ANALYSIS OF VIBRATIONAL SPECTRA OF PHENYLPHOSPHINE, DIPHENYLPHOSPHINE AND THEIR CHLORO DERIVATIVES. OVERLAY TECHNIQUE CALCULATION OF THEIR FORCE FIELD IN THE "REDUCED MODEL" APPROXIMATION.

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A normal coordinate analysis using the "reduced model" of benzene ring was carried out with $(C_6H_5)_nPX_{3-n}$ ($n = 1, 2$; $X = H, Cl$) compounds. 46 wavenumbers of vibrational transitions of the phenyl- and phosphine group were determined by means of the overlay technique. The transferability of force constants used in this calculation is discussed and an improved assignment of vibrations in the phenyl and phosphine group, based on PED calculations is presented.

In an earlier paper[1] we were concerned with the measurement and detailed interpretation of infrared and Raman spectra of diphenylphosphine $(C_6H_5)_2PH$, phenyldichlorophosphine $C_6H_5PCl_2$ and diphenylchlorophosphine $(C_6H_5)_2PCl$, using chlorobenzene as the model compound. Shortly after that article was submitted, the results of spectral analysis for a similar set of compounds were published by Hassler and Höfler[2]. The assignment offered by these authors[2] is based on experimental C_6H_5/C_6D_5 isotopic shifts, as well as on calculations of the characteristicity of some low frequency fundamental vibrations $(600-100 \text{ cm}^{-1})$. In this paper we attempt to reproduce the wave numbers of selected fundamental vibrations by a set of valence force constants. The results are compared with the assignments of Hassler and Höfler[2].

Information about structure of the phenylphosphine derivatives studied in this paper is very limited. Phenyldichlorophosphine[3] is the only compound the structure of which was so far elucidated (by electron diffraction). The structure of all other compounds was described by various structural models based on the C_s point symmetry group, derived from Raman line depolarisation measurements[4], band splitting in the liquid[5] and solid[6] state and the character of the envelopes of gas phase spectra bands[5]. A normal coordinate analysis in the harmonic approximation of the force field was carried out for chloro derivatives of benzene[7], phosphine methyl derivatives[8] and dichlorophosphine methyl derivatives[9]; but no force constants were given by Hassler and Höfler[2].

The assumption of transferability of force constants within the benzene chloro derivatives was already verified[7] for the case that it is possible to define the local environment of the corresponding internal coordinate[10]. Therefore, in present paper the calculation was limited to frequencies of several X-sensitive vibrations of the monosubstituted benzene ring[11] and to vibrations of the phosphine substituent. It was found advantageous to use for this calculation the "reduced model" of the phenyl group, introduced by Becher and Höfler[12]. The geometric parameters required for estimation of the G matrix elements were assumed to be the same as those for chlorobenzene[7] and the methyl derivatives of phosphine[8,13] and diphosphine[9]. The mutual orientation of both benzene rings in diphenylphosphine and its chloro derivatives, which is not specified in their paper[2], was taken from work of Steger and Stoperka[6].

The wavenumbers of vibrational transitions were determined by solving the inverse secular problem[11] using the overlay technique. The iteration procedures were terminated after a 2−5% mean deviation between the experimental and theoretical wavenumbers had been reached.

EXPERIMENTAL

The measurement of infrared and Raman spectra and the conditions for sample storage of the rather unstable compounds were described earlier[1]. An IBM-7040 computer was used for the calculations, executed in Fortran IV language.

RESULTS

The details of spectral analysis of the compounds under discussion and the force constants calculation were described previously[1]. The geometry and intermal coordinates employed in this paper are shown in Fig. 1; Fig. 1c presents the configuration of a molecule, in which the angle between the plane of symmetry σ_{xz} and the plane YCY is identical with the projection of the angle $\delta/2$ into the plane σ_{yz}. Numerical values of the atomic masses were taken from reference[14] and the Y atom mass was chosen as twice the mass of atom C. The geometrical parameters applied in the calculations are given in Table I. The symmetry coordinates and their correlation with fundamental vibrations are given in Table II.

