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Vibration Spectra and Structures of the Simplest Aromatic Derivatives of Group I-VI Elements

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The review gives a general and systematic account of experimental and calculated data on the vibration spectra and structures of the simplest aromatic derivatives of non-transition Group I-VI elements. Particular attention has been devoted to "M-sensitive" vibrations, i.e. vibrations involving the element M, the frequencies of the corresponding bands, their activites, and the splittings of the components as a function of molecular structure. The monosubstituted benzene approximation is shown to have poor suitability for the interpretation of the spectra of derivatives of polyvalent elements. The bibliography includes 145 references

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I. INTRODUCTION

The extremely common occurrence of aromatic compounds in natural and synthetic materials is generally known. The specific features of aromatic molecules associated with the delocalisation of π electrons and the transmission of electronic effects from one part of the molecule to the entire conjugated system have found extremely wide applications in science and engineering. The creation of new materials with specified properties requires a profound study of the various factors which affect the structure and physicochemical characteristics of aromatic molecules. One of the physical methods most widely employed is that of vibration spectroscopy with which it is often possible to determine the structure of the compound, the type and nature of the substituent, the stability and structure of the complexes, etc.

Therefore this method has been widely used in the last 10–20 years in analytical and structural studies on numerous aromatic compounds, particularly in view of its availability to a wide circle of not only spectroscopists but also chemists working on synthesis. Monographs devoted fully or partly to the vibration spectra of aromatic derivatives have been published in recent years both in the USSR and abroad[1-3]. However, the vibration spectra of purely aromatic molecules of different structures are as a rule discussed in these general texts. In those cases where a substituent is introduced into the aromatic system it usually consists of hydrocarbon groups (aliphatic, unsaturated, etc.) or halogen atoms.

There has now been an appreciable growth of interest in heteroaromatic molecules containing heteroatoms of different types. Studies have been made in recent years on the vibration spectra of compounds of this type but so far these have been non-systematic and sometimes contradictory.

The present review attempts to compile and arrange systematically the original studies on the vibration spectra and structures of the simplest aromatic derivatives of Group I–VI elements and to demonstrate the possibility of employing these spectra for the identification of the individual Ar–M bonds, to determine their strength, and to investigate the molecular structure.

A single system of notation for vibrations is at present lacking in the literature on the vibration spectra of the simplest aromatic compounds (monosubstituted benzenes). In the discussion of the vibration spectra of aromatic compounds with hydrocarbon substituents, one usually employs the notation proposed by Herzberg[2] or Wilson[4]. However, in most studies on the vibration spectra of aromatic derivatives of the elements, Whiffen's notation has been used[5]. Since the present review deals with the spectra of compounds of the second type, we shall continue to employ Whiffen's notation for the vibrations of monosubstituted benzenes in order to simplify comparison with the original studies.

The conversion from one system of notation for monosubstituted benzene vibrations to the other is illustrated in Table 1 which includes in addition the vibration symmetries and approximate absorption regions.

Analysis of the experimental and theoretical data on the vibration spectra of many phenyl derivatives of various elements shows the complexity of the majority of vibration modes. Thus, in contrast to aliphatic derivatives of the elements where stretching and deformation vibrations of the C–M bond can be more or less clearly distinguished, in aromatic derivatives there are as a rule several vibrations in which the Ph–M group is involved to different extents.

According to Whiffen's suggestion[5], these vibrations are called "M-sensitive". These vibrations are in fact of greatest interest in the study of the nature of the substituent and molecular structure and therefore they will be henceforth discussed in greatest detail. On the other hand, the vibrations of the benzene ring, which do not involve the heteroatom, will be considered only where they throw light on the structure of molecules or their complexes.

It is noteworthy that, in contrast to phenyl derivatives of univalent Group VII elements, the spectra of which were studied by Whiffen[5], for polyvalent heteroatoms (with several substituents linked to a single heteroatom), one

must take into account the overall molecular symmetry; this may lead to the splitting of the bands owing to the interaction of the vibrations of adjacent groups via the central atom.

Table 1. The notation, symmetry, and absorption regions of the vibrations of monosubstituted benzenes (C_{2v}).

