical dimers in the crystals. This leads to the doublet splitting of a large number of singlet (in the spectra of liquid) bands and lines (Table 9). The components of the doublets

Table 9. Characteristic frequencies of the stretching vibrations of PCl bonds in the spectra of several organophosphorus compounds.

Molecule	Assignment	Raman	IR
CH_3PCl_2	$\nu_s(PCl_2)$, $\delta(PCl_2)$	483, vs, p (l)	479, vs (cr)
	$\nu_{as}(PCl_2)$, $t(PCl_2)$	483, vs, p (l)	479, vs (cr)
$C_2H_5PCl_2$	$\nu_s(PCl_2)$, δ(CCP)	499, vs, p (g)	506, vs (g)
	$\nu_{as}(PCl_2)$	478, s, p (g)	498, vs (g)
n-$C_3H_7PCl_2$	$\nu_s(PCl_2)$, ν_{as}[PCl_2(*Gt*)]		512, vs (g)
	ν_s[PCl_2(*Tt*)]	497, vs, p (l)	498, vs (g)
	$\nu_{as}(PCl_2)$	479, s, p (l)	482, s, sh (g)
$ClCH_2PCl_2$	$\nu_{as}(PCl_2)$, ν_s[PCl_2(*G*)]	494, vs (l)	508, vs (g)
	$\nu_s(PCl_2)$, $\nu_{\hat{o}s}$[PCl_2(*G*)]	494, vs, p (l)	498, vs (g)
CF_3PCl_2	$\nu_{as}(PCl_2)$, $\delta_{as}(CF_3)$	523, w, dp (l)	526, vs (g)
	$\nu_s(PCl_2)$, $\delta_{as}(CF_3)$	516, vs, p (l)	520, vs (g)
$(CH_3)_2PCl$	ν(PCl), $w(PC_2)$	462, s, p (l)	533, vw, sh (cr) 460, s (cr)
	$w(PC_2)$, ν(PCl)	301, w, p (l)	306, m (cr)

correspond to the in-phase and antiphase molecular vibrations in the dimers. Normal coordinate analysis for the molecule **17** [57] was based on the known experimental data,[67] which are somewhat different from those reported earlier.[49]

Since vibrational spectra of CF_3PH_2 (**18**) and its deuterium-substituted analogue revealed no reduction of the C_{3v} local symmetry of the CF_3 group due to the addition of the PH_2 group, a normal coordinate analysis for this molecule was performed assuming this symmetry. An interpretation of the vibrational spectra of molecule **18**, based on the results obtained by Bürger *et al.*,[68] is given in Table 10; however, the description of the vibrations of the PH_2 fragment is somewhat changed to accord with the true C_s symmetry of the entire molecule.

Table 10. Interpretation of vibrational spectra of (trifluoromethyl)phosphine.

No.	Symmetry	Assignment	Raman (g)	IR (g)
10	A″	$\nu_{as}(PH_2)$		2348,vs
1	A′	$\nu_s(PH_2)$		2305, vs
2	A′	$\nu_{as}(CF_3)$, $\delta_{as}(CF_3)$	1184, w	1187, vs
11	A″	$\nu_{as}(CF_3)$, $\delta_{as}(CF_3)$	1184, w	1187, vs
3	A′	$\nu_s(CF_3)$, $\delta_s(CF_3)$, $\nu(P-C)$	1140, w	1154, vs
4	A′	$\delta(PH_2)$	1072, w	1072, s
12	A″	$t(PH_2)$	848, m	833, vs
5	A′	$w(PH_2)$		833, vs
6	A′	$\delta_s(CF_3)$, $\nu_s(CF_3)$, $\nu(P-C)$	745, s	743, m
7	A′	$\delta_{as}(CF_3)$	524, w	525, m
13	A″	$\delta_{as}(CF_3)$	524, w	525, m
8	A′	$\nu(P-C)$, $\delta_s(CF_3)$	422, vs	419, s
9	A′	$r(CF_3)$	290, w	284, w
14	A″	$r(CF_3)$	290, w	284, w

Spectra of $(CF_3)_2PH$ (**19**) and its deuterio analogue, as well as those of $(CF_3)_3P$ (**20**) have been interpreted on the basis of normal coordinate analysis.[69,70] Vibrational spectra [54,71] of compounds CF_3PF_2 (**21**), CF_3PCl_2 (**22**), CF_3PBr_2 (**23**) and CF_3PI_2 (**24**) have been analysed.[72]

Unlike vibrational spectra of unsubstituted alkylphosphines, those of alkyl(halogeno)phosphines are strongly dependent on the state of aggregation of the substances (see Tables 1–10). This can be rationalised by self-association of the molecules. Since routine spectral experiments usually do not include strong heating or cooling of specimens, the spectral indications of particular vibrations presented below are given for those states of aggregation, in which the compounds under study exist at ambient temperature.

Compared to unsubstituted compounds, spectral regions corresponding to vibrations of structural fragments constituting the molecules of alkyl(halogeno)phosphines become much wider. This is due to not only intermolecular interactions, but also relatively strong coupling of vibrations and strong substituents effects. Mention has been made [1] that the IR spectra of compounds of the type RPF_2 reveal two strong bands in the frequency ranges 806–869 and 860–947 cm^{-1}, which correspond to the vibrations $\nu_{as}(PF_2)$ and the $\nu_s(PF_2)$, respectively (see Table 6). As can be seen in Table 6, only the frequencies in the spectra of molecule **21** fall within the above-mentioned limits. Probably, a tendency of compounds containing the PF_2 group to undergo an autocatalytic disproportionation [73,74] can be a reason for violation of the known correlations.[1] Analysis of the IR spectra of alkyl(difluoro)phosphines showed that both stretching vibrations of the PF_2 group are observed in the same characteristic region $\sim$ 780–830 cm^{-1}. When assigning the vibrations, one should take into account that the $\nu(PF_2)$ frequencies can increase substantially on going from the liquid to vapour phase. In addition, our experience suggests that in the Raman spectra the $\nu_s(PF_2)$ lines are of medium or weak intensity and are polarised, while the $\nu_{as}(PF_2)$ lines are weak and depolarised (though quantitative differences between the degrees of depolarisation of these lines can be rather small). Introduction of halogen atoms into molecules causes an increase in the force constants of the P–F bonds, so that the $\nu(PF_2)$ frequencies can be as high as 870 cm^{-1}.

The frequencies of stretching vibrations of the PCl_2 groups lie in the region 420–526 cm^{-1} (see the monograph [1]). For alkyl(halogeno)phosphines, they are usually close to the upper bound of this spectral region ($\sim$ 450–526 cm^{-1}). The frequencies of the vibrations $\nu_s(PCl_2)$ of alkyl(dichloro)phosphines are somewhat higher than those of the vibrations $\nu_{as}(PCl_2)$ [the opposite is observed for molecules **16** and **22** (see Table 9)]; in the spectra of liquids the corresponding peaks usually coalesce into an unresolved contour. These compounds are characterised by an increase in the frequencies of stretching vibrations of the PCl_2 group on going to the gas phase. However, both the IR spectral bands and the Raman lines remain very strong, which facilitates the identification of these $\nu(PCl_2)$ vibration in spite of their strong coupling with other vibrations (see Table 9).

The vibrations $\nu(P-Cl)$ of the molecule **17** are strongly mixed with the rocking vibrations of the $(CH_3)_2P$ group, which gives rise to two co-operative vibrations. Among them, the vibration with the higher frequency can be rather arbitrarily associated with the $\nu(P-Cl)$ stretch (see Table 9). Analysis of scarce spectral data for dialkyl(chloro)phosphines suggests that the frequencies of the vibrations $\nu(P-Cl)$ of these compounds lie in nearly the same spectral region as those of the vibrations $\nu(PCl_2)$ (see above). Therefore, the most pronounced distinction between the corresponding spectra is reduced to the appearance of two vibrations, *viz.*, $\nu_s(PC_2)$ and $\nu_{as}(PC_2)$, in the spectra of dialkyl(chloro)phosphines instead of one $\nu(P-C)$ vibration in the spectra of alkyl(dichloro)phosphines. The frequencies of the vibrations $\nu(PC_2)$ and $\nu(P-C)$ in the spectra of alkyl(halogeno)-phosphines (see Table 5) are observed near the upper bounds of the corresponding spectral regions (see Section II) for alkylphosphines. (The molecules containing the CH_2Cl and CF_3P groups are exceptions to this rule. Their spectra are discussed below.) The intensities of the corresponding bands in the IR spectra of alkyl(halogeno)phosphines are usually higher than those in the spectra of unsubstituted analogues. Other parameters of these spectral peaks are similar to those discussed above (see Section II).

Spectral indications of the CH_3P and C_2H_5P groups are nearly identical for alkylphosphines and their halogeno-substituted derivatives. The exceptions are the vibrations with predominant contribution of the $r(CH_3P)$ vibration, since their frequencies decrease from $\sim$ 940–985 down to $\sim$ 880 cm^{-1} upon introduction of halogen atoms to the phosphorus atom in the last-named molecules. The intensities of the corresponding bands in the IR spectra are rather high.

The peaks in the region 1380–1410 cm^{-1}, corresponding to the $\delta(CH_2)$ vibrations, are characteristic of the CH_2Cl group. (This spectral region is characteristic of the vibrations of CH_2X groups, where X is a rather heavy atom; *e.g.*, X = P or S). Stretching vibrations of the C–Cl bond of the CH_2Cl group strongly interact with the vibrations $\nu(P-C)$ and give rise to two new vibrations. Among them, the vibration with the lower frequency is observed in the region typical of the vibration $\nu(P-C)$ and has all the specific spectral indications (see Section II). The peaks corresponding to the second stretching vibration of the PCCl group are observed in the region $\sim$ 740–790 cm^{-1} and have variable intensities.

The vibrations of the CF_3P group are readily identified in the spectra of any organophosphorus compounds. Mention has been made [4] that very strong IR absorption bands in the region 1100–1300 cm^{-1} correspond to the stretching vibrations of trifluoromethyl groups. For phosphines, this correlation has specific details.

Two very strong bands in the region 1140–1235 cm^{-1} of the IR spectra of phosphines can be arbitrarily assigned to the vibrations $\nu_{as}(CF_3)$ (Table 11), which result from the mixing of the stretching and deformation [$\delta_{as}(CF_3)$] vibrations. They are

Table 11. Vibration $\nu_{as}(CF_3)$ in the spectra of organophosphorus compounds.

Molecule	Assignment	Raman	IR
CF_3PH_2	$\nu_{as}(CF_3)$, $\delta_{as}(CF_3)$ (‖)	1184, w (g)	1187, vs (g)
	$\nu_{as}(CF_3)$, $\delta_{as}(CF_3)$ (⊥)	1184, w (g)	1187, vs (g)
CF_3PI_2	$\nu_{as}(CF_3)$, $\delta_{as}(CF_3)$ (‖)		1177, vs (g)
	$\nu_{as}(CF_3)$, $\delta_{as}(CF_3)$ (⊥)		1140, vs (g)
CF_3PBr_2	$\nu_{as}(CF_3)$, $\delta_{as}(CF_3)$ (‖)	1184, m (l)	1190, vs (g)
	$\nu_{as}(CF_3)$, $\delta_{as}(CF_3)$ (⊥)	1156, sh (l)	1160, sh (g)
CF_3PCl_2	$\nu_{as}(CF_3)$, $\delta_{as}(CF_3)$ (‖)	1200, w (l)	1200, vs (g)
	$\nu_{as}(CF_3)$, $\delta_{as}(CF_3)$ (⊥)	1184, m (l)	1176, m (g)
CF_3PF_2	$\nu_{as}(CF_3)$, $\delta_{as}(CF_3)$ (‖)	1222, m (g)	1222, vs (g)
	$\nu_{as}(CF_3)$, $\delta_{as}(CF_3)$ (⊥)	1166, m (g)	1170, sh (g)
$(CF_3)_2PH$	$\nu_{as}(CF_3)$, $\delta_{as}(CF_3)$		1212, vs (g)
	$\nu_{as}(CF_3)$, $r(CF_3)$		1180, vs (g)
$(CF_3)_3P$	$\nu_{as}(CF_3)$, $\delta_{as}(CF_3)$ (‖)		1235, s (g)
	$\nu_{as}(CF_3)$, $\delta_{as}(CF_3)$ (⊥)	1176, w, br (g)	1189, s (g)

Note. Hereafter (‖) and (⊥) respectively denote the vibrations, which occur parallel and perpendicular to the molecular symmetry plane.

localised within one CF_3P group and do not interact kinematically with the motions of adjacent fragments. Therefore, variations of the frequencies of the vibrations $\nu_{as}(CF_3)$ are due to dynamic reasons alone and, hence, reflect the changes in the electronic structure of the phosphorus-containing fragment of the molecule. The $\nu_{as}(CF_3)$ frequencies increase as the electronegativities of substituents at the phosphorus atom increase (see Table 11).

Symmetrical stretching vibrations $\nu_s(CF_3)$ mix with the bending vibrations $\delta_s(CF_3)$ and the vibrations $\nu(P-C)$ (see Table 10). The involvement of the phosphorus atom in the vibrations provides the possibility for kinematic interactions between adjacent groups to occur, which is particularly effective in the case of equal 'individual' frequencies. That is why the number of bands corresponding to the vibration $\nu_s(CF_3)$ in the IR spectra of compounds with one CF_3P group and with two (or three) CF_3P groups is different, namely, one very strong band in the region 1100–1160 cm^{-1} *vs*. two bands in the same spectral region, respectively.