The preliminary calculation based on force constants presented in the literature[7−9,13] proved that only 11 types of interaction constants were of significance; all the remaining non-diagonal constants were neglected since their absolute values were less than their three times deviations. The force constants and their deviations are summarized in Table III, the calculated wavenumbers, their relative deviations from experimental values and the potential energy distribution data (further only PED) are given in Table IV.

DISCUSSION

The vibrational spectra of the phenyl derivatives contain bands, the wave numbers of which are not sensitive to mass and chemical character of the substituents, as well as bands of so called "X-sensitive vibrations" with wavenumbers strongly depending on the substituent properties. Assignment of the mass insensitive vibrations was described in the previous paper[1] and agrees with the results in reference[4-6].

On the other hand, the assignment of X-sensitive vibrations and of vibrations of the phosphorus containing substituent does not agree well with the published results, especially in a low-frequency region. For example, the lowest band of the
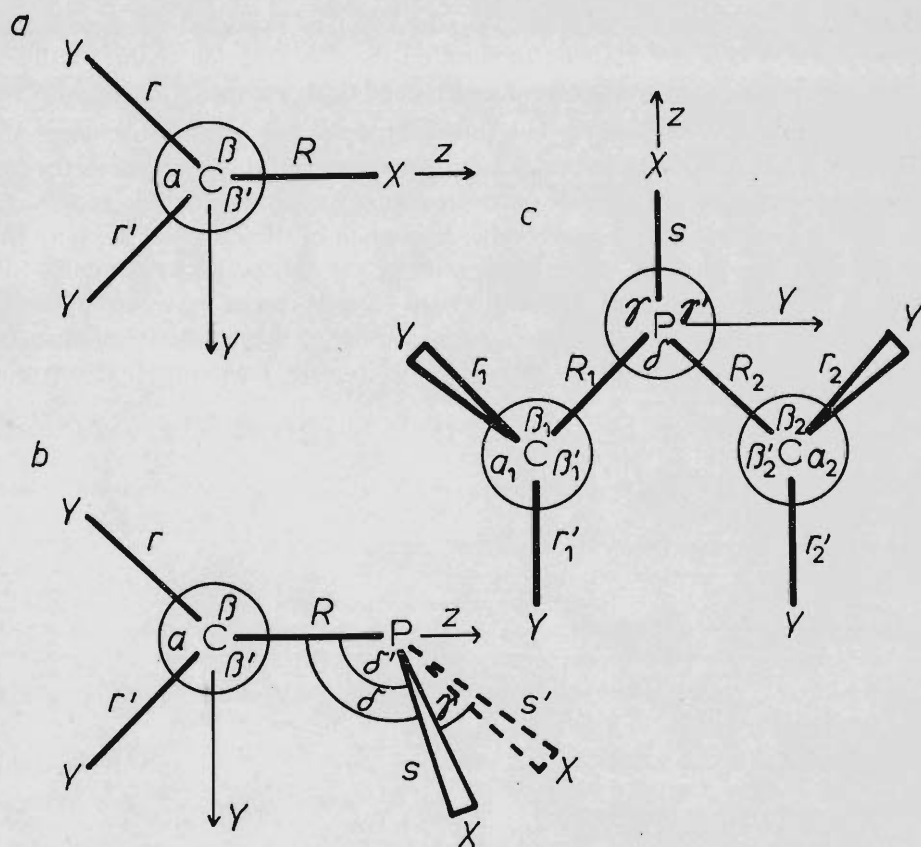

FIG. 1

The orientation of coordinate system and the selection of valence force coordinates: *a*) mono-substituted benzene *b*) phenylphosphine skelet *c*) diphenylphosphine skelet