Notation according to Refs.						Notation according to Refs.					
2	4	5	based on vibration modes	Vibration symmetry	Absorption region, cm^{-1}	2	4	5	based on vibration modes	Vibration symmetry	Absorption region, cm^{-1}
1	2	z_1	ν_{C-H}	a_1	3060	13′	19*a*	*n*	ν_{C-C}	a_1	1450
2	1	*r*	ν_{C-X}	a_1	650—800	14	18*a*	*b*	β_{C-H}	a_1	1030
3	3	*e*	β_{C-H}	a_1	1270	14′	18*a*	*u*	β_{C-X}	a_1	200—500
4	11	*f*	γ_{C-H}	a_2	750	15	7*a*	z_5	ν_{C-H}	a_1	3045
5	13	z_2	ν_{C-H}	a_1	3060	15′	7*a*	z_3	ν_{C-H}	a_1	3045
6	12	*p*	α_{CCC}	a_1	1000	16	8*a*	*l*	ν_{C-C}	a_1	1590
7	5	*j*	γ_{C-H}	a_2	982	16′	8*a*	*k*	ν_{C-C}	a_1	1605
8	4	*v*	δ_{C-C}	a_2	697	17	9*a*	*c*	β_{C-H}	a_1	1155
9	14	*o*	ν_{C-C}	a_1	1325	17′	9*a*	*a*	β_{C-H}	a_1	1175
10	15	*d*	β_{C-H}	a_1	1070	18	6*a*	*s*	α_{CCC}	a_1	620
11	10*a*	*g*	γ_{C-H}	a_2	835	18′	6*a*	*t*	α_{CCX}	a_1	250—625
11′	10*a*	*i*	γ_{C-H}	a_2	910	19	17*a*	*h*	γ_{C-H}	a_2	960
12	20*a*	*q*	ν_{C-X}	a_1	1050—1220	19′	17*a*	*y*	γ_{CCX}	a_2	430—500
12′	20*a*	z_4	ν_{C-H}	a_1	3080	20	16*a*	ω	γ_{CC}	a_2	405
13	19*a*	*m*	ν_{C-C}	a_1	1500	20′	16*a*	*x*	γ_{CCX}	a_2	150—250

Table 2.

Type of compound	Symmetry point groups	M-sensitive vibrations active in	
		i.r.spectra	Raman spectra
Ph_2M, $PhMX$, Ph_2MX, $PhMX_2$, Ph_2MX_2	C_{2v}	$A_1+B_1+B_2$	$A_1(p) + B_1(d) + B_2(p)$
Ph_2M, Ph_2MX	C_2	A+B	A(p) + B(d)
Ph_3M, Ph_3MX, $PhMX_3$	C_{3v}	A_1+E	$A_1(p) + E(d)$
Ph_3M	C_3	A+E	A(p) + B(d)
Ph_2M	D_{2h}	$B_{1u}+B_{2u}+B_{3u}$	$A_g(p) + B_{1g}(d) + B_{2g}(d) + B_{3g}(d)$
Ph_2M	D_2	$B_1+B_2+B_3$	$A(p) + B_1(d) + B_2(d) + B_3(d)$
Ph_3M	D_{3h}	E′	$A'_1(p) + E'(d) + E''(d)$
Ph_3M	D_3	A_2+E	$A_1(p) + E(d)$
Ph_4M	Td	F_2	$A_1(p) + E(d) + F_2(d)$
Ph_4M	S_4	A+E	A(p) + B(d) + E(d)

Notation. p = polarised; d = depolarised.

This effect should probably be shown most markedly in vibrations involving the heteroatom, i.e. in M-sensitive vibrations. Depending on molecular symmetry, the components of the split band can appear in different ways in the infrared and Raman spectra. Table 2 gives the selection rules for the infrared and Raman spectra of M-sensitive vibrations corresponding to different molecular symmetries.