Previously (see Section II), particular attention was paid to the vibrations $\nu(P-C)$ and it was shown that the corresponding Raman lines have distinctive spectral indications, which are common to various organophosphorus compounds with the $P-C(sp^3)$ valence bonds. Unfortunately, compounds with the CF_3P group are exceptions to this rule, since all attempts to discriminate between the vibrations with predominant contribution of the P–C bond and other normal coordinates have failed. The vibrations denoted [4] as $\nu(P-C)$ are in fact coupled vibrations with nearly equal contributions of the vibrations $\delta_s(CF_3)$ and $\nu_s(CF_3)$ and with a some contributions of the vibrations $\nu(P-C)$ (see Table 10). The corresponding bands in the vibrational spectra of organophosphorus compounds are observed in the region between 650 and 750 cm^{-1}. For phosphines, this region is much narrower, namely, one or two strong IR absorption bands are observed in the frequency range $\sim$ 720–750 cm^{-1}. The corresponding Raman lines are polarised and intense.

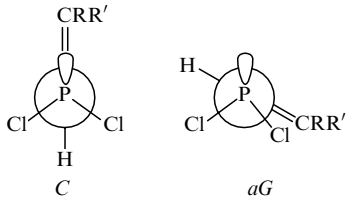
Vibrations of the P–C bonds make somewhat greater contributions to the coupled vibrations denoted [4] as $\delta(C-F)$. The corresponding IR absorption bands and Raman lines ($\sim$ 410–470 cm^{-1}) are rather strong, the latter being polarised, which facilitates vibrational assignments.

We suggest that the Raman lines of medium or weak intensity, which are observed in the region 520–570 cm^{-1} and correspond to the vibrations with the predominant contribution of the vibrations $\delta_{as}(CF_3)$, can also be used for identification of compounds under consideration. The intensities of the $\delta_{as}(CF_3)$ bands in the IR spectrum can vary from very weak to strong.

IV. Phosphines with unsaturated groups at the phosphorus atom

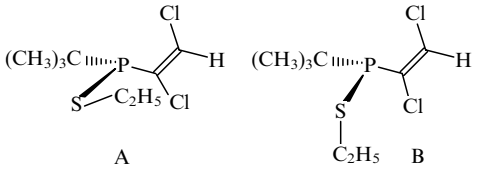
To date, a normal coordinate analysis has been performed only for three groups of the trivalent phosphorus compounds with unsaturated fragments. These are the molecules with the P–C = C fragment, ethynylphosphines and cyano derivatives of phosphines.

The first group comprises alkenyl(dichloro)phosphines. Their molecules can adopt both the *cis* (*C*) and *anti*,*gauche* (*aG*) conformations.



C *aG*

According to the vibrational spectroscopy data,[75] the *cis* conformers of the molecules $CH_2 = CHPCl_2$ (**25**) and $(CH_3)_2C = CHPCl_2$ (**26**) are dominant in the condensed phase, whereas liquid dichloro(styryl)phosphine (**27**) is a mixture of both conformers. Because of steric hindrances, in the molecule of *S*-ethyl *tert*-butyl(1,2-dichlorovinyl)phosphinothioite (**28**) the C = C bond is in *cis* position with respect to the lone electron pair (LEP) of the phosphorus atom.[76] However, it is believed that a mixture of conformers can exist in the liquid owing to internal rotation of the C_2H_5S fragment



A B

The interpreted vibrational spectra [75] of the simplest representative of this group of compounds, *viz*., compound **25**, are listed in Table 12.

Triethynylphosphine (**29**) is a representative of the second group of the trivalent phosphorus compounds with unsaturated fragments. Its molecule has a C_{3v} symmetry and the vibrations of the A_2 type are optically inactive and not observed in vibrational spectra. Table 13 lists the experimental [77] vibrational spectra of compound **29** and the assignments [78] based on the results of normal coordinate analysis. Unfortunately, neither the eigenvectors of the vibrations nor the potential energy distribution over the

Table 12. Interpretation of vibrational spectra of dichloro(vinyl)phosphine.

No.	Symmetry	Assignment	Raman (l)	IR (l)
4	A′	ν(C = C), $\delta(CH_2)$, δ(PCH)	1605, sh, w, 0.20	1592, vw
		ν(P–C)	1595, m, 0.17	
5	A′	$\delta(CH_2)$, ν(C = C)	1392, m, 0.22	1391, m
6	A′	δ(PCH), $r(CH_2)$, $\delta(CH_2)$	1255, m, 0.21	1255, w
13	A″	$\gamma(CH_2)$	1028, vw	1037, vw
7	A′	$r(CH_2)$, r(P–C)	1010, w	1011, m
14	A″	χ(C = C), $\gamma(CH_2)$, γ(PCH)	971, w	965/976, w
8	A′	ν(PC), $r(CH_2)$	720, m, 0.42	719, s
15	A″	γ(PCH), $t(PCl_2)$	587, w, 0.74	585, s
9	A′	$\nu_s(PCl_2)$, $\delta(PCl_2)$	502, vs, 0.25	504, vs
16	A″	$\nu_{as}(PCl_2)$	473, s, 0.42	473, vs
10	A′	r(C = C)	348, vs, 0.15	347, w
11	A′	$\delta(PCl_2)$	255, m, 0.50	258, m
17	A″	$t(PCl_2)$, γ(PCH)	218, m, 0.86	218, m
12	A′	$w(PCl_2)$	190, s, 0.83	188, m

Table 13. Interpretation of vibrational spectra of triethynylphosphine.

No.	Symmetry	Assignment	Raman (s) [a]	IR (s) [b]
2	A_1	$\nu(C\equiv C)$	2054, 100, p	2053, m
10	E	$\delta(C\equiv C)$	2054, 100, p	2053, m
3	A_1	$\delta(C\equiv CH)$ ($\parallel$)	702, 2	696, vs
11	E	$\delta(C\equiv CH)$ ($\parallel$)	702, 2	696, vs
12	E	$\delta(C\equiv CH)$ ($\perp$)	654, 1	651, s, sh
13	E	$\nu_{as}(PC_3)$	643, 3	639, vs
4	A_1	$\nu_s(PC_3)$		614, w
5	A_1	$\delta(PC\equiv C)$ ($\parallel$)	449, 2	444, m
14	E	$\delta(PC\equiv C)$ ($\parallel$)		423, m
15	E	$\delta(PC\equiv C)$ ($\perp$)	273, 4	270, m
6	A_1	$\delta_s(PC_3)$		131, m, v.br
16	E	$\delta_{as}(PC_3)$	106, 71, dp	100.5, vw [c]

[a] The frequencies were averaged over the spectra of solutions in CCl_4 and furan. [b] The frequencies were averaged over the spectra of solutions in CCl_4 and CS_2. [c] From the gas-phase spectrum.

vibrational coordinates have been reported,[78] therefore the assignments listed in Table 13 seem to be tentative.

Vibrational spectra of dicyano(methyl)phosphine (**30**)[79] and tricyanophosphine (**31**)[80–82] have been studied. The spectra reported by Goubeau, Haeberle and Ulmer[80] differ appreciably from those reported in the other studies.[81,82] This is probably due to chemical transformations of the substances during the preparation of the samples.[82] In the condensed phase, both compounds can be involved in strong intermolecular interactions, which can cause rather large shifts of the spectral peaks (Table 14) and even be responsible for the appearance of new bands as compared to the gas-phase spectra. For instance, an intense peak at ~ 630 cm^{-1} (see Refs 79, 81, 82) in the spectra of liquid and crystalline cyanophosphines and their solutions in CH_3CN is not observed in the spectra of vapours or solutions in other solvents. This peak results from intermolecular interactions involving the cyano groups.[79,82] Such strong effects hamper the interpretation of the spectra of these molecules in the liquid or crystalline phase. It should be noted that the molecule **31** has a C_{3v} symmetry and vibrations belonging to the A_2 type are optically inactive and not observed in vibrational spectra. The force field of the molecule **31** has been first evaluated by Unnikrishnan and Aruldhas.[83] However, calculations performed using this force field have led to unrealistic values of the root-mean-square vibrational amplitudes.[84] Therefore, Table 14 lists the theoretical interpretation of the spectra of compound **31** according to other studies.[84,85] The results of normal coordinate analysis for the spectra of dicyano(methyl)phosphine **30** have been reported.[86]

Table 14. Interpretation of vibrational spectra of phosphorus tricyanide.

No.	Symmetry	Assignment	Raman (g)	Raman (s) [a]	Raman (cr)	IR (cr)
1	A_1	$\nu(C\equiv N)$	2197, s, p	2196, s, p	2210, w 2205, w	
6	E	$\nu(C\equiv N)$		2190, vw		2201.2, s
2	A_1	$\nu_s(PC_3)$, $\delta(PCN)$ ($\perp$), $\delta_s(PC_3)$	625, w, p	606, s, p	604, s	603, s
7	E	$\nu_{as}(PC_3)$		581, w, dp	577, w	
3	A_1	$\delta(PCN)$ ($\perp$), $\nu_s(PC_3)$,	451, w, p	464, w, dp	469, m	468, w
8	E	$\delta(PCN)$ ($\perp$), $\delta_{as}(PC_3)$	442, vw	452, w, p	453, w	452, w
9	E	$\delta(PCN)$ ($\parallel$), $\delta_{as}(PC_3)$		312, w, dp	318, w	314, w
4	A_1	$\delta_s(PC_3)$, $\delta(PCN)$ ($\perp$)	128, m, dp		(148, w)	(145, w)
10	E	$d_{as}(PC_3)$, $\delta(PCN)$ ($\parallel$)	105, s, dp	(130, m, dp)	(112, vw)	

Note. The frequencies assigned tentatively are given in parentheses.
[a] A solution in CH_3CN.

A common feature of the spectra of the three groups of compounds considered in this Section is that the frequencies of stretching vibrations of the multiple bonds at the trivalent phosphorus atom are lower than those for the corresponding organic molecules. For instance, the frequencies of stretching vibrations of the C=C(P) group (see Table 12) are lower than the lower bound of the spectral region 1620–1680 cm^{-1} typical of alkenes.[87] As is known, the introduction of halogens also leads to a decrease in the frequency of the stretching vibrations ν(C=C); however, this effect is not so strong as that observed after introduction of the phosphorus atom. For instance, the frequency of the vibrations ν(C=C) in $CCl_2=CHCl$ is 1589 cm^{-1} (*cf.* 1539 cm^{-1} for the molecule **28**). The same is also observed for the frequency of the vibrations $\nu(C\equiv C)$ in compound **29** (see Table 13), which is lower than the corresponding frequencies in acetylene and haloacetylenes ($\sim 2085-2270$ cm^{-1}).[87,88] The frequencies of the stretching vibrations $\nu(C\equiv N)$ of molecules **30** and **31** also lie far below the spectral region 2215–2260 cm^{-1} typical of organic cyanides.[87] It should be noted that the peaks at $\sim 2180-2217$ cm^{-1} are 'fingerprint' of the PCN groups in the spectra of neat liquids or crystals (see monograph [1]). A small overlap of the two spectral regions [1,87] is of no concern for trivalent phosphorus compounds, since the corresponding frequencies of stretching vibrations of the PCN group always lie below 2215 cm^{-1}. At the same time, it should be remembered that the $\nu(C\equiv N)$ frequencies of halonitriles [89] lie nearly in the same region as the ν(PCN) frequencies. The ν(C=C), $\nu(C\equiv C)$ and $\nu(C\equiv N)$ bands in the IR spectra can be of weak intensity, therefore it is more convenient to identify these groups using the Raman spectra in which the corresponding lines always are sufficiently strong and polarised.

Raman spectroscopy can also be used to assign the vibrations denoted [87] as $\delta(CH_2)$ and δ(C–H), since the lines associated with them are polarised and are of medium intensity. The frequency of the vibration $\delta(CH_2)$ of the vinyl radical at the phosphorus atom is observed in the region 1390–1410 cm^{-1} (*cf.* 1410–1420 cm^{-1} in the spectra of terminal alkenes). The frequencies of the vibrations δ(C–H) of monosubstituted styrenes [87] lie in the region 1295–1310 cm^{-1} [*cf.* 1335 cm^{-1} for dichloro(styryl)phosphine **27**]. The δ(C–H) vibrations in the molecules of terminal alkenes are observed in the spectral region 1290–1300 cm^{-1} (see Ref. 87), while the frequency of the vibration δ(PCH) of the vinyl group at the phosphorus atom varies between 1250 and 1260 cm^{-1} (see Table 12). The $\gamma(CH_2)$ and χ(C=C) frequencies also 'drop out' of the corresponding spectral regions typical of alkenes.[87] Changes in the 'fingerprint' vibrational frequencies of alkenylphosphines as compared to those of alkenes are due to the effect of the phosphorus atom on the force constants of the alkenyl fragment rather than kinematic effects.

V. Alkoxy derivatives of trivalent phosphorus

The spectra of both cyclic and acyclic alkoxy derivatives of trivalent phosphorus have been studied. According to *ab initio* calculations,[90–92] the simplest acyclic molecules such as methyl dimethylphosphinite (**32**), methyl phosphorodifluoridite (**33**) and methyl phosphorodichloridite (**3**) can adopt both the *T* and *G* conformations (see Fig. 1; X = CH_3, F, Cl; Y = O; Z = CH_3). Studies of the vibrational spectra of molecule **32** and its isotopomers $CD_3OP(CH_3)_2$, $CH_3OP(CD_3)_2$ and $CD_3OP(CD_3)_2$ showed that both conformers were present in the liquid and gas states,[93] while only the *trans* conformer was retained in crystals. It should be noted that the interpretation of incomplete spectra of methyl dimethylphosphinite **32** (see Seel and Velleman [94]) is in agreement

Table 15. Interpretation of vibrational spectra of methyl phosphorodichloridite.