PH_2 group was assigned to the wagging mode $v_5(A')$ in analogy with anilin[11] $C_6H_5NH_2$. The band at 605 cm^{-1} in phenylphosphine (and the band of similar nature at 505 cm^{-1} in diphenylphosphine) were in previous papers assigned to the combination frequencies[4,5]. Furthermore, the strong infrared band in the diphenyl-phosphine spectrum was assigned to the twisting vibration $\delta_{as,CPH} - v_6(A'')$, the polarized Raman line at 256 cm^{-1} to the scissoring vibration $\delta_{PC_2} - v_4(A')$ in analogy with trimethylphosphine[1]. The band at 170 cm^{-1}, which had been formerly assigned to this scissoring vibration[2] was re-assigned to the vibration $v_{17b}(B_1) - y$.

The twisting vibration is the only deformation vibration of the PH_2 group in the $C_6H_5PH_2$ molecule which changes its wavenumber according to orientation of this group against the benzene ring plane; a change of the angle between the axis of the HPH angle and this plane from 0 to 90° leads to a wavenumber decrease from 821 to 795 cm^{-1}. The insensitivity of other vibrations can be explained by almost total independence of G and F matrix structures on the conformation change, resulting from a relatively weak interaction between PH_2 and C_6H_5 groups.

The attempts to reproduce the low frequency vibrations of phenyldichloro- and diphenylchlorophosphine by the calculation were unsuccesful. Nevertheless, the cor-responding vibrations are mutually strongly coupled and the harmonic approxima-tion used is therefore not an appropriate description of the collective motion. This conclusion is supported by the estimate value of the anharmonicity constant[1] (de-termined for phenyldichlorophosphine from the wavenumber of the second harmonic of wagging vibration $v_5(A')$), which is by one order of magnitude larger than the anharmonicity constant value for phenyl group in-plane vibrations[23]. It was pos-

TABLE I

Structural parameters used for OVFF calculations (see Fig. 1)

Model	geometrical parameter[m]							
	r_{CC}	$R_{CX,CP}$	s_{PX}	α_{YCY}	$\beta_{YC}\binom{X}{P}$	$\binom{\delta}{\gamma}_{CPX}$	γ_{XPX}	δ_{CPC}
Y_2C-Cl	$139\cdot7^a$	170^b		120^c	120^c			
Y_2C-PH_2	$139\cdot7$	$183\cdot3$	$141\cdot4^e$	120	120	118^f	$93°12'^g$	
Y_2C-PCl_2	$139\cdot7$	$183\cdot3^d$	$207\cdot2^h$	120	120	$120°54'^i$	$100°24'^j$	
$(Y_2C)_2.PH$	$139\cdot7$	$183\cdot3$	$141\cdot9^l$	120	120	118		$103°18'^k$
$(Y_2C)_2.PCl$	$139\cdot7$	$183\cdot3$	$207\cdot2$	120	120	$120°54'$		$103°18'$

[a] ref.[15], [b] ref.[16], [c] ref.[7], [d] ref.[3], [e] ref.[17], [f] estimate, [g] ref.[18], [h] ref.[3], [i] ref.[3], [j] ref.[3], [k] ref.[19], [l] ref.[20]; [m] bond distances given in pm, bond angles in degrees.

TABLE II

Symmetry coordinates for Y_2C-X and $(Y_2C)_nPX_{3-n}$ ($n = 1, 2$; $X = H, Cl$)