II. VIBRATION SPECTRA AND STRUCTURES OF PHENYL DERIVATIVES OF GROUP I ELEMENTS

The structures of aromatic derivatives of Group I elements have been hardly investigated at all. The formation of stable dimers has been demonstrated for the lithium derivatives [6,7]. There is no unanimous view as to the nature and structures of these association complexes. Wittig suggests that the structure of the phenyl-lithium dimer be regarded as that of the autocomplex $(Ph_2Li)^-Li^+$, [6] while in other studies it is believed that a cyclic dimer may exist as a result of "electron-deficient" bonds [7]. An increase of the C–M bond polarity in the series Li → Na → K → Rb, Cs is known to occur in alkali metal compounds and therefore, starting with sodium, the C–M bond is usually regarded as mainly ionic.

Lanpher [8] measured the infrared spectra of phenyl derivatives of lithium, sodium, and potassium and found an intense band in the range 1160–1260 cm^{-1} which he assigned to the C–M bond vibration on the basis of its shift when one metal is replaced by another. However, it has been shown [7,9,10] that the band near 1250 cm^{-1} in the spectra of PhLi does not undergo an isotopic shift on replacement of lithium-7 by lithium-6 and therefore cannot be assigned to the C–Li stretching vibration. The use of compounds containing different proportions of the lithium-7 and lithium-6 isotopes made it possible to isolate in the spectra bands associated with the Ar–Li vibration in the dimers (Table 3).

Table 3. C–Li... absorption bands in the infrared spectra of dimeric lithium aryls (cm^{-1}). [7]

Compound	Medium	
	in liquid paraffin	in butyl ether
[^{7}Li]-Phenyl-lithium	280, 320, 350, 427	352, 390, 440
[^{6}Li]-Phenyl-lithium	290, 326, 357, 430	no data available
[^{7}Li]-*o*-Tolyl-lithium	327, 390, 420	345, 383, 421, 432
[^{6}Li]-*o*-Tolyl-lithium	338, 400, 420	278, 354, 387, 440
[^{7}Li]-*p*-Tolyl-lithium	275, 310, 353	357, 395
[^{6}Li]-*p*-Tolyl-lithium	297, 318, 362	365, 416
[^{7}Li]Mesityl-lithium	278, 314, 342	—
[^{6}Li]Mesityl-lithium	290, 326, 357	—
[^{7}Li]-α-Naphthyl-lithium	335, 383, 407	352, 390
[^{6}Li]-α-Naphthyl-lithium	350, 390, 410	360, 410

Comparison of the infrared spectra of the PhLi and monosubstituted benzenes with a substituent of similar mass revealed the absence from the spectra of the former of bands sensitive to the substituent in the region above 700 cm^{-1} [for example the 1220 cm^{-1} (*q*-vibration) and 806 cm^{-1} (*r*-vibration) bands in the infrared spectrum of PhF]. [11] This effect is observed in the spectra of all the aromatic lithium derivatives investigated and can probably be accounted for by a weakening of the C–Li bonds owing to stable association of the electron-deficient type. Calculations on in-plane vibrations for the monomeric model of PhLi indeed showed that, even without taking into account the change in molecular configuration on dimerisation, when the force constant K_{Ph-Li} decreases to 1.5×10^6 cm^{-2} the bands in the regions expected for *q*- and *r*-vibrations cease to shift on isotopic substitution of lithium-7 by lithium-6 [12] and, in agreement with experimental data, the isotopic shift occurs only in the long-wavelength part of the spectrum (374 and 259 cm^{-1} for lithium-7 and 400 and 270 cm^{-1} for lithium-6). Moreover, it is noteworthy that the infrared spectra of all the lithium aryls investigated show additional bands in the C–H stretching region displaced towards longer wavelengths by 50–100 cm^{-1}

together with bands in the normal ν_{C-H} region (3030 to 3100 cm^{-1}). The decrease of the ν_{C-H} band intensity in the infrared spectra of lithium aryls is probably associated with a weakening of the C–H bonds in the *ortho*-position relative to the C–Li group, which is satisfactorily correlated with the effect observed in the ^1H NMR spectra of PhLi (Ladd[13]) and is consistent with the decrease in the frequency of the α-C–H bonds in the infrared spectra of aliphatic organolithium compounds[14,15].