No.	Symmetry	Assignment	Raman (l)	IR (g)
5	A′	$r(CH_3)$, $\nu_{as}(POC)$	1181, 15, p	1181, s
14	A″	$r(CH_3)$	1154, 50, dp	1151, m [a]
6	A′	$\nu_{as}(POC)$, $r(CH_3)$	1044, 50, p	1057, vs
7	A′	$\nu_s(PF_2)$	816, 100, p	829, vs
15	A″	$\nu_{as}(PF_2)$	778, 5, dp	797, vs
8	A′	$\nu_s(POC)$	778, 39, p	784, m
9	A′	$r(PF_2)$, $\delta(POC)$, $\delta(PF_2)$	536, 40, p	539, m
16	A″	$t(PF_2)$, $\chi(PO)$	370, 20, p	370, s
10	A′	$\delta(PF_2)$	351, 10, p	358, sh
11	A′	$\delta(POC)$, $r(PF_2)$	218, 30, p	214, s
17	A′	$\chi(PO)$, $\chi(O-CH_3)$, $t(PF_2)$	128,10, dp	120, m
18	A″	$\chi(O-CH_3)$, $\chi(PO)$	81, 14, dp	

[a] From the spectrum of crystals.

with the assignments suggested on the basis of *ab initio* quantum-chemical calculations.[90, 93]

Both vibrational [91, 95] and microwave [96] spectral studies as well as a gas-phase electron diffraction study [97] revealed no indications of the *gauche* conformers of the molecule of methyl phosphorodifluoridite **33**. Therefore, the interpretation of the IR absorption bands and Raman lines in the spectra of compound **33** (Table 15) is based on the results of *ab initio* calculations of the vibrations of the *trans* conformer.[91]

Data on rotational isomerism in the molecule of methyl phosphorodichloridite **3** are contradictory.[92, 98–103] In spite of this, the existence of *trans* conformers of molecule **3** is doubtless,[92, 102, 103] and the interpretation of the spectra of *trans* conformer was based on the results of *ab initio* calculations of the vibrations.[92]

The molecule of ethyl phosphorodichloridite (**34**) can adopt five stable conformations [104] (see Fig. 2; X = Cl, Y = O); however, this has not been confirmed experimentally. Using normal coordinate analysis, it has been shown [104] that the observed spectra can be attributed to the *Tt* and/or *Gt* conformers. The interpretation of the spectra (see Table 16) is based on the results of normal coordinate analysis for the *Tt* conformer.[26]

The molecule of β-thiocyanatoethyl phosphorodichloridite (**35**) can adopt twenty-three stable conformations. In the liquid state, compound **35** exists as a mixture of at least three conformers, while in the crystalline state (at low temperatures) the number of conformers equals at least two.[105] Since conformational analysis of compound **35** is too complicated, attempts to determine unambiguously the number and type of observable conformers of molecule **35** have failed. It has only been shown [105] that the mutual *gauche*-orientation of the O–C and C–S bonds is energetically favourable. The interpretation of the IR absorption bands and Raman lines in the spectra of β-thiocyanatoethyl phosphorodichloridite **35** is based on the results of normal coordinate analysis for all possible conformers.[105]

A few studies devoted to the normal coordinate analysis of cyclic alkoxy derivatives of trivalent phosphorus has been reported. Five-, six- and seven-membered phosphacycles with the P–O–C fragment have been studied. First, consider the spectra and conformations of five-membered organophosphorus compounds. According to the vibrational spectroscopy data,[106] the molecule of 2-chloro-1,3,2-dioxaphospholane (**36**) adopts a single conformation. Gas-phase electron diffraction study [107] of compound **36** revealed a stable (in the gas phase) conformation of molecule **36** shown in Fig. 3 (*a*-E_O, X = Y = O). Earlier, a normal coordinate analysis for 2-chloro-1,3,2-dioxaphospholane **36** has been performed for a symmetrical 'envelope' conformation in which the phosphorus atom deviates from the plane passing through the other ring atoms [106] (*a*-E_P). Next to the publication cited,[107] a normal coordinate analysis for the non-symmetrical *a*-E_O conformer (see Fig. 3) has been reported.[108] It is this version of the interpretation of the spectra that is listed in Table 17.

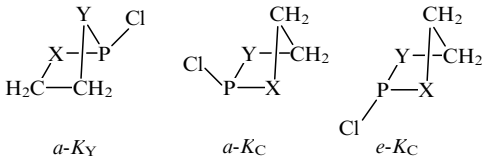


Figure 3. The 'envelope' conformations of the molecules of 2-chloro-1,3,2-dioxa(thia)phospholanes: with apical Y atom and pseudoaxial orientation of the P–Cl bond (*a*-E_Y), with apical C atom and axial orientation of the P–Cl bond (*a*-E_C) and with apical C atom and equatorial orientation of the P–Cl bond (*e*-E_C).

Table 16. Interpretation of vibrational spectra of ethyl phosphorodichloridite.

No.	Symmetry	Assignment	Raman (l)	IR (l) [a]
8	A′	$\nu(OC)$, $\nu(CC)$, $\delta(POC)$, $\delta(OCC)$	1095, vw, 0.4	1095, vw
9	A′	$\nu_{as}(POC)$, $\nu(CC)$, $w(CH_2)$	1022, vw	1022, vs
10	A′	$\nu(CC)$, $\nu(PO)$, $w(CH_3)$		963, s
22	A″	$r(CH_2)$, $r(CH_3)$	727, m, 0.6	735, m
11	A′	$\nu_s(POC)$, $\nu(CC)$, $\delta(POC)$, $w(CH_2)$	727, m, 0.6	735, m
12	A′	$\nu_s(PCl_2)$	493, vs, 0.3	500, s
23	A″	$\nu_{as}(PCl_2)$	443, m, dp	450, s
13	A′	$\delta(POC)$, $\delta(OCC)$, $w(PCl_2)$	422, m, 0.8	430, sh
14	A′	$\delta(OCC)$, $\delta(POC)$, $w(PCl_2)$	300, vw	
24	A″	$t(PCl_2)$, $\chi(PO)$, $\chi(OC)$	300, vw	
15	A′	$\delta(PCl_2)$	192, s, 0.6	
25	A″	$t(PCl_2)$, $\chi(CC)$	150, w, 0.67	
16	A′	$\delta(POC)$, $\omega(PCl_2)$, $\delta(PCl_2)$	125, vw, dp	

[a] Spectral region below 400 cm^{-1} has not been recorded.

2-Chloro-1,3,2-oxathiaphospholane (**37**) exists in the liquid state and in solutions as a mixture of two non-symmetrical conformers shown in Fig. 3 (*a*-E_C and *e*-E_C; X = O, Y = S).[108, 109] Their vibrational spectra [108, 109] have been interpreted theoretically.[108]

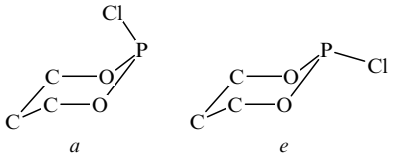
The molecule of 2-chloro-1,3,2-dioxaphosphorinane (**38**) adopts a single conformation.[110] Based on the results of the gas-phase electron diffraction study,[111] the conformation *a* was suggested for its molecule; at the same time, the band-shape

Table 17. Interpretation of vibrational spectra of 2-chloro-1,3,2-dioxaphospholane.

No.	Assignment	Raman (l)	IR (l) [a]
11	$\nu_{as}(POC)$		1048, sh
12	$\nu_{as}(CCO)$	1009, 20, p	1010, s
13	$r(CH_2)$		984, sh
14	$\nu(CC)$, $\nu_{as}(POC)$, $\delta(CCO)$	922, 20, p	928, s
15	$\nu_s(POC)$, $\nu_{as}(POC)$, $r_{as}(CH_2)$	805, 100, p	809, m
16	$\nu_{as}(POC)$, $r(CH_2)$, $\delta(POC)$	767, 5	764, s
17	$\nu(PO)$, $r(CH_2)$	754, 5	750, sh
18	$\delta_{as}(CCO)$, $\delta_{as}(POC)$	602, 10, p	597, m
19	$\nu(PCl)$	443, 70, p	445 s
20	$\delta(OPO)$, $\delta_s(POC)$	330, 60, p	
21	$\delta_{as}(OPCl)$	258, 10, p	

[a] Spectral region below 400 cm^{-1} has not been recorded.

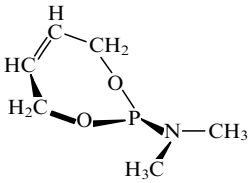
analysis of the IR spectra of compound **38** in the vapour phase counts in favour of conformation *e*.[110]



a *e*

A normal coordinate analysis for both conformers of the molecule of 2-chloro-1,3,2-dioxaphosphorinane **38** has been performed.[110, 112]

The molecule of 4,7-dihydro-2-dimethylamino-1,3,2-dioxaphosphepin (**39**) adopts mainly an non-symmetrical conformation,[113]



for which theoretical interpretation of the vibrational spectra has been carried out.[113]

Based on the results of normal coordinate analyses (see Tables 15–17), it is possible to establish the origin of the bands used as spectral indications of the presence of different AlkOP groups in the molecules under study. It is known that the methoxy group at the phosphorus atom is responsible for the appearance of a strong band at $\sim 1010-1050$ cm^{-1}, a strong or medium band in the region $\sim 700-800$ cm^{-1} and a medium or weak (often multiplet) band in the region $\sim 1150-1200$ cm^{-1} in the IR spectra. The first two bands are associated with the antiphase and in-phase stretching vibrations of the P—O and O—C bonds, respectively. The former bond makes the major contribution to the symmetric vibration ν_s(POC), while the latter contributes largely to the antisymmetric vibration ν_{as}(POC). Mention may be made that the vibrations ν_s(POC) can also be readily identified using the Raman spectra, since the corresponding line is of rather high intensity and polarised. Weak Raman lines and IR absorption bands in the spectral region $\sim 1150-1200$ cm^{-1} are mainly due to the rocking vibrations of the methyl group.

Spectral 'fingerprints' of the C_2H_5OP group are well known.[1–5] These are the strong bands in the IR spectra in the regions $\sim 900-970$, $\sim 1010-1040$ cm^{-1} and the bands of medium or weak intensity in the regions $\sim 1090-1110$ and $\sim 1150-1170$ cm^{-1}. All of them are due to strongly coupled vibrations (Table 16). The vibration with the highest frequency is associated with the rocking motion $r(CH_2)$. The frequencies of stretching vibrations of the OCC fragment usually lie in the range $\sim 1090-1110$ cm^{-1}. Strong bands in the IR spectrum are to a certain degree due to the antiphase stretching vibrations of the P—O, O—C and C—C bonds (see Table 16, stretching vibrations Nos 9 and 10). The vibration ν_s(POC) gives rise to the appearance of rather intense spectral peaks both in the IR and Raman spectra (stretching vibration No. 11). They are observed in the region $\sim 700-800$ cm^{-1}, the corresponding Raman line being polarised.

This spectral region is characteristic of the frequencies of the vibrations ν_s(POC) for not only the ethoxy group, but almost any alkoxy groups at the trivalent phosphorus atom. Only for cyclic alkoxy derivatives does the region extend to $\sim 690-820$ cm^{-1}. Because of the possibility that the molecules of compounds under study adopt several conformations owing to internal rotation about the P—O bond, the bands corresponding to the vibrations ν_s(POC) can split into doublets. It should be noted that if a molecule contains two POC groups at the phosphorus atom, their stretching vibrations effectively interact through this atom (see Section I). For instance, the frequencies of the ring 'breathing' vibrations corresponding to the synchronous stretch or contraction of the bonds in both POC groups (see Table 17, vibrations No. 15) and to the antiphase vibrations of these fragments (vibrations No. 16) are observed in this region of the spectra of 2-chloro-1,3,2-dioxaphospholane. The IR absorption bands associated with the antiphase vibrations ν_s(POC) are usually more intense than those corresponding to the in-phase vibrations. At the same time, the lines of the in-phase vibrations in the Raman spectra are symmetrical, very strong and strongly polarised, while those of the antiphase vibrations are, as a rule, of weak intensity.

It should be noted that the ring 'breathing' vibrational frequencies of 1,3,2-dioxaphospholanes are always higher than the frequencies of the in-phase vibrations ν_s(POC) of related acyclic organophosphorus compounds, as well as those of the ring 'breathing' vibrations of 1,3,2-dioxaphosphorinanes[112] and other related unstrained phosphacyclanes (provided that the exocyclic groups in the dioxaphospholane and in the larger ring to be compared are the same). A remarkable feature of 1,3,2-dioxaphospholanes is that the frequencies of the ring 'breathing' vibrations are higher than those of the antiphase vibrations ν(POC). The opposite is observed for 1,3,2-dioxaphosphorinanes and acyclic dialkoxy derivatives. These distinctions can be used for analytical purposes. If the molecules under study have exocyclic P—Cl bonds, then the strong IR absorption bands and very strong polarised Raman lines in the spectral region $\sim 440-460$ cm^{-1} provide reliable spectral indications of the 1,3,2-dioxaphospholane rings. These spectral bands and lines are due to the stretching vibrations of the P—Cl bond. In the molecules of 1,3,2-dioxaphosphorinanes, the vibrations ν(P—Cl) interact with the ring deformation vibrations. Two resultant vibrations appear in the spectra as the intense IR absorption bands and Raman lines in the regions $\sim 400-430$ and $\sim 460-490$ cm^{-1}. The most characteristic of the spectra of acyclic phosphorochloridites are intense IR absorption bands in the region $\sim 490-510$ cm^{-1}. Thus, the readily identifiable vibrations ν(P—Cl) can be used for the discrimination not only between 1,3,2-dioxaphospholanes and 1,3,2-dioxaphosphorinanes, but also between these cyclic and corresponding acyclic compounds.

The vibrations of the PCl_2 group (see Table 16) have marked spectral indications. Symmetrical stretching vibrations $\nu_s(PCl_2)$ of the molecules of alkyl phosphorodichloridites appear as very strong IR absorption bands and Raman lines in the region $\sim 490-510$ cm^{-1}. The less intense peaks in the region $\sim 440-480$ cm^{-1} are associated with antisymmetric vibrations. Identification of these vibrations using the Raman spectra is facilitated by the fact that the lines corresponding to $\nu_s(PCl_2)$ are strongly polarised while those corresponding to $\nu_{as}(PCl_2)$ are depolarised or nearly depolarised. It should be noted that the appearance of additional intense peaks in these spectral regions, which are due to the deformation vibrations of non-branched alkoxy groups at the phosphorus atom (see Table 16) prevents easy interpretation.