Symmetry	Coordinate	Assignment[a]	Description
	model Y_2C-X		
A_1	$S_1 = 1/\sqrt{2}\,(\Delta r + \Delta r')$	20a,X	$\nu_{CC,s}$
	$S_2 = 1/\sqrt{6}\,(2\Delta\alpha - \Delta\beta - \Delta\beta')$	6a,X	δ_{CCC}
	$S_3 = \Delta R$	1,X	ν_{CP}
	$S_4 = 1/\sqrt{3}\,(\Delta\alpha + \Delta\beta + \Delta\beta')$	redund.	
B_2	$S_5 = 1/\sqrt{2}\,(\Delta r - \Delta r')$	14	$\nu_{CC,as}$
	$S_6 = 1/\sqrt{2}\,(\Delta\beta - \Delta\beta')$	18b,X	δ_{CCP}
	model Y_2C-PX_2		
A'	$S_1 = 1/\sqrt{2}\,(\Delta r + \Delta r')$	20a,X	ν_{CC}
	$S_2 = 1/\sqrt{6}\,(2\Delta\alpha - \Delta\beta - \Delta\beta')$	6a,X	δ_{CCC}
	$S_3 = \Delta R$	1,X	ν_{CP}
	$S_4 = 1/\sqrt{2}\,(\Delta s + \Delta s')$	2	$\nu_{PX,s}$
	$S_5 = \Delta\gamma$	4	δ_{PX_2}, sciss.
	$S_6 = 1/\sqrt{2}\,(\Delta r - \Delta r')$	14	$\nu_{CC,as}$
	$S_7 = 1/\sqrt{2}\,(\Delta\beta - \Delta\beta')$	18b,X	δ_{CCP}
	$S_8 = 1/\sqrt{2}\,(\Delta\delta + \Delta\delta')$	5	δ_{CPX}, wagg.
	$S_9 = 1/\sqrt{3}\,(\Delta\alpha + \Delta\beta + \Delta\beta')$	redund.	
A''	$S_{10} = 1/\sqrt{2}\,(\Delta s - \Delta s')$	3	$\nu_{PX,as}$
	$S_{11} = 1/\sqrt{2}\,(\Delta\delta - \Delta\delta')$	6	δ_{CPX}, twist.
	model $(Y_2C)_2PX$		
A'	$S_1 = 1/\sqrt{2}\,(\Delta R_1 + \Delta R_2)$	1,s,X	$\nu_{CP,s}$
	$S_2 = 1/2(\Delta r_1 + \Delta r'_1 + \Delta r_2 + \Delta r'_2)$	20a,s,X	$\nu_{CC,s}$
	$S_3 = 1/2(\Delta r_1 - \Delta r'_1 + \Delta r_2 - \Delta r'_2)$	14,s	$\nu_{CC,as}$
	$S_4 = \Delta s$	1	ν_{PX}
	$S_5 = 1/2\sqrt{3}\,(2\Delta\alpha_1 - \Delta\beta_1 - \Delta\beta'_1 +$ $+ 2\Delta\alpha_2 - \Delta\beta_2 - \Delta\beta'_2)$	6a,s,X	δ_{CCC}
	$S_6 = 1/2(\Delta\beta_1 - \Delta\beta'_1 + \Delta\beta_2 - \Delta\beta'_2)$	18b,s,X	δ_{CCP}
	$S_7 = \Delta\delta$	4	δ_{PC_2}, sciss.
	$S_8 = 1/\sqrt{2}\,(\Delta\gamma + \Delta\gamma')$	5	δ_{CPX}, wagg.
	$S_9 = 1/\sqrt{6}\,(\Delta\alpha_1 + \Delta\beta_1 + \Delta\beta'_1 +$ $+ \Delta\alpha_2 + \Delta\beta_2 + \Delta\beta'_2)$	redund.	
A''	$S_{10} = 1/\sqrt{2}\,(\Delta R_1 - \Delta R_2)$	1,as,X	$\nu_{CP,as}$
	$S_{11} = 1/2(\Delta r_1 + \Delta r'_1 - \Delta r_2 - \Delta r'_2)$	20a,as,X	$\nu_{CC,s}$
	$S_{12} = 1/2(\Delta r_1 - \Delta r'_1 - \Delta r_2 + \Delta r'_2)$	14,as	$\nu_{CC,as}$
	$S_{13} = 1/2\sqrt{3}\,(2\Delta\alpha_1 - \Delta\beta_1 - \Delta\beta'_1 -$ $- 2\Delta\alpha_2 + \Delta\beta_2 + \Delta\beta'_2)$	6a,as,X	δ_{CCC}
	$S_{14} = 1/2(\Delta\beta_1 - \Delta\beta'_1 - \Delta\beta_2 + \Delta\beta'_2)$	18b,as,X	δ_{CCP}
	$S_{15} = 1/\sqrt{2}\,(\Delta\gamma - \Delta\gamma')$	6	δ_{CPX}, twist.
	$S_{16} = 1/\sqrt{6}\,(\Delta\alpha_1 + \Delta\beta_1 + \Delta\beta'_1 -$ $- \Delta\alpha_2 - \Delta\beta_2 - \Delta\beta'_2)$	redund.	