III. VIBRATION SPECTRA AND STRUCTURES OF PHENYL DERIVATIVES OF GROUP II ELEMENTS

The presence of vacant p-orbitals and the relatively low electronegativity of beryllium and magnesium result in a fairly stable association of organic derivatives of these elements. The structures of the association complexes of $(CH_3)_2Be$ and $(CH_3)_2Mg$ have been investigated and an appreciable departure of the molecular framework from linearity has been noted ($\angle CBeC \simeq 114°$; $\angle CMgC \simeq 105°$).[16]

Table 4. Experimental and calculated frequencies (wave-numbers, cm^{-1}) of the M-sensitive vibrations in the spectra of Ph_2Be and Ph_2Mg (Rodionov et al.[18]).

Designation of vibration according to Whiffen (Ref.5)	Symmetry (C_2)	Ph_2Be		Ph_2Mg	
		i.r. spectra	calc. for $\alpha = 120°$	i.r. spectra	calc. for $\alpha = 120°$
q	B	1250 m.	1265	1045 m.s.	1060
	A	1200 m.	1198		1075
r	B	902 s.	900	670 m.	675
	A	780 m.	800		685
t	B	570 m.	582	425 s.	415
	A	545 m.	540	310 s.	358
		250 w.	236	200 w.	200
u	B	410 m.	380	255 m.	257
		225 m.	202		185
y	B	475 m.		425 s.	

Note. The following designation of band intensities has been adopted in Tables 4–15: s = strong (intense), m = medium, w = weak, p = polarised, d = depolarised.

We were unable to find direct data concerning the structure of compounds of the type Ph_2M but the fairly large dipole moment of Ph_2Be in benzene[17] and X-ray diffraction data for the crystalline ether adduct of PhMgBr suggest that aromatic derivatives of beryllium and magnesium also have a bent structure with $\angle CMC$ smaller than 180° but probably somewhat larger than for methyl derivatives. In this case structures with C_{2v} or C_2 symmetries are possible. For C_{2v} symmetry, class A_2 vibrations are inactive in the infrared. The decrease of molecular symmetry to C_2 results in all the vibrations becoming active in the infrared and Raman spectra.

We investigated the infrared spectra of Ph_2Be and Ph_2Mg in the range 200–3500 cm^{-1} [18] and assigned the principal bands and confirmed the bent structure of the molecules by comparison of experimental data with the frequencies and vibration modes calculated for different conformations of the Ph_2M molecules.

Table 4 presents bands assigned to the components of the M-sensitive vibrations in the above investigation. In accordance with the selection rules for the proposed molecular symmetry, both components of the M-sensitive vibrations are fairly intense in the infrared spectra, the splitting between them depending significantly on the C–M–C angle. It is noteworthy that, as for PhLi, the association of aromatic derivatives of beryllium and particularly of magnesium leads to a decrease of the force constant K_{C-M} and the appearance in the C–H stretching region in the infrared of C–H bands displaced towards longer wavelengths, in agreement with the ^1H NMR data for PhMgX solutions[13].

The band near 365–383 cm^{-1} in the infrared spectra of ethereal solutions of Ph_2Mg and PhMgBr, assigned by Salinger and Mosher[19] to the stretching PhMg vibration, is probably the B component of the t-vibration with its frequency reduced owing to the formation of an ether adduct.