The deformation vibration of the PCl_2 group is also characteristic of alkyl phosphorodichloridites. The corresponding line is observed in the region $\sim 190-220$ cm^{-1} and can be identified with ease in the Raman spectra, since it is always strong and has a depolarisation ratio of about 0.6.

It should be noted that vibrational spectra of phosphorochloridites change as the state of aggregation of compounds under study changes or on dissolution, which is mainly due to intermolecular interactions. The frequencies of the vibrations involving the P—Cl bonds change to the greatest extent. All the above-mentioned characteristic spectral regions refer to the spectra of neat liquids at room temperature.

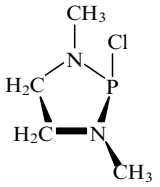
VI. Dialkylphosphoramidites

To date, a normal coordinate analysis has been performed only for four compounds containing Alk_2NP^{III} groups. The simplest molecules, such as dimethylphosphoramidodifluoridite

(**40**)[114–116] and dimethylphosphoramidodichloridite (**41**),[117] adopt single conformations. The structure of molecule **40** was studied by X-ray analysis,[118] gas-phase electron diffraction,[119] and microwave spectroscopy.[116,120] However, two structures of the $(CH_3)_2NP$ fragment were proposed, a planar[118] and a pyramidal one.[119] Later, the results obtained in the former study[119] were critically reviewed[116,120] since structural parameters of the molecule **40** obtained in more recent studies appeared to be in agreement with the data of the X-ray study.[118] The results of gas-phase electron diffraction investigations[121–123] of molecules **41**, $[(CH_3)_2N]_2PCl$ (**42**) and 2-chloro-1,3-dimethyl-1,3,2-diazaphospholane (**43**) also suggested that the dialkylamino group at the trivalent phosphorus atom has a nearly planar structure. It was found that this group in the molecule **40** is oriented parallel to the LEP of the phosphorus atom.[116,118,120] Based on the results obtained in studies on the vibrational[117] and NMR spectra,[124] a similar conformation was suggested for the molecule of compound **41**. At the same time, it was stated[121] that the $(CH_3)_2NP$ group is oriented perpendicular to the LEP of the phosphorus atom. Spectra of molecules **40**, **41** and fully deuterated derivative of compound **41** have been studied[114,117] and a normal coordinate analysis was performed[125] for the conformations with eclipsed arrangement of the plane of the dimethylamino groups and the LEP of the phosphorus atom. It was also assumed that the molecules have no symmetry elements because of the non-symmetrical orientation of methyl groups.

The initial empirical interpretation of the spectra of dimethylphosphoramidodifluoridite **40** (see Ref. 117) was essentially different from that based on the results of normal coordinate analysis (see Ref. 125). In addition, the experimental vibrational spectra reported by Durig and Casper[117] contained some 'extra' Raman lines and IR absorption bands as compared with the spectra reported earlier.[114] Probably, they are due to impurities formed as a result of partial hydrolysis. Because of this, Table 18 lists the experimental results[114] interpreted on the basis of normal coordinate analysis.[125] After publication of the study cited (Ref. 125), new spectra of dimethylphosphoramidodifluoridite **40** and its D-isotopomers have been reported,[116] which are somewhat different from those published previously.[114]

The molecules of tetramethylphosphorodiamidochloridite and 2-chloro-1,3-dimethyl-1,3,2-diazaphospholane adopt single conformations.[126,127] The equilibrium conformation of the molecule **43** has a C_s symmetry (see Refs 123, 127).



The vibrational spectra of compound **42** (Table 19) have been interpreted[127] assuming that both dimethylamino groups in the molecule are arranged so that they are nearly eclipsed by the LEP of the phosphorus atom. The results of normal coordinate analysis for this conformer with C_s symmetry are in good agreement with experimental data.[127] At the same time, it should be noted that, according to the electron diffraction data,[122] molecule **42** has an non-symmetrical conformation. The spectra of compound **43** listed in Table 20 are given in accordance with the known interpretation.[127]

Analysis of the spectra of phosphoramides based on the results of normal coordinate analysis (see Table 18–20) made it possible to establish the nature of the bands characteristic of the $(CH_3)_2NP$ group. It is known[1–5] that the bands of medium or high intensity in the frequency range $\sim 1260-1320$ cm^{-1} are observed in the IR spectra of compounds with these groups. These bands are associated with the vibration in which a symmetric stretch of both N–C bonds [the $\nu_s(NC_2)$ vibration] is accompanied by contraction of the P–N bond [the ν(P–N) vibration]. The frequency of synchronous stretch of the three bonds lies in the range $\sim 650-700$ cm^{-1}. The corresponding IR absorption bands

Table 18. Interpretation of vibrational spectra of dimethylphosphoramidodifluoridite.

No.	Assignment	Raman (l)	IR (g)
13	$r(CH_3)$, ν(PN), $\nu_s(NC_2)$, $\delta(NC_2)$	1306, m, p	1307, m
14	$\nu_{as}(NC_2)$, $r(CH_3)$		1195, m
15	$r(CH_3)$	1103, vw	
16	$r(CH_3)$	1071, w, dp?	1073, w
17	$r(CH_3)$, $\nu_{as}(NC_2)$		1002, sh [a]
18	ν_{as}(PNC), $r(CH_3)$	989, m, dp?	989, s
19	$\nu_s(PF_2)$	792, m, p?	814, s
20	$\nu_{as}(PF_2)$	743, m, dp?	770, s
21	$\nu_s(NC_2)$, ν(PN)	705, vs, p	704, m
22	$\delta(PF_2)$, $r(NC_2)$	495, m	501, w, br
23	$\delta(NC_2)$, $\delta(PF_2)$	393, w	
24	$t(PF_2)$, φ [b,c]	393, w	
25	$r(NC_2)$, $\delta(PF_2)$	336, m	
26	$w(PF_2)$, $r(NC_2)$	239, w	
27	φ, [b] χ [b]	173, w	
28	χ, [b] φ [b,d]	97, vw	

[a] From the spectrum of crystals.

[b] The character φ denotes the out-of-plane deviation of the P–N bond with respect to the CNC plane and the character χ denotes torsional vibrations about the P–N bond.

[c] A strong band at 343 cm^{-1} in the IR spectrum and a weak Raman line at 346 cm^{-1} in the spectra of low-temperature crystals were also associated with this vibration.[116]

[d] Weak peaks at ~ 116 cm^{-1} in the IR spectra were also associated with this vibration.[116]

Table 19. Interpretation of vibrational spectra of tetramethylphosphoramidochloridite.

No.	Symmetry	Assignment	Raman (l)	IR (l) [a]
13	A′	$r(CH_3)$, ν(PN) – $\nu_s(NC_2)$		1280, sh
41	A″	$r(CH_3)$, ν(PN) – $\nu_s(NC_2)$	1275, 6, 0.3	1271, s
14	A′	$\nu_{as}(NC_2)$, $r(CH_3)$	1185, vw	1192, s
42	A″	$\nu_{as}(NC_2)$, $r(CH_3)$	1140, vw, 0.8	1140, w
43	A″	$r(CH_3)$	1090, vw	1095, w
15	A′	$r(CH_3)$		1082, vw
16	A′	$r(CH_3)$	1060, 6, 0.8	1061, m
44	A″	$r(CH_3)$		1029, vs
17	A′	$r(CH_3)$		1029, vw
45	A″	$r(CH_3)$		1029, vs
46	A″	$\nu_s(NC_2)$ – ν(PN), $r(CH_3)$	980, 9, 0.8	980, vs
18	A′	$\nu_s(NC_2)$ – ν(PN), $r(CH_3)$	960, 7, 0.8	960, vs
47	A″	$\nu_s(NC_2)$ + ν(PN)	695, w, sh	698, s
19	A′	$\nu_s(NC_2)$ + ν(PN)	670, 100, 0.12	671, m
20	A′	ν(PCl), $r(NC_2)$	490, vw	488, m, br
21	A′	ν(PCl), $\delta(PN_2)$	410, 9, 0.4	415, m, br
48	A″	$\delta(PN_2)$, $w(NC_2)$	410, 9, 0.4	
22	A′	ν(PCl), $w(NC_2)$	385, 6, 0.4	
49	A″	$r(NC_2)$, $w(NC_2)$	385, 6, 0.4	
23	A′	ν(PCl), $\delta(NC_2)$	335, 67, 0.25	
50	A″	$r(NC_2)$, $\delta(NC_2)$	335, 67, 0.25	
24	A′	$w(NC_2)$, χ(N–CH_3)	292, 52, 0.3	
51	A″	$w(NC_2)$, χ(N–CH_3)	292, 52, 0.3	
52	A″	$w(NC_2)$	125, 3.7, dp	

[a] Spectral region below 400 cm^{-1} has not been recorded.

Table 20. Interpretation of vibrational spectra of 2-chloro-1,3-dimethyl-1,3,2-diazaphospholane.

No.	Symmetry	Assignment	Raman (l)	IR (l) [a]
10	A′	$w(CH_2)$, $\nu(P-N)$	1250, 1.6, p	
11	A′	$\nu(N-CH_3)$, $t(CH_2)$	1238, 1.8, p	1235, s
36	A″	$\nu(N-CH_3)$, $t(CH_2)$		1217, s
37	A″	$\nu_{as}(PNCH_3)$, $t(CH_2)$	1205, 2.9, dp	1205, w, sh
12	A′	$\nu_{as}(PNCH_3)$, $t(CH_2)$	1180, 3.3, p	1180, vw
13	A′	$\nu(N-CH_2)$, $r(CH_3)$, $w(CH_2)$		1148, s
38	A″	$\nu(N-CH_2)$, $r(CH_3)$, $w(CH_2)$	1125, 1.6, 0.7	
39	A″	$r(CH_3)$	1085, 0.8, 0.8	
14	A′	$r(CH_3)$		1055, w
15	A′	$r(CH_3)$, $\nu(C-C)$	1030, 9.5, 0.4	1030, s
40	A″	$r(CH_2)$	1012, sh, dp	1010, m
41	A″	$\nu(N-CH_2)$	948, 2, 0.7	946, s
16	A′	$\nu(N-CH_2)$, $\nu(C-C)$	855, 1.4, 0.8	855, br, sh
17	A′	$r(CH_2)$	830, 0.3	
18	A′	ν pulse	710, 100, 0.08	706, m
42	A″	$\nu(P-N)$	692, sh	692, m
43	A″	ring δ	597, 10.5, 0.86	595, w
19	A′	$\nu(P-Cl)$, $r(P-Cl)$	490, 18.4, 0.34	490, m
20	A′	$\nu(P-Cl)$	392, 12.6, 0.3	
44	A″	$r(N-CH_3)$	355, 11, 0.83	
45	A″	$\gamma(N-CH_3)$, ring χ	310, sh	
21	A′	ring δ	300, 29.5, p	
22	A′	$r(N-CH_3)$	268, 27.9, 0.25	
46	A″	$\chi(N-CH_3)$	245, br. sh	
25	A′	$\gamma(N-CH_3)$	112, 30, 0.6	

[a] Spectral region below 400 cm^{-1} has not been recorded.

are, as a rule, rather weak, while the Raman lines are intense and strongly polarised.

The vibration $\nu_{as}(NC_2)$ with predominant contributions of the antiphase stretch and tension of the N–C bonds interacts with the stretching vibration $\nu(P-N)$. One of the two resultant vibration appears as a band of strong or medium intensity in the IR spectrum in the region 1140–1210 cm^{-1}. For the trivalent phosphorus compounds, this band is shifted towards high frequencies in this spectral region. The other resultant vibration gives rise to a strong IR absorption band[1] in the region $\sim$ 935–1008 cm^{-1} (a narrower spectral region $\sim$ 940–980 cm^{-1} has also been reported[4,5]). The corresponding Raman lines are usually weak, as are the lines corresponding to the $r(CH_3)$ rocking vibrations, which appear in the IR spectra of molecules containing the $(CH_3)_2NP$ groups as bands of medium intensity in the frequency range $\sim$ 1050–1080 cm^{-1}.

Two or even three peaks can be observed in these spectral regions for diamides and triamides (see Tables 19, 20). The bands due to the vibrations with the contributions of the vibrations $\nu(P-N)$ and $\nu_{as}(NC_2)$ in the frequency range 1140–1210 cm^{-1} or the vibration $\nu_s(NC_2)$ in the frequency ranges 935–1008 and 650–700 cm^{-1} are mainly split. The splitting is to a great extent caused by the kinematic interaction between the dimethylamino groups through the shared phosphorus atom.[127]

It is of interest to compare the spectra of acyclic compound **42** (see Table 19) and its cyclic analogue **43** (see Table 20). A distinctive feature of the vibrational spectra of 2-chloro-1,3-dimethyl-1,3,2-diazaphospholane **43** is that they contain the lines at 1370, 1342 and 830 cm^{-1} corresponding to the methylene groups, as well as the lines at 855 and 597 cm^{-1} caused by the ring vibrations. As in the case of acyclic compound **42**, the strongest line in the Raman spectrum of the phospholane **43** is associated with the totally symmetrical vibration with the contribution of the P–N bonds. However, for compound **43** the frequency of this line (710 cm^{-1}) is shifted as compared with that of tetramethylphosphoramidochloridite **42** (670 cm^{-1}), whereas the frequencies of the corresponding antisymmetrical vibrations (692 cm^{-1}) remain virtually unchanged.