[a] Notation accepted from literature[21,22]; indices s, as denote in-phase and out-of-phase vibrations.

TABLE III

Valence force constants ϕ_i and deviations $\sigma(\phi_1)$ for $Y_2C–X$ and $(Y_2C)_nPX_{3-n}$ ($n = 1, 2$; $X = H,Cl$)

Description	$\phi_i{}^a$	$\sigma(\phi_i)^b$	Published values
	stretching force constants		
$r(Y–C)$	7·40		6·76^c
$R(C–P)$	3·81		3·08^d, 2·88^e
$R(C–Cl)$	3·70		3·73^c
$s(P–H)$	3·01		3·08^e
$s(P–Cl)$	2·10		2·44^d
	deformation force constants		
$\alpha(YCY)$	1·43		0·86^c
$\beta(YCCl)$	0·70		0·83^c
$\beta^1(YCP_H)^g$	0·52	0·02	
$\beta^2(YCP_H)$	0·30	0·02	
$\beta^1(YCP_{Cl})$	0·50	0·09	
$\beta^2(YCP_{Cl})$	0·46	0·01	
$\gamma(HPH)$	0·53		0·68^e
$\gamma(ClPCl)$	2·75?		1·02^d
$\delta^1(CPH)$	0·71	0·01	0·81^e
$\delta^2(CPH)$	0·54	0·03	
$\delta^1(CPCl)$	0·55	0·05	1·22^d
$\delta^2(CPCl)$	0·96	0·02	
$\gamma(CPC)$	0·82		0·97^f
	interaction force constants		
$rr(YC,YC)$	1·05		0·83^c
$rR(YC,CX)$	0·45		0·41^c
$Rs(CP,PH)$	0·04		0^e
$Rs(CP,PCl)$	0·38		0·38^d
$RR(CP,CP)$	−0·008		−0·03^f
$ss(PH,PH)$	−0·008		−0·002^e
$ss(PCl,PCl)$	0·08		0·38^d
$r\alpha(YC,YCY)$	0·87		0·29^c
$r\beta(YC,YCCl)$	0·18		0·20^c
$r\beta(YC,YCP_H)$	0·19		
$r\beta(YC,YCP_{Cl})$	0·15	0·01	
$R\beta(CCl,YCCl)$	0·40		0·65^c
$R\beta(CP,YCP_H)$	0·32	0·05	
$R\beta(CP,YCP_{Cl})$	0·54	0·01	

TABLE III
(*Continued*)

Description	$\phi_i{}^a$	$\sigma(\phi_i)^b$	Published values
$s\gamma$(PH, HPH)	−0·01		0^e
$s\gamma$(PCl,ClPCl)	0·17		$0·17^d$
$s\delta$(PCl,CPCl)	0·17		$0·17^d$
$\gamma\delta$(HPH,CPH)	0·018	0·004	0^e

^{a} Stretching force constants in $N\,cm^{-1}$, deformation constants in $10^{-18}\,J\,rad^{-2}$, constants of interaction between the stretching and deformation motions in $10^{-8}\,N\,rad^{-1}$; ^{b} when no value is listed, the constant was obtained by direct calculation; ^{c} ref.[7], ^{d} ref.[9], ^{e} ref.[8], ^{f} ref.[13], ^{g} the indices 1 and 2 denote the mono- and diphenyl derivative, symbols H and Cl the type of substitution.