VII. Phosphorothioites

A rather large number of studies dedicated to the interpretation of the spectra of phosphorothioites has been reported. Normal coordinate analyses were performed for cyclic and acyclic molecules with one, two and three RSP groups, where R are various alkyl, dithiocarbamoyl and dithiophosphoryl radicals. The simplest representative of phosphorothioites, methyl phosphorodichloridothioite (**44**), exists in the liquid and gas phases as a mixture of the *T* and *G* conformers (see Fig. 1; X = Cl, Y = S, Z = CH_3).[103,128] Vibrational spectra of compound **44** have been interpreted[129] assuming that the molecule adopts a single conformation. Then, it was established[103] that the molecule adopts several conformations, the previous assignments[129] were refined and a normal coordinate analysis was performed for the spectrum of compound **44**. These results are listed in Table 21.

Table 21. Interpretation of vibrational spectra of methyl phosphorodichloridothioite.[a]

No.	Symmetry	Assignment	Raman (l)	IR (l) [b]
		$\nu_s[PCl_2(G)]$	516, m	520, sh
7	A′	$\nu_s(PCl_2)$	496, m	496, s, br
		$\nu_{as}[PCl_2(G)]$	481, sh	
15	A″	$\nu_{as}(PCl_2)$	474, s	472, s
8	A′	$\nu(P-S)$	461, m	466, s, br
9	A′	$\delta(PSC)$	318, s	
		$\delta[PSC(G)]$	262, s	
16	A″	$t(PCl_2)$	202, vs	
10	A′	$\delta(PCl_2)$	185, m	
		$w[PCl_2(G)]$	168, w	
11	A′	$w(PCl_2)$	150, sh	

[a] See note to Table 2. [b] Spectral region below 400 cm^{-1} has not been recorded.

The molecule of ethyl phosphorodichloridothioite (**45**) can adopt five stable conformations[130] (see Fig. 2; X = Cl, Y = S). Vibrational spectra of compound **45** have been interpreted using the results of normal coordinate analysis.[130] It has been shown that internal rotation about both the P–S and S–C bonds occurs in the neat liquid and in solutions. However, it was not established whether the *Gg* and *Gg′* conformations or at least one of them do exist (we only can say that the existence of these conformers does not contradict experimental data). Keeping this in mind, the spectra of ethyl phosphorodichloridothioite **45** can be interpreted in different ways, since some of the frequencies can be attributed to either the *Tg* conformers or the *Tg*, *Gg* and *Gg′* conformers simultaneously. These frequencies are denoted by a character '*g*'. The bands, which can be attributed to the *Gt*, *Gg* and *Gg′* conformers are denoted by a character '*G*'. A version[130,131] of the interpretation of the spectra of compound **45** is listed in Table 22.

The molecule of propyl phosphorodichloridothioite (**46**) can adopt 14 spectroscopically discernible conformations, of which three are shown in Fig. 4. It was established that the *T*, *G*, *gt′*, *tt′*, *gg′* and tg′ conformers of the molecule **46** (for the meaning of notations, see Fig. 4) exist in the liquid and in solutions and a normal coordinate analysis was performed for all possible conformers.[132] Attempts to establish exact composition of such a complex mixture of conformers have failed.

The molecule of isopropyl phosphorodichloridothioite (**47**) can adopt five spectroscopically discernible conformations (Fig. 5). The bands associated with internal rotation about the P–S and S–C bonds of the molecule are observed in the vibra-

Table 22. Interpretation of vibrational spectra of ethyl phosphorodichloridothioite.[a]

No.	Symmetry	Assignment	Raman (l)	IR (l) [b]
		$r[CH_2(g)]$		780, vw
22	A″	$r(CH_2)$	765, 1	765, w
10	A′	ν(SC), δ(SCC), δ(PSC)	655, 18, p	655, w
		δ(SC), δ(SCC), δ[PSC(g)]	645, 21, p	645, w
		$\nu_s[Cl_2PS(G)]$	510, 36, p	514, vs
11	A′	$\nu_s(Cl_2PS)$	500, sh, p	500, vs
12	A′	$\nu_s(PCl_2)$, ν(P−S)	474, 100, p	476, vs
		$\nu_{as}[PCl_2(Tg,Gt,Gg,Gg)]$	493, sh, dp	
23	A″	$\nu_{as}(PCl_2)$	460, sh, dp	
		δ(SCC), δ[PSC(g)]	340, 11, p	
13	A′	δ(SCC), δ(PSC)	320, 4, p	
14	A′	δ(PSC), δ(SCC)	260, 27, p	
		δ(PSC), δ[SCC(G)]	248, 32, p	
24	A″	$t(PCl_2)$	190, 44, dp	
15	A′	$\delta(PCl_2)$		
16	A′	$w(PCl_2)$, δ(SCC)	135, 10, p	

[a] See note to Table 3.
[b] Spectral region below 400 cm^{-1} has not been recorded.

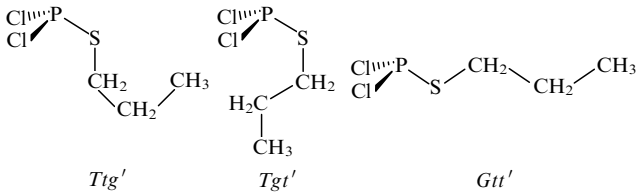


Figure 4. Conformers of the molecule of propyl phosphorodichloridothioite:
Ttg′ stands for *trans*,*trans*,*gauche*, *Tgt′* for *trans*,*gauche*,*trans* and *Gtt′* for *gauche*,*trans*,*trans*; *T* and *G* denote the *trans* and *gauche* conformers formed owing to rotation about the P−S bond; *t* and *g* denote the *trans* and *gauche* conformers formed owing to rotation about the S−C bond and t′ and g′ denote the *trans* and *gauche* conformers formed owing to rotation about the C−C bond.

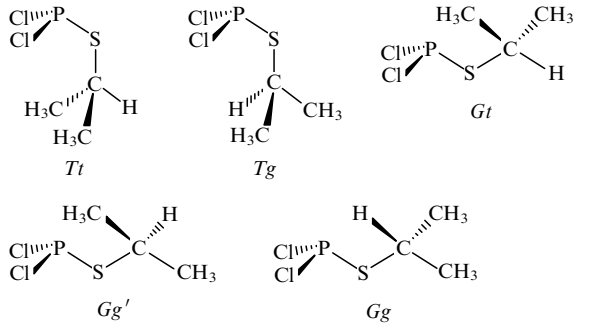
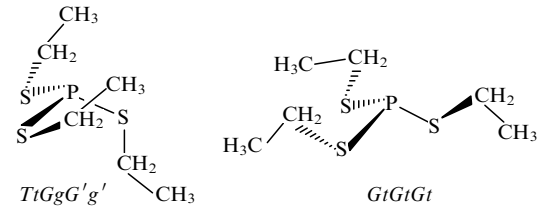


Figure 5. Conformers of the molecule of isopropyl phosphorodichloridothioite:
Tt stands for *trans*,*trans*, *Tg* for *trans*,*gauche*, *Gt* for *gauche*,*trans*, *Gg* for *gauche*,*gauche* and *Gg′* for *gauche*,*gauche′*.

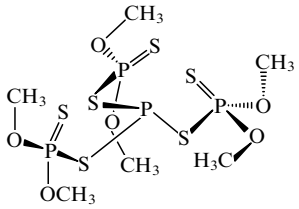
tional spectra of liquid **47**.[132] Only the *Tg* conformer is retained upon crystallisation.

The number of possible conformers of the molecule of triethyl phosphorothioite (**48**) is as large as 36. Nevertheless, experimental spectra of neat (liquid) compound **48** and its solutions can be interpreted [130] assuming that its molecule has only two conformers.

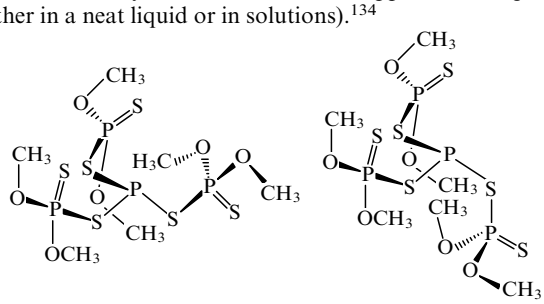


Here, the first two characters denote the conformation of one C_2H_5SP group of the molecule **48**, while the next two pairs of characters denote the conformations of the other two identical groups. It has been reported that only the *TtGgG′g′* conformer is retained upon crystallisation.[130]

In the crystalline phase, the equilibrium conformation of the molecule of *S*,*S′*,*S″*-tris(dimethoxythiophosphoryl) phosphorotrithioite (**49**) has a C_3 symmetry (see Ref. 133)

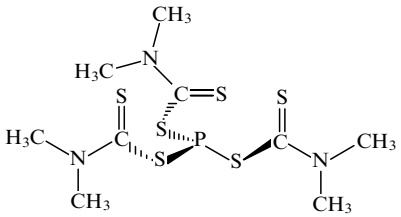


Other, non-symmetrical conformers appear in the liquid phase (either in a neat liquid or in solutions).[134]



This gives rise to additional peaks in the spectra. Normal coordinate analysis for all possible conformers of the molecule **49** shows [134] that additional bands can be attributed to the non-symmetrical conformers. Some bands were assigned to those conformers which can be formed from all the three conformers shown above by changing the arrangement of the methoxy groups of the $(CH_3O)_2P(=S)$ fragment from *gauche′*, *gauche* with respect to the P=S bond to the *gauche*, *gauche* or *gauche*, *trans* with respect to the same bond. The presence of other conformers also does not contradict the results of spectral experiments.[134]

The equilibrium conformation of the molecule of *S*,*S′*,*S″*-tris-(*N*,*N′*-dimethylthiocarbamoyl) phosphorotrithioite (**50**) in the crystalline phase has a C_3 symmetry group (see Ref. 135).



According to the vibrational spectroscopy data,[136] the molecule of compound **50** in solutions retains a single conformation.

According to the results of the gas-phase electron diffraction study,[137] the molecule of 2-chloro-1,3,2-dithiaphospholane (**51**) adopts a symmetrical 'envelope' conformation with an apical phosphorus atom and an axial P−Cl bond. On the other hand, data obtained in the NMR [138] and vibrational spectroscopic [108] studies indicate that the molecule of compound **51** adopts a non-symmetrical conformation. Calculations by the molecular mechanics method predict the *a*-E_C conformation of molecule **51**

Table 23. Interpretation of vibrational spectra of 2-chloro-1,3,2-dithiophospholane.

No.	Assignment	Raman (l)	IR (l) [a]
11	ν(C−C)	987, 0, 0.73	990, w
12	r(CH_2)	938, 0, 0.45	942, m
13	r(CH_2), δ(CCS)	825, 0, 0.78	830, w
14	ν(C−S), δ(CCS), r(CH_2)	664, 10, 0.43	665, w
15	ν(C−S), δ(CCS)	646, 50, 0.13	647, m, s
16	ν(P−Cl), ν_s(PS_2)	480, 100, 0.1	482, w, br
17	δ(PSC), δ(CCS)	440, 40, 0.76	442, w
18	ν(P−S), δ(CCS)	415, 40, 0.30	420, w, br
19	ν(PS_2)	362, 50, 0.27	352, ms
20	δ(PSC), δ(SPS), δ(SPCl)	255, 10, 0.67	256, w
21	δ(SPS), δ(CCS)	196, 30, 0.63	
22	δ(SPCl)	175, 40, 0.85	
23	ring puckering [b]	102, 20, 0.78	
24	ring puckering [b]	102, 20, 0.78	

[a] Spectral region below 400 cm^{-1} has not been recorded.
[b] Nonplanar vibration.

(see Fig. 3; X = Y = S). Table 23 lists the interpretation of the vibrational spectra of 2-chloro-1,3,2-dithiaphospholane **51** for this conformation.[108] Experimental spectral parameters[108] of liquid compound **51** coincide with previously reported data,[139] except for the degrees of depolarisation of the Raman lines.

Stretching vibrations of the P−S and S−C bonds are most pronounced in the spectra of all the above-mentioned alkyl phosphorothioites. The vibrations ν(S−C) can mix with the deformations of the alkylthio group and PSC fragment (Table 24), which is responsible for the variations in the intensities of the corresponding IR absorption bands (from weak to medium) and Raman lines (from medium to strong). The phosphorus-containing fragment of the molecule contributes negligibly to the potential energy of this vibration, therefore its frequency depends on the structure of the alkylthio group. Because of this, the ν(S−C) 'fingerprint' spectral regions[87] of phosphorothioites nearly coincide with those of different organosulfur compounds. It is more convenient to identify stretching vibrations of the S−C bond using the Raman spectra, since the corresponding lines are rather strong and polarised. If internal rotation of the alkylthio groups about the S−C bond can lead to inequivalent orientations of these groups with respect to the P−S bond, the Raman lines become multiplets.

It is also desirable to identify the P−S bonds using the Raman spectroscopy. The stretching vibrations ν(P−S) in the molecules of alkyl phosphorodichloridothioites are strongly coupled with symmetrical stretching vibrations of the PCl_2 group. One of the two resultant vibrations appears as strong bands in the IR spectrum and polarised Raman lines of medium or strong intensity in the region $\sim 490-530$ cm^{-1}. The second vibration is associated with very strong polarised Raman lines and strong IR absorption bands in the region $\sim 460-480$ cm^{-1}. If the molecules of compounds under study can adopt several conformations, all these bands are, as a rule, multiplets; it is noteworthy that polarised Raman lines can have depolarised 'shoulders'.

The vibrations ν(P−S) can also interact with vibrations of other groups at the phosphorus atom (see Table 24). Nevertheless, the presence of both a strong polarised Raman line and an IR absorption band of medium or strong intensity in the region $\sim 470-540$ cm^{-1} can be considered to be a reliable spectral indicator of the single P−S bond, while multiplet IR and Raman spectra in this spectral region can be regarded as an indicator of the existence of different conformers due to the internal rotation about this bond. This spectral region is characteristic of acyclic molecules. For cyclic phosphorothioites, the frequencies of the stretching vibrations P−S can be substantially lower.