sible to assign without ambiguity only the twisting vibration of the diphenylchlorophosphine, since it belongs to the symmetry block without strong coupling. Concerning the assignment of other vibrations, we favor the results obtained directly by spectral analysis[1], as presented in Table V. The calculation should involve also the remaining X-sensitive vibrations $\nu_{16b}(B_1) - x$ and especially $\nu_{17b}(B_1) - y$. We assign the latter vibration to a depolarized Raman line in the 425 cm^{-1} region, the $\nu_{6a}(A_1) -$ $- t$ vibration to a polarized line at 455 cm^{-1} − which is overlapped in the dichloroderivative spectrum by the antisymmetric stretching vibration $\nu_{as,PCl}$; this overlap explains the rather high value of the depolarization factor of this line (0·53). The torsional vibration τ_{CCPX} (X = H,Cl) was observed only in the spectrum of phenyldichlorophosphine at 99 cm^{-1}; in the same region a torsional vibration band appeared in the spectrum of a structurally similar Cl_2P-PCl_2 molecule[25]. A splitting of the phenyl group X-sensitive vibrations into the in-phase and out-of-phase component was determined by calculation for the diphenyl derivatives[1]. The splitting does not exceed 30 cm^{-1}, in agreement with conclusions of Hassler and Höfler[2].

The structural model used for the normal coordinate calculation is too oversimplified to be used for a detailed discussion of differences between the calculated and published[7−9] force constants values. To a certain extent, the transferability of force constants can be assesed: For example, the stretching force constants connected with the vibrations of significant characteristicity are transferable within this series, with equivalent substituents. The force constants of the ν(C—P) vibration suggests (in comparison with the C—P force constant from methylphosphine[8]) an existence of conjugation between the P atom and phenyl group. The transferabil-

TABLE IV

The calculated wave numbers (σ), their relative deviation from experimental values ($\varrho\sigma$) and PED values for Y_2C–Cl and $(Y_2C)_n PX_{3-n}$ ($n = 1, 2$; $X = H,Cl$)

Number	σ, cm^{-1}	$\varrho\sigma$, %	PED^a
		model Y_2C–Cl	
1	1 100	−1·33	$69(\nu_{CC,s})$, $27(\nu_{CP})$
2	408	1·98	$68(\delta_{CCC})$, $32(\nu_{CC,s})$
3	679	3·06	$41(\nu_{CP})$, $31(\nu_{CC,s})$, $28(\delta_{CCC})$
5	1 328	0·23	$97(\nu_{CC,as})$
6	303	−2·57	$97(\delta_{CCP})$
		model Y_2C–PH$_2$	
1	1 120	−1·17	$51(\nu_{CC,s})$, $28(\nu_{CP})$, $11(\delta_{PH_2})$
2	401	−2·30	$72(\delta_{CCC})$, $28(\nu_{CP})$
3	692	−0·44	$40(\nu_{CP})$, $33(\nu_{CC,s})$, $22(\delta_{CCC})$
4	2 284	0·22	$100(\nu_{PH,s})$
5	1 074	−0·09	$55(\delta_{PH_2})$, $25(\delta_{CPH,s})$, $15(\nu_{CC,s})$
6	1 321	0·53	$96(\nu_{CC,as})$
7	248	0·40	$99(\delta_{CCP})$
8	604	0·17	$63(\delta_{CPH,s})$, $30(\delta_{PH_2})$
10	2 292	0·09	$100(\nu_{PH,as})$
11	823	−0·24	$100(\delta_{CPH,as})$
		model $(Y_2C)_2 PH$	
1	678	1·45	$42(\nu_{CP,s})$, $31(\nu_{CC,s})$, $25(\delta_{CCC})$
2	1 102	−0·09	$69(\nu_{CC,s})$, $29(\nu_{CP,s})$
3	1 303	1·73	$100(\nu_{CC,as})$
4	2 288	0·13	$100(\nu_{PH,s})$
5	405	−3·31	$58(\delta_{CCC})$, $20(\delta_{PC_2})$, $18(\nu_{CP,s})$
6	202	−0·50	$92(\delta_{CCP})$, $4(_{CPH,s})$
7	258	−0·78	$69(\delta_{PC_2})$, $12(\delta_{CCC})$, $11(\nu_{CP,s})$
8	495	1·98	$90(\delta_{CPH,s})$, $5(\delta_{PC_2})$
10	693	−0·73	$42(\nu_{CP,as})$, $33(\nu_{CC,s})$, $19(\delta_{CCC})$
11	1 116	−0·72	$63(\nu_{CC,s})$, $34(\nu_{CP,as})$
12	1 316	0·75	$100(\nu_{CC,as})$
13	411	−5·93	$78(\delta_{CCC})$, $22(\nu_{CP,as})$
14	170	1·73	$100(\delta_{CCP})$
15	883	0·67	$90(\delta_{CPH,as})$, $6(\nu_{CC,s})$

Number	σ, cm^{-1}	$\varrho\sigma$, %	PED^a
		model $Y_2C\text{–}PCl_2$	
1	1 089	−0·09	$77(\nu_{CC,s})$, $24(\nu_{CP})$
3	695	0·29	$54(\nu_{CP})$, $21(\nu_{CC,s})$, $11(\delta_{CCC})$
4	504	−1·00	$42(\nu_{PCl,s})$, $40(\delta_{CCC})$, $13(\delta_{PCl_2})$
6	1 325	0·30	$98(\nu_{CC,as})$
10	461	−2·22	$94(\nu_{PCl,as})$
		model $(Y_2C)_2PCl$	
1	671	2·89	$53(\nu_{CP,s})$, $23(\delta_{CCC})$, $19(\nu_{CC,s})$
2	1 075	1·64	$80(\nu_{CC,s})$, $22(\nu_{CP,s})$
3	1 325	0·23	$98(\nu_{C,as})$
4	509	−1·80	$48(\nu_{PCl})$, $32(\delta_{CCC})$, $11(\delta_{PC_2})$
10	699	−1·16	$58(\nu_{CP,as})$, $28(\nu_{CC,s})$, $10(\delta_{CCC})$
11	1 093	0·27	$74(\nu_{CC,s})$, $28(\nu_{CP,s})$
12	1 325	0·23	$99(\nu_{CC,as})$
13	467	−2·41	$84(\delta_{CCC})$, $13(\delta_{CPCl,as})$
14	195	−3·00	$71(\delta_{CCP})$, $25(\delta_{CPCl,as})$
15	234	−2·18	$57(\delta_{CPCl,as})$, $29(\nu_{CP,as})$

^{a} The in-phase and out-of-phase vibrations are not distinguished with diphenyl derivatives, the notation corresponds to Table II.

ity of the force constants connected with deformation motions is also determined by the geometry of the phosphine-group pyramide, in addition to the character of the substituent.

The potential energy distribution shows increased coupling between the phenyl- and phosphine group vibrations (when passing from phenylphosphine to diphenyl-phosphine and their corresponding chloro derivatives). The estimation of the HPH valence angle by Linnett[26], based on this fact, led to 93°10′ for phenylphosphine, in good agreement with the experimental value[18]. With chloroderivatives, the $\nu_{s,PCl}$ vibration seems to be coupled not only with deformation vibrations of the chlorophosphine group, but also with the $\nu_{6a}(A_1)$ vibration. The remaining totally symmetric X-sensitive vibrations of the phenyl group ν_{20a} and $\nu_1(A_1)$ (so called q and r vibrations) are mutually coupled in all the compounds studied; the assumption of their entire characteristicity[2] was not verified.