Table 24. Vibrations of fragments of the molecules with contributions of the P−S, P−Cl and S−C bonds in the spectra of organophosphorus compounds.

Molecule	Assignment	Raman (l)	IR (l)
CH_3SPCl_2	ν_s[$PCl_2(G)$]	516, m	520, sh
	ν_s[$PCl_2(T)$]	496, m	496, s, br
	ν_{as}[$PCl_2(G)$]	481, sh	472
	ν_{as}[$PCl_2(T)$]	474, s	
	ν(P−S)	461, m	466, s, br
$C_2H_5SPCl_2$	ν(S−C), δ(SCC), δ[PSC(t)]	655, m, p	655, w
	ν(S−C), δ(SCC), δ[PSC(g)]	645, m, p	645, w
	ν_s[$Cl_2PS(G)$]	510, s, p	514, vs
	ν_s[$Cl_2PS(T)$]	500, sh, p	500, vs
	ν_s(PCl_2), ν(P−S)	474, vs, p	476, vs
	ν_{as}[PCl_2(Tg,Gt,Gg)]	493, sh, dp	
	ν_{as}[$PCl_2(Tt)$]	460, sh, dp	
n-$C_3H_7SPCl_2$	ν(S−C), δ[SCC(tt')]	720, sh	
	ν(S−C), δ[SCC(tg')]	645, w, p	
	ν(S−C), δ[SCC(gg')]	635, w, p	
	ν_s[$Cl_2PS(G)$]	510, s, p	
	ν_s[$Cl_2PS(T)$]	500, sh	
	ν_s(PCl_2), ν(P−S)	475, vs, p	
	ν_{as}[PCl_2(Tg,Gt,Gg)]	492, sh, dp	
	ν_{as}[$PCl_2(Tt)$]	455, s, dp	
iso-$C_3H_7SPCl_2$	ν[S−C(g)]	615, w, p	
	ν[S−C(t)]	610, sh	
	ν_s[$Cl_2PS(G)$]	527, s, p	
	ν_s[$Cl_2PS(T)$]	505, sh, p	
	ν_s(PCl_2), ν(P−S)	475, vs, p	
	ν_{as}[$PCl_2(G)$]	490, sh, dp	
	ν_{as}[$PCl_2(T)$]	450, sh, dp	
	ν(S−C), δ(SCC), δ[PSC(t)]	665, sh, 0.5	
	ν(S−C), δ(SCC), δ[PSC(g)]	650, s, 0.3	650, w
	ν(P−S), r[PCCl(G)]	498, vs, 0.1	503, m
	ν(P−S), r[PCCl(T)]	482, sh, 0.3	486, m
	ν(C−S), δ(CCS), δ(CCO)	679, s, 0.35	680, w
	ν(P−Cl)	469, vs, br, 0.3	470, vs
	ν(P−S)	414, vs, br, 0.3	415, vs
	ν(C−S), δ(CCS), r(CH_2)	664, w, 0.4	665, w
	ν(C−S), δ(CCS)	646, w, 0.1	647, ms
	ν(P−Cl), ν_s(PS_2)	480, vs, br, 0.1	482, w, br
	ν(P−S), δ(CCS)	415, s, br, 0.3	420, w, br
	ν(PS_2)	362, s, 0.3	352, ms
$(C_2H_5S)_3P$	ν_{as}(PS_3)	515, sh, p?	513, s
	ν_{as}(PS_3)	485, s, dp?	485, vs
	ν_s(PS_3)	485, vs, p	455, s
$[(CH_3O)_2P(S)S]_3P$	ν_s[PS_3(gg)], ν_s(PS_3) ν_s(PSP)	523, s [a] 498, vs, p [a]	523, m [a] 498, sh [a]
	ν(P^vS) ν_{as}(PSP)	485, sh, dp [a]	485, w [a]
$[(CH_3)_2NC(S)S]_3P$	ν_s(PS_3)	483, s [b]	485, vw [b]
	ν_{as}(PS_3)	464, s [b]	465, m [b]

[a] Melt. [b] Crystals.

Effective coupling of the stretching vibrations of three P−S bonds in the molecules of trialkyl phosphorotrithioites gives rise to three new resultant motions (see Table 24). Symmetrical

stretching vibrations of all the three P—S bonds of the PS_3 group appear in the spectral region ~ 430–470 cm^{-1}. The corresponding Raman lines are very intense and strongly polarised and the IR absorption bands are of medium or strong intensity. Two antisymmetric vibrations $\nu_{as}(PS_3)$ appear as very strong bands in the IR spectrum and strong Raman lines in the region ~ 460–500 cm^{-1} and as peaks of medium intensity in the region ~ 500–570 cm^{-1}. All the above-mentioned vibrations can be 'conformationally sensitive', therefore some 'extra' peaks can be observed in these regions of the spectra of those trialkyl phosphorotrithioites which can exist as a mixture of conformers.

If the molecules of trialkyl phosphorotrithioites have a C_3 symmetry, both antisymmetric vibrations $\nu_{as}(PS_3)$ become degenerate, *i.e.*, have equal frequencies. This is the case for *S*,*S*′,*S*″-tris-(*N*,*N*-dimethylthiocarbamoyl) phosphorotrithioite **50** (see Table 24), for which a singlet IR absorption band and a singlet Raman line corresponding to the vibration $\nu_{as}(PS_3)$ are observed. Unlike the spectra of trialkyl phosphorotrithioites, the frequency of symmetric vibration $\nu_s(PS_3)$ in these spectra is higher than that of antisymmetric vibration $\nu_{as}(PS_3)$ (~ 485 *vs.* ~ 465 cm^{-1}, respectively).

This also holds for compound **49** (see Table 24) that is, the $\nu_s(PS_3)$ frequency is as high as nearly 500 cm^{-1}, while the $\nu_{as}(PS_3)$ frequency is 485 cm^{-1}. According to Thomas,[1] the IR absorption bands and Raman lines characteristic of compounds with the $P^{III}SP$ group are usually observed in nearly the same spectral region (~ 480–510 cm^{-1}). As can be seen from the data listed in Table 24, they should be attributed to the stretching vibrations of this group.

VIII. Compounds with Si—P, Ge—P and P—P bonds

Silylphosphine (**52**), (trifluorosilyl)phosphine (**53**) and germylphosphine (**54**) are rare examples of the trivalent phosphorus compounds with Group IV elements for which normal coordinate analysis has been performed. The spectra of compound **52** and its fully deuterated analogue have been interpreted.[140,141] Analysis of the spectra of both these molecules [141] has led to some changes in the vibrational assignments suggested earlier.[140] Vibrational spectra of compound **53** and its fully deuterated analogue were interpreted using the results of normal coordinate analysis [142] and the spectra of phosphine **54** and its three D-isotopomers were studied.[143]

A salient feature of the vibrational spectra of silyl- and germylphosphines is that they contain the peaks which correspond to the stretching vibrations ν(Si—P) and ν(Ge—P). The vibration ν(Si—P) appears in the region ~ 300–530 cm^{-1}, while the vibration ν(Ge—P) appears in the region ~ 290–410 cm^{-1}. Both stretching vibrations can mix with skeletal deformations of the molecules (Table 25). This probably results in substantial variations of the intensities of the corresponding peaks. The vibrations ν(Si—P) in the molecules of acyclic organophosphorus compounds appear in a somewhat narrower spectral region ~ 380–530 cm^{-1}. The vibrations $\nu_{as}(PH_2)$, $\nu_s(PH_2)$, $\delta(PH_2)$, characteristic of all primary phosphines, appear in the spectra of compounds under consideration in nearly the same way as in the spectra of alkylphosphines. For primary phosphines, the $\nu(PH_2)$ frequencies are somewhat higher while the $\delta(PH_2)$ frequencies are somewhat lower than those indicated in Section II.

In Table 25, the frequencies of these characteristic vibrations of the phosphino group are also given for the molecule of diphosphane (**55**). As can be seen, the frequencies of stretching and deformation vibrations of the PH_2 groups of the molecule **55** lie far beyond the limits of the spectral regions characteristic of alkyl-, silyl- and germylphosphines and their halogen-substituted derivatives.

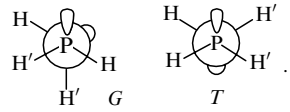
Only the *G* conformers have been detected in diphosphane **55** (see Refs 144–146). Vibrational spectra of diphosphane have been studied.[144,147–149] Table 25 lists the interpretation [144] of the spectra, which is based on the results of normal coordinate analysis for molecules **55** and $P_2H_2D_2$. Vibrational assignments made in the framework of *ab initio* calculations [146] of the force field of the molecule **55** differ only slightly from those listed above.

Table 25. Spectral indications of characteristic vibrations of molecules X_nAPY_m (A = Si, Ge, P).

Molecule	Assignment	Raman	IR
H_3SiPH_2	$\nu_{as}(PH_2)$		2312 (g)
	$\nu_s(PH_2)$		2312 (g)
	$\delta(PH_2)$		1072 (g)
	ν(Si—P)		454 (g)
F_3SiPH_2	$\nu_{as}(PH_2)$		2318, s (g)
	$\nu_s(PH_2)$	2310, s (l)	2312, s (g)
	$\delta(PH_2)$	1062, vw (l)	1069, s (g)
	ν(Si—P), $\delta_s(SiF_3)$	507, vs (l)	512, vs (g)
H_3GePH_2	$\nu_{as}(PH_2)$	2304, dp (l)	2320, s (g)
	$\nu_s(PH_2)$	2293, p (l)	2310, s (g)
	$\delta(PH_2)$		1080, R mw (g) [a] 1065, P vw (g) [a]
	ν(Ge—P), $w(PH_2)$	363, p	371, R? 352, P?
H_2PPH_2	ν_{as}(P—H)		2299, vs (cr)
	ν_s(P—H)	2295, vs (cr)	2312, vs (g)
	ν_{as}(P—H′) [b]	2320, vs (g)	2281, vs (cr)
	ν_s(P—H′) [b]	2268, vs (cr)	
	$\delta(PH_2)$, δ(PPH) (B) [c]	1054, s (cr)	1081 (g)
	$\delta(PH_2)$, δ(PPH) (A) [c]	1037, s (cr)	
	ν(P—P)	438, s (g)	
I_2PPI_2	ν(P—P), ν(P—I)	319, vw (cr)	
	ν(P—I), ν(P—P)	307, vs (cr)	
$(CF_3)_2PP(CF_3)_2$	ν(P—P), $\nu_s(PC_2)$	486, m, p (l)	~ 497, vw (g)

[a] Characters R and P denote the branches of the contours of the IR absorption bands.

[b] The meaning of notation H′ is clearly seen from the Newman projections of possible conformations of diphosphane and its derivatives:



[c] Symmetry species of vibrations.

Initially, the spectra of solutions of tetraiododiphosphane (**56**) were interpreted assuming the *gauche* conformation of the molecule.[150] However, it was shown later [151] that the *trans* conformation exists in fact both in the crystal and in solutions. Taking into account the results of normal coordinate analysis of the molecule **56** (see Ref. 152), some vibrational assignments in the low-frequency region were changed compared to those reported earlier.[150]

Vibrational spectra of tetrakis(trifluoromethyl)diphosphane (**57**) have been interpreted [153] assuming that the molecule **57** has only the *trans*-conformation with a C_{2h} symmetry. Under this symmetry group, the vibrations of the A_g and B_g types should be Raman active while the vibrations of the A_u and B_u types should be IR active (the so-called principle of alternative exclusion). However, the results of spectroscopic studies [153] indicate that this principle is not obeyed. The fact that the IR absorption band corresponding to the vibration ν(P—P) (see Table 25) is weak is not always a consequence of alternative exclusion. It is known that these bands can also be of weak intensity if the molecules with the P—P bond adopt non-symmetrical conformations. Therefore, the conclusion [153] that the molecule **57** has a C_{2h} symmetry, which is based on the weak intensity of the ν(P—P) band, casts some doubts. Correspondingly, the results of theoretical interpretation of the spectra [153] can appear to be not sufficiently rigorous.

It is convenient to identify the P—P bond in diphosphanes using Raman spectra where the line corresponding to the vibration ν(P—P) is observed in the region $\sim 300-530$ cm^{-1}, has a medium or strong intensity and is polarised (for gases, liquids or solutions).

IX. Rotational isomerism of trivalent phosphorus compounds and its manifestation in vibrational spectra

1. General

If interconversions between stable conformations of a molecule can occur owing to hindered internal rotation and if the conformers are not mirror images, their vibrational frequencies can differ from one another. Because of this, the number of bands and lines in the vibrational spectra of organophosphorus compounds, whose molecules can adopt several conformations, is larger than it should be expected for a single molecular conformation. As a rule, the 'sensitivity' to rotations of a particular molecular fragment about an X—Y bond with respect to another molecular fragment is characteristic of those vibrations to which the bond in question contributes. Usually, the frequencies of other vibrations depend only slightly on the molecular conformation, so that the corresponding IR absorption bands or Raman lines in the spectra of different conformers coincide. Therefore, an equilibrium between N conformers rarely, if ever, leads to the N-fold increase in the number of spectral peaks; rather, it causes multiplet splittings of particular peaks, *e.g.*, the ν(X—Y) or δ(XYZ) peaks. However, the frequencies of vibrations with predominant contribution by a particular molecular fragment can also be dependent on the conformation of another molecular fragment. This dependence is due to changes in either or both the spatial mass distribution and the force constants of the molecule on interconversions between different conformations. Sometimes, the effect of conformations on the vibrational frequencies is so weak that it can be detected only in the low-temperature experiments. In this case, the spectral contours become much narrower and the peaks of different conformers which have been unresolved at room temperature, can be observed as multiplets or as separated bands. In other cases, shifts in the vibrational frequencies due to conformational effects are as large as tens of cm^{-1}. Usually, crystallisation leads to simplification of the conformational composition of most compounds and disappearance of particular spectral bands. The conformational composition depends also on the temperature and polarity of the medium. Therefore, the conditions of spectroscopic experiments can strongly affect the spectra of organophosphorus compounds, whose molecules can adopt several conformations. This should be taken into account when interpreting the spectra.