TABLE V

The assignment of deformation vibrations for $(Y_2C)_nPCl_{3-n}$ $(n = 1, 2)$

σ, cm^{-1} ϱ_σ	Assignment	Description	Bases for assignment
	model Y_2C–PCl_2		
188 (0·83)	6 (A'')	δ_{CPCl}, twist.	$v_4(E) - PCl_3{}^a$
243 (0·80)	18b (B_2)	δ_{CCP}, X	18b (B_2)
257 (0·21)	4 (A')	$\delta_{PCl,PCl}$, sciss.	$v_2(A_1) - PCl_3{}^a$
291 (0·08)	5 (A')	δ_{CPCl}, wagg.	$v_5(A') - CH_3PCl_2{}^c$
451 (0·53)	6a $(A_1) +$	δ_{CCC}, X	depol. factor
	3 (A'')	$v_{PCl,as}$	$v_3(E) - PCl_3{}^a$
	model $(Y_2C)_2PCl$		
201 (—)	18b (B_2)	δ_{CCP}, X	18b $(B_2)^b$
229 (0·86)	6 (A'')	δ_{CPCl}, twist.	$v_6(A'')^b$
261 (0·12)	4 (A')	δ_{CPC}, sciss.	$v_2(A_1) - P(CH_3)_3{}^c$
283 (0·16)	5 (A')	δ_{CPCl}, wagg.	$v_5(A'') - (CH_3)_2PCl^c$
456 (0·20)	6a (A_1)	δ_{CCC}, X	depol. factor

^{a} Ref.[1], ^{b} ref.[4], ^{c} ref.[24].

TABLE VI

Vibrational assignment and corresponding calculated wave numbers in dimethylphenylphosphine

σ_{exp}, cm^{-1}		Assignment	σ_{calc}, cm^{-1}	ϱ_σ, %	Assignment^c
R	IR				
125 m			137	−9·6	16b (B_1), X?
253 s	260 m,br	18b $(B_2)^b$	267	−3·9	4 (A'), sciss.
282 s		$\delta_{PC}{}^a$	291	−3·2	5 (A'), wagg.?
325 s	330 vs	$\delta_{PC}{}^b$	295	9·2	6 (A''), twist.
396 m	400 s		412	−3·4	6a (A_1), X
	434 m	$v_{PC}{}^a$			16a (A_2), Γ_{CCC}
481 vs	485 vs	$\gamma_{PC}{}^a$			17b (B_1), X
653 s	653 m	$v_{PC}{}^a$	622	4·7	2 (A'), $v_{PC,s}$
693 sh	685 vs				4 (B_1), Γ_{CCC}
707 m	707 sh	comb.^{a}	715	−1·1	3 (A''), $v_{PC,as}$
760 vs	760 m	comb.^{a}	747	1·7	1 (A_1), X
890 s	890 vs	comb.^{a}			10b (B_1), γ_{CH}
1 103 s	1 103 s	$v_{CP}{}^a$	1 110	−0·63	20a (A_1), X
	1 315s		1 317	−0·15	14 (B_2), v_{CC}

The results of this paper outline the applicability of the overlay valence force field calculation for the phenylphosphine derivatives. In addition, the calculations were extended to P-methyl derivatives of phenylphosphine; in these calculations the methyl group was approximated by a mass center with 16·04 relative atom mass units[27]. The normal coordinate calculations allow a more accurate assignment of vibrations[28,29] in the case of dimethylphenylphosphine $C_6H_5P(CH_3)_2$. The wavenumbers calculated by means of this procedure are presented along with experimental values and the suggested assignments in Table VI.

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[a] ref.[28]; [b] ref.[29]; [c] presented is the assignment obtained by the analysis of experimental data and by calculation, vibrations denoted ? were not verified by the calculation, other vibrations were assigned on basis of comparison with the model compounds (chlorobenzene, substituted methylphosphine).

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