For instance, the intensities of the bands of conformers of greater polarity usually increase in polar media and decrease on going to non-polar solutions. This correlation can be used for the assignment of spectral peaks to the conformers of different polarities. However, the assignments based on both the experimental results and the results of normal coordinate analysis for possible conformers are the most reliable. It is these vibrational assignments that are generalised in this review and serve as the basis for simple empirical rules which facilitate the interpretation of the spectra of organophosphorus compounds, whose molecules can adopt several conformations.

2. Internal rotation of Alk—P fragments

Alkylphosphines and their derivatives with the general formula $AlkPX_2$ (Alk = C_2H_5, n-C_3H_7, iso-C_3H_7; X = H, F, Cl, CH_3), which are liquids or gases at room temperature, are characterised by the existence of an equilibrium between the G and T conformers formed owing to internal rotation about the P—C bond (see Figs 1, 2). The T conformers are more energetically favourable than the G conformers,[15–21,23,56–61] except for the molecule of ethyl(dimethyl)phosphine;[46,154,155] the energy 'gain' is nearly 1.6 kJ mol^{-1} in the liquid phase and 0.8 kJ mol^{-1} in the gas phase. It should be noted that the enthalpy differences (ΔH) between the T and G conformers are small: they vary from ~ 0.4 to ~ 4.2 kJ mol^{-1} and decrease on going from the liquid to the gas phase. Therefore, liquid or gaseous alkylphosphines exist at room temperature as mixtures of the G and T conformers in comparable proportions.

Many of the vibrations of the T and G conformers have different frequencies (see Tables 2–4). The simplest rule is valid for the conformational 'sensitivity' of the P—C stretching vibrations (Alk = C_2H_5, *iso*-C_3H_7): the frequency of the vibrations ν[P—C(T)] is always lower than that of the vibrations ν[P—C(G)]. The ν[P—C(G)] — ν[P—C(T)] difference for compounds $C_2H_5PX_2$ (X = CH_3, Cl, F) varies between ~ 30 and 60 cm^{-1}. For the molecule **6**, this value decreases to ~ 20 cm^{-1} and is only 7 cm^{-1} for ethylphosphine **4**, so that the doublet band corresponding to the vibrations ν(P—C) can only be observed in the spectra of a solution of ethylphosphine **4** in liquid xenon.[20]

The appearance of *gauche* and *trans* conformers in n-$C_3H_7PX_2$ is due to not only internal rotation about the P—C bond (the G and T conformers, respectively, see Fig. 2; Y = CH_2), but also the rotation with respect to the C—C bond (the g and t conformers, see Fig. 2). The t conformers are ~ 1.3 to 2.9 kJ mol^{-1} more energetically stable than the g conformers, the ΔH values decrease on going from the liquid to the gas phase or to solutions in liquid xenon. It is noteworthy that the enthalpy difference between the *gauche* and *trans* conformers of butane measured in the gas phase [~ 4.2 kJ mol^{-1} (see Ref. 156)] is much larger than the ΔH values for the corresponding n-propylphosphine conformers. Thus, substitution of a methyl group in the butane molecule by a bulky PX_2 group causes a decrease rather than an increase in the probability of the appearance of the *trans* conformers owing to internal rotation about the C—C bond.

The frequencies of the vibrations ν(P—C) of propylphosphines are 'sensitive' to conformational transitions of both the $G \rightleftarrows T$ and $g \rightleftarrows t$ types. For $G \rightarrow T$ transition, the ν(P—C) frequency decreases, as is the case of $C_2H_5PX_2$, whereas the $g \rightarrow t$ transition leads to an increase in this frequency. As a result, the highest-frequency IR absorption band (or Raman line) in the spectra of propylphosphines, corresponding to the vibrations ν(P—C), is characteristic of the Gt conformers, while the frequencies of the peaks of the Tt conformers are $\sim 20-50$ cm^{-1} lower and the peaks of the Gg and Tg conformers are even more shifted towards the low-frequency region (see Table 5). All these correlations between the changes in the frequency of the vibrations ν(P—C) and the conformations of the ethylphosphino and propylphosphino groups are caused mainly by kinematic factors.

Orientations of alkyl groups (*gauche* and *trans*) with respect to the lone electron pair of the phosphorus atom are also characteristic of the molecules of the Alk_2PX or Alk_3P types. In the liquid or gas phase, the molecules of secondary and tertiary phosphines adopt usually several conformations, which is responsible for the appearance of multiplet IR absorption bands and Raman lines corresponding to the symmetrical and antisymmetrical stretching vibrations of the P—C bonds and to some other vibrations (see Table 5). However, all attempts to find general correlations between the molecular conformations and frequencies of any vibrations have failed.

3. Internal rotation of AlkOP fragments

The molecules of compounds with the general formula $ROPX_2$ can adopt either *trans* or *gauche* conformations, which is due to internal rotation about the P—O bond (see Fig. 1; X = CH_3, F, Cl; Y = O; Z = R). The *gauche* conformers are more favourable for X = CH_3, though a detectable amount of *trans* conformers is also present in the liquid phase. On the contrary, the *trans* conformers of alkyl phosphorodichloridites or alkyl phosphorodifluoridites are much more stable. According to the data of *ab initio* quantum-chemical calculations,[91,92] the energy difference between the G and T conformers for X = F is larger than for

X = Cl. In the former case, it is so large that the *G* conformer cannot be detected experimentally.[91,95–97]

No spectral indications of the existence of several conformers was observed for alkyl phosphorodichloridites $ROPCl_2$ (R = CH_3, C_2H_5) in the liquid or gas phase at room temperature.[98–100,103,104] Based on the results of a gas-phase electron diffraction study [101] and measurements of the dipole moments,[99] it was assumed that the molecule **3** adopts a nearly *gauche* conformation. However, a more detailed gas-phase electron diffraction study showed that this molecule adopts the *trans* conformation in the gas phase.[102] Later, additional bands which cannot be attributed to the *trans* conformer were found in the spectra of glassy films of compound **3** and its solutions.[103] The high-frequency component of the doublet at 748/754 cm^{-1} corresponding to the vibrations ν_s(POC) was attributed to the *gauche* conformer. The enthalpy difference between the *gauche* and *trans* conformers determined in CS_2 from the temperature dependence of the relative intensities of the bands at 748 and 754 cm^{-1} was found to be ~ 0.8 kJ mol^{-1} in favour of the latter. However, studies of methyl phosphorodichloridite **3** dissolved in liquid xenon revealed [92] disappearance of some of the bands attributed to the *gauche* conformer.[103] Probably, these bands belong to molecular associates. However, the doublet band at 773/754 cm^{-1} corresponding to the stretching vibrations ν_s(POC) retained in the solution in liquid xenon. It was suggested that this doublet is due to the Fermi resonance, since the relative intensities of the bands at 773 and 754 cm^{-1} were found to be temperature-independent.[92]

It should be emphasised that the enthalpy differences between the *G* and *T* conformers of molecules $AlkOPX_2$ (X = CH_3, F, Cl) have not been measured as yet. The same is also true for the enthalpy differences between the *g* and *t* conformers, which are formed due to internal rotation about the O–C bond in this type of molecules (see Fig. 2, Y = O). These differences seem to be so large that only *t* conformers are observed in the liquid phase at room temperature.[104] This is also typical of the dialkyl ether molecules for which the *trans* conformers formed by internal rotation about the O–C bond are much more energetically favourable ($\Delta H \simeq 4.6–6.3$ kJ mol^{-1}).[157–160] However, their *gauche* conformers are also present in detectable amounts both in the liquid and gas phase at room temperature.

Relative stabilities of the *gauche* and *trans* conformers change drastically upon introduction of the SCN group into the alkyl substituent of the $ROPCl_2$ molecules. The enthalpies of the *G* and *g* conformers of the molecule **35** become much lower than those of the *T* and *t* conformers, respectively.[105] The fact that the 'twist' conformers of the molecule **35** are more energetically favourable was attributed [105] to the effects of hypervalent intramolecular 1–5-attraction between the phosphorus and sulfur atoms. It should be noted that a doublet at 730 to $\sim$ 715 cm^{-1} is observed in the spectra of liquid β-thiocyanatoethyl phosphorodichloridite **35** in the region characteristic of vibrations with predominant contribution of the ν_s(POC) vibration and that the low-frequency line of the doublet disappears upon crystallisation.

Doublet IR absorption bands and Raman lines, assigned to the P–O stretching vibrations, are also observed in the spectra of liquid 2-chloro-1,3,2-oxathiaphospholane **37** ($\sim$ 760 to $\sim$ 750 cm^{-1}), whose molecule can adopt several conformations owing to internal rotation about the P–O bond (see Fig. 3; conformers *a*-E_C and *e*-E_C, X = O, Y = S).[108] The *a*-E_C conformer, which is an analogue of the *T* conformers of acyclic alkoxy derivatives of the trivalent phosphorus compounds, was found to be ~ 2 kJ mol^{-1} more stable than the *e*-E_C conformer (an analogue of the *G* conformers).

Thus, despite some uncertainty in the data on the spectral indications of interconversions of the molecules containing one Alk–O–P group, one can say that they can be detected using the readily identifiable band corresponding to the POC stretching vibrations. However, the corresponding effects are weak and often remain unnoticed in the spectra of liquids measured at room temperature. These effects can be observed if the spectral resolution is improved compared to that of the routine experiments. This can be attained in the low-temperature experiments. The kinematic effect of the $G \rightarrow T$ transition results in a decrease in the ν_s(POC) frequency. However, for 2-chloro-1,3,2-oxathiaphospholane **37** an increase rather than a decrease in this frequency was observed, which is probably due to changes in the force field of the molecule in the course of interconversion of its conformers.

4. Internal rotation of AlkSP fragments

Alkyl phosphorodichloridothioites $AlkSPCl_2$ exist in the liquid and gas phases as mixtures of *T* and *G* conformers [103,128,130–132] which are formed owing to internal rotation about the P–S bond (see Fig. 1; X = Cl, Y = S, Z = Alk). In the liquid phase, the *T* conformers are more energetically favourable [130–132] (*e.g.*, $\Delta H \sim 3.3$ kJ mol^{-1} for Alk = C_2H_5). Nevertheless, the amount of the *G* conformers at room temperature is comparable with that of the *T* conformers. For the molecule **28**, it is possible that great steric hindrances to the formation of the *trans* conformers (conformer A, see Section IV) lead to a decrease in their concentration in the equilibrium mixture. This can be assessed from the intensity ratio of the Raman lines corresponding to the vibrations ν(P–S) of the *gauche* and *trans* conformers (see Table 25).

Rotation about the S–C bond can also be responsible for the formation of the *g* and *t* conformers (see Fig. 2; Y = S; Fig. 4, 5), the *trans* arrangement of the P–S and C–C bonds being more favourable for liquid alkyl phosphorodichloridothioites [130–132] (*e.g.*, $\Delta H_{g-t} \simeq 1.6$ kJ mol^{-1} for Alk = C_2H_5). For Alk = n-C_3H_7, the g' and t' conformers were also detected in the liquid phase [132] which appear due to internal rotation about the C–C bond (see Fig. 4).

The molecules of alkyl phosphorodichloridothioites can adopt several conformations. A distinctive feature of their spectra is that the number of the IR absorption bands and Raman lines is much larger than one could expect. In particular, a complicated spectrum is observed in the region characteristic of the 'cooperative' stretching vibrations of the Cl_2PS fragment at $\sim 450–530$ cm^{-1}. The totally symmetric stretching vibration $\nu_s(Cl_2PS)$ is 'sensitive' only to rotation about the P–S bond and the frequencies of this vibration for the *T* conformers are always lower than those of the *G* conformers ($\sim 495–505$ *vs.* $\sim 510–530$ cm^{-1}, respectively). A similar type of conformational 'sensitivity' was also observed for the frequencies of the vibrations ν(P–S) of the molecule **28** (see Table 25). A decrease in the frequencies of vibrations with contribution of the P–S bond on going from the *G* to *T* conformers is mainly due to changes in the kinematic interactions in the molecule upon this transition.

The frequencies of the antisymmetric vibrations $\nu_{as}(PCl_2)$ of alkyl phosphorodichloridothioites depend on the conformations of the Cl_2PSC and PSCC fragments. The conformation in which the lone electron pair of the phosphorus atom lies in the plane of the PSCC fragment (the *Tt* conformation, see Figs 2 and 4; or the *Tg* conformation, see Fig. 5) is characterised by a frequency in the range between ~ 450 and 460 cm^{-1}. For all other conformations, the characteristic frequency $\nu_{as}(PCl_2)$ is observed at ≈ 490 to 495 cm^{-1} (see Table 25). The corresponding bands in the IR spectrum are masked by a very strong band corresponding to the antiphase stretching vibration of the P–S bond and PCl_2 fragment ($\sim 460–480$ cm^{-1}), which is conformationally 'insensitive'. Because of this, the vibrations $\nu_{as}(PCl_2)$ of different conformers can be identified only in the Raman spectra in which they appear as depolarised shoulders on either side of a very strong polarised line at $\sim 460–480$ cm^{-1} corresponding to the above-mentioned antiphase stretching vibration of the P–S bond and PCl_2 group.

It is also convenient to use the Raman spectra for the attribution of the lines corresponding to the stretching vibrations S–C, the frequency of which depends on not only the structure of the alkyl radical at the sulfur atom, but also the conformation of the PSCC fragment. The conformer with *trans* arrangement of the P–S and C–C bonds (*t*, see Figs. 2 and 4; *g*, see Fig. 5) is

characterised by a higher frequency ν(S−C) than the *gauche* conformer (*g*, see Figs. 2 and 4; *t*, see Fig. 5). Therefore, in the case of a mixture of the *g* and *t* conformers, the vibrations ν(S−C) appear as doublets. For *S*-propyl phosphorodichloridothioite, a triplet rather than a doublet corresponding to the vibrations ν(S−C) is observed (see Table 25). This may be due to the fact that the frequency of this vibration depends on internal rotation about not only the S−C bond, but also the C−C bond. Nevertheless, the high-frequency components of the triplet correspond to the *t* conformation of the PSCC fragment.

The molecules of S,S′,S″-trialkyl phosphorotrithioites $(AlkS)_3P$ are also characterised by the *G* and *T* orientations of the S−C bonds with respect to the LEP of the phosphorus atom and either a *g* or *t* arrangement of the C−C bonds with respect to the P−S bonds. Usually, S,S′,S″-trialkyl phosphorotrithioites exist in the liquid or gas phase as mixtures of the *TGG* and/or *TGG′* conformers with the *GGG* conformers.[130, 131, 161] The latter are less energetically favourable, but are present in considerable amounts at room temperature. Since the molecules of S,S′,S″-trialkyl phosphorotrithioites can adopt several conformations, some of the bands in their vibrational spectra become split into multiplets. However, only correlations between the conformations of the C_2H_5SP fragments and the frequencies of the CH_2 rocking vibrations were found.[130, 131] The *g* arrangement of the C−C bond with respect to the P−S bond corresponds to the $r(CH_2)$ frequency ≈ 780 cm^{-1}, while the *t* arrangement corresponds to the $r(CH_2)$ frequency ~ 760 cm^{-1}. The same is also true for the molecule **45** (see Table 22).

X. Force constants of molecules containing trivalent phosphorus atoms

Among different classes of organophosphorus compounds, the force constants of alkylphosphines and their halogen-substituted derivatives have been studied in most detail. The potential fields of all these molecules share the common property that the effect of the phosphorus atom is confined to the distance to the α-C atom. For instance, the force constants of the CH_3 group of ethyl radical at the phosphorus atom remain virtually the same as in the ethane molecule. Because of this, only frequencies of the vibrations with predominant contribution of the P−C bonds, and those of the methyl and methylene groups bound to the phosphorus atom are specific to alkylphosphines and, hence, can be regarded as having an analytical value.

On the other hand, variation of the alkyl radical in the $AlkPX_2$ molecules affects not only the force constants of the AlkP group, but also the parameters of the potential field of the PX_2 fragment. For instance, the force constants of the P−C and P−X bonds decrease simultaneously as the chain length of the alkyl radical increases.

Force constant	CH_3PF_2	$C_2H_5PF_2$	CH_3PCl_2	$C_2H_5PCl_2$
K_{PC}	2.76	2.54	2.94	2.65
K_{PF}	4.34	4.15		
K_{PCl}			2.08	1.94

For X = H, this dependence can be expressed quantitatively in the form of linear relationships (recall that the force constants are given in 10^2 N m^{-1})[22]

$$K_{PH} = 0.126\,\sigma^* + 3.063,$$

$$K_{PC} = 0.235\,\sigma^* + 2.664,$$

where σ^* is the Taft constant of the alkyl group.[162]

Introduction of halogens into the AlkP fragment leads to a pronounced decrease in the force constant K_{PC} and simultaneous increase in K_{PX}. For instance, the K_{PC} and K_{PCl} values respectively change from 2.94 and 2.08 for CH_3PCl_2[57] to 2.34 and 2.20 for $ClCH_2PCl_2$.[64]

For the same alkyl radical, the force constant K_{PC} depends on the type of substituents X at the phosphorus atom; however, its magnitude changes only slightly and does not obey simple rules. Thus for the CH_3PX_2 molecules the K_{PC} value increases from 2.66 to 2.94 on going from X = H,[13, 14] to CH_3,[13, 14, 43] F[51] and Cl.[57]

The force constants of phosphorus-containing molecules can also be conformation dependent. For instance, the *gauche* → *trans* transition in the molecule **6** causes a decrease in the force constant K_{PH} from 3.05 to 3.01.[22] Despite the small difference between these values, it was found to be reliable, since the P−H stretching vibrations are known to be characteristic.[22] Changes in the conformation of the polar $ClCH_2P$ group has a more pronounced effect on the potential field of the molecule **15**: K_{PF}(*gauche*) = 4.43; K_{PF}'(*gauche*) = 4.51; K_{PF}(*trans*) = 4.08; K_{PC}(*gauche*) = 2.81; K_{PC}(*trans*) = 2.84; K_{CCl}(*gauche*) = 3.09; K_{CCl}(*trans*) = 2.97.

Thus, analysis of the force constants of the molecules of alkylphosphines and their halogen-substituted compounds suggests that the potential field of the phosphorus-containing fragment of the molecule strongly depends on the type and spatial orientation of each substituent at the phosphorus atom. On the other hand, the effect of the phosphorus-containing fragment on the force constants of adjacent groups is confined to the nearest environment of the phosphorus atom.

For phosphines with unsaturated groups at the phosphorus atom, the effect of the latter can likely extend to distances longer than the distance to the α-C atom. The force constants of the fragment $=C(CH_3)_2$ of molecules $Cl_2PCH=C(CH_3)_2$ (see Ref. 75) and $CH_2=C(CH_3)_2$ (see Ref. 160) differ appreciably, thus providing an explanation for the specific values of the characteristic vibrational frequencies of the alkenyl groups at the phosphorus atom. The potential fields of all these molecules share the common property that the force constants of the multiple carbon–carbon bonds at the trivalent phosphorus atom are smaller than those for the corresponding hydrocarbon molecules. The force constant $K_{C=C}$ for the molecules of alkenyl(dichloro)-phosphines is much smaller than those for ethylene and various alkenes and halogen-substituted alkenes [7.9 (Ref. 75) *vs.* 8.3–10.0 (Ref. 163), respectively]. On the other hand, the constants $K_{PC} \simeq 3.1-3.5$ (see Ref. 75) and $K_{PCl} \simeq 2.3$ (see Ref. 75) are larger than the corresponding force constants of alkyl(dichloro)-phosphines [*e.g.*, $K_{PC} = 2.94$ and $K_{PCl} = 2.08$ for the molecule **11** (see Ref. 57)].

A similar situation is also observed for the molecule **29**: the value of the constant $K_{C\equiv C} = 13.85$ (see Ref. 78) 'drops out' of the range between 14.22 and 15.62 (see Refs 164–167), which is characteristic of acetylene and its alkyl- and halogen-substituted derivatives; while the value of the constant $K_{PC} \approx 3.3$ (see Ref. 78) far exceeds the corresponding value [2.9 (see Ref. 43)] for the molecule **8**.

On the other hand, numerical values of the force constants K_{PC} and $K_{C\equiv N}$ for molecules **30** (see Ref. 79) and **31** (see Refs 84, 85) lie within the limits of conventional ranges, which are characteristic of trialkylphosphines and cyanogen halides.[167] Probably, this indicates that the phosphorus atom affects the electronic systems of adjacent C≡N and C≡C groups in a different manner.

For the AlkOP groups, this effect is most likely confined to the distance to the α-C atom of the ester group. In any case, the force constants of the ethyl fragments of molecules $C_2H_5OPCl_2$ (see Ref. 104) and $C_2H_5OC_2H_5$ (see Ref. 168) are nearly equal. On the other hand, the force constant K_{PO} increases by about one unit on going from the ethyl to the methyl substituent.[103, 104] Usually, variation of the nearest environment of the trivalent phosphorus atom has little effect on the force field of the AlkOP groups. For instance, $K_{PO} = 5.97$ and $K_{OC} = 4.91$ for CH_3OPCl_2,[92] while for CH_3OPF_2 these values are $K_{PO} = 5.99$ and $K_{OC} = 4.51$.[91]

For the molecules of dialkylphosphoramides, the dependence of the force constant K_{PN} on the nature of substituents at the phosphorus atom is much more pronounced; for instance, the K_{PN} value increases from 4.5 to 5.1 on going from $(CH_3)_2NPCl_2$ to $(CH_3)_2NPF_2$.[125]

Analysis of the force fields of the molecules of S-alkyl phosphorothioites shows that the phosphorus atom has no effect not only on the alkyl fragment of the molecule, but also on the force constant of the S–C bond. This seems to be reason why the spectral characteristics of the AlkS groups in the molecules of organophosphorus compounds coincide with the spectral indications of these groups in organosulfur compounds. Alkyl phosphorothioites are also characterised by the absence of pronounced effect of the alkyl radical on the force field of the phosphorus-containing fragment of the molecule. All acyclic compounds studied belonging to this class are characterised by the same force constant $K_{PS} = 2.0$.[130–132] It should be noted that even passage to strained five-membered rings with endocyclic P–S bond [108] or replacement of the alkyl radical in the AlkSP group by the dimethoxythiophosphoryl fragment [133, 134] decrease the K_{PS} value by only $\sim 10\%$.

As for the force fields of the molecules with the Si–P, Ge–P and P–P bonds, the corresponding data are too scarce to be used as a basis for any generalisation.

Closing the discussion of the force constants of the molecules of organophosphorus compounds, it should be emphasised that they can be used to predict the molecular spectra of related compounds for which studies by conventional methods of vibrational spectroscopy give no unambiguous solutions.[169] Additionally, rapid progress of computer industry opened the way to routine quantum-chemical calculations of the force constants. The first systematic studies of the so-called scaled 'quantum-chemical' potential fields of phosphines gave encouraging results.[170] Taken together, this allows one to hope that computer-assisted predictions of vibrational spectra of various organophosphorus compounds will become a routine procedure already in the near future.

XI. Conclusion

Trivalent tricoordinate phosphorus compounds contain no structural elements with such distinct spectral indications as, *e.g.*, the phosphoryl group. However, analysis of the published data shows that the efficiency of vibrational spectroscopy in studying the structure of trivalent phosphorus compounds can be as high as in the case of pentavalent phosphorus compounds. This requires that the following salient features of the vibrational spectra of organophosphorus compounds be taken into account.

The effect of the phosphorus-containing fragment of the molecule is confined to the force constants of adjacent molecular fragments. This leads to a nearly complete additivity in that part of the spectral region which is due to the vibrations of more distant groups. For instance, the spectra of molecule $[(CH_3O)_2P(S)S]_3P$ nearly coincide with those of the corresponding *O*,*O*′-dimethyl phosphoroditioate $(CH_3O)_2P(S)SH$ (see Ref. 171) in the whole frequency range, except for the region corresponding to the stretching (485–585 cm^{-1}) and bending vibrations (108–150 and 350–405 cm^{-1}) of the PSP fragments. Therefore, the spectrum of a phosphorus-containing molecule can be represented as the sum of the spectra of the fragments constituting the molecule minus the region corresponding to the vibrations of the nearest environment of the phosphorus atom. Therefore, the use of the data listed in Tables 1–25 can make the interpretation of vibrational spectra of trivalent phosphorus compounds much easier. For instance, spectral parameters of the C_2H_5OP fragment of an arbitrary molecule will coincide with the corresponding parameters of the *O*-ethyl fragment of ethyl phosphorodichloridite **34**. Vibrations of the POC fragment can appear to be an exception to this rule, since they can interact with vibrations of some other substituents through the shared phosphorus atom.

This example shows that consideration of the interactions between individual oscillators is of great importance to the analysis of the 'fingerprint' spectral regions. The data on the characteristic vibrations of different phosphorus-containing groups collected in this review will also help in predicting these effects correctly. Stretching vibrations of the C–C bond in the C_2H_5P fragment of dichloro(ethyl)phosphine may serve as an example. This bond is connected to the PCl_2 group through the P–C valence bond. Nevertheless, no interaction between the vibration ν(C–C) and the vibrations of the PCl_2 group occurs (see Table 7). The reason is that the vibrational frequencies of the PCl_2 fragment are much lower than the frequency of the vibrations ν(C–C). A similar situation will be observed for any other molecules with heavy substituents at the phosphorus atom. Therefore, the frequencies of the vibrations ν(C–C) in the molecules **9**, **12** and **13** are equal. On the other hand, this frequency can vary on introduction of the C_2H_5P fragment into a molecule with light substituents at the phosphorus atom, since the character of the interaction between vibrations in the new molecule may be different. For instance, characteristic frequencies of the bending vibrations of the PH_2 group (1073–1097 cm^{-1}) are close to the frequency of the vibrations ν(C–C). Therefore, one can expect that in the molecule of ethylphosphine **4** these individual oscillators will interact, thus changing the frequency of the vibration ν(C–C) as compared to those of the same vibrations of molecules **9**, **12** and **13**. The data listed in Table 2 confirm this assumption.

Vibrations with contributions of the nearest environment of the phosphorus atom can change on going from one compound to another since the force constants of the phosphorus-containing molecular fragment depend on the types and conformations of all substituents at the phosphorus atom. Turning our attention to the above-mentioned example with the C_2H_5P fragment, one can say that the frequency of the stretching vibrations ν(P–C) will change from 636 cm^{-1} for ethylphosphine **4** to 631/663 cm^{-1} for the molecule **12** or to 655/682 cm^{-1} on going to ethyldifluorophosphine **13**.

Reliability of spectral–structural correlations for the 'fingerprint' region increases substantially, if the Raman spectra are used in combination with the IR spectra. For instance, several IR absorption bands in the region 550–710 cm^{-1} can indicate two or three P–C bonds in the molecule under study. However, if the molecules of compounds under study contain one P–C bond but can adopt several conformations, more than one IR absorption band will be observed in the above-mentioned spectral region. It is easy to discriminate between these two variants using the Raman spectrum. In the first case, an intense, strongly polarised Raman line will correspond to only one of the bands in the IR spectrum [see, *e.g.*, $(CH_3)_2PCl$ or $(CH_3)_3P$ in Table 5], while the number of polarised lines in the Raman spectrum of the second compound will be equal to the number of peaks in the IR spectrum (*e.g.*, n-$C_3H_7PCl_2$ or n-$C_3H_7PH_2$, see Table 5).

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