IV. VIBRATION SPECTRA AND STRUCTURES OF PHENYL DERIVATIVES OF GROUP IIB ELEMENTS

1. Compounds of the Type Ph_2M

Aromatic derivatives of zinc, cadmium, and mercury are monomeric[20–22]. There are X-ray diffraction data demonstrating the linearity of the C–M–C framework of aliphatic derivatives of these elements[23] and also of Ph_2Hg.[24,25] On this basis a planar structure with D_{2h} symmetry has been adopted for Ph_2Zn, Ph_2Cd, and Ph_2Hg, but, as a result of the presence of a centre of symmetry, it should lead to an alternative prohibition: B_u vibrations are active only in the infrared and class Ag and Bg vibrations are active only in the Raman spectra. Unfortunately only the infrared spectra of these compounds have been studied sufficiently fully and the spectra have been interpreted by analogy with monosubstituted benzenes without taking into account the overall molecular symmetry. Therefore the infrared bands assigned[21,26,27] to M-sensitive vibrations should probably be regarded as B_u components of these vibrations active in the infrared spectra. Although the Raman spectra of Ph_2Zn (Kubas and Shriver[28]) and Ph_2Hg (Rodionov et al.[12]) published recently are in fact very incomplete, when combined with calculations on the in-plane vibrations of these molecules[12] they make it possible to detect certain symmetrical components of the M-sensitive vibrations. Table 5 lists the experimental and calculated wave-numbers of the M-sensitive vibrations of diphenyl compounds of zinc, cadmium, and mercury. The results show that the t-vibration, which appears in the range from 200 to 330 cm^{-1} with all the components, shows the maximum splitting of the B_{3u} and Ag components and the greatest sensitivity to the replacement of one metal by another. The 462 and 496 cm^{-1} bands, assigned[29] to the C–Hg–C stretching vibrations in the infrared spectra of $(C_6H_5)_2Hg$ and $(C_6F_5)_2Hg$ respectively, are probably associated with an out-of-plane y-vibration.

The effect of the deuteriation of the benzene rings on the position of the M-sensitive bands in the infrared spectra of $(C_6D_5)_2Zn$ and $(C_6D_5)_2Hg$ has been investigated[21,26]. It has been shown that the B_{3u} components of the t-vibration hardly change on deuteriation, while the r- and q-vibrations shift towards longer wavelengths by 30–40 cm^{-1}; on the other hand, according to Mink et al.[26] the wave-number of the q-vibration of $(C_6D_5)_2Hg$ decreases by approximately 100 cm^{-1}.

2. Compounds of the Type PhMX

X-Ray diffraction data demonstrated the linearity of the C–Hg–Cl and PhHgCl frameworks [30]. The structures of the analogous zinc and cadmium compounds are unknown. If it is assumed that all the compounds discussed in this section have a monomeric linear structure with C_{2v} symmetry, then, in contrast to compounds of the type Ph_2M, only class A_2 vibrations are inactive in the infrared.

Table 5. Experimental and calculated frequencies (wavenumbers, cm^{-1}) of the M-sensitive vibrations in the spectra of Ph_2M (M = Zn, Cd, or Hg).

Vibration		Ph_2Zn			Ph_2Cd		Ph_2Hg		
		expt.					expt.		
Designation	Symmetry (D_{2h})	i.r. spectra according to (Ref.21)	Raman spectra according to (Ref.28)	Calcn. based on Ref.18	i.r. spectra according to (Ref.21)	Calcn. based on Ref.18	i.r. spectra according to (Ref.21)	Raman spectra according to (Ref.18)	Calcn. based on (Ref.18)
q	B_{3u}	1076 s.		1070	1070 m	1065	1075 m.	—	1070
	A_g	—	—	1085	—	1080	—		1080
r	B_{3u}	677 s.		679	672 s.	670	670 s.	—	672
	A_g	—	666 m.	687	—	680	—	670 m.	685
t	B_{3u}	305 s.	—	325	270 s.	280	252 s.	—	253
	A_g	—	210 s(p)	210	—	205	—	212 s(p)	210
u	B_{2u}	220 m.	—	235	—	227	—	—	237
	B_{1g}	202 w.	—	197	—	190	—	—	193
y	B_{1u}; B_{2g}	430 s.		—	445 m	—	452 s.	—	—
		445 s.	455 w.				462 s.	—	—
x	B_{1u}; B_{2g}	170	170	—	—	—			

Table 6. Experimental and calculated frequencies (wavenumbers, cm^{-1}) of the M-sensitive vibrations in the spectra of PhMX (M = Zn, Cd, or Hg; X = Cl, Br, or I).

Designation of vibration according to Whiffen (Ref.5)	Vibration symmetry (C_{2v})	PhZnI (Ref.21)		PhCdI (Ref.21)		PhHgCl(Ref.26)		PhHgBr (Ref.26)		PhHgI (Ref.26)	
		i.r. spectra	calc.	i.r. spectra	calc.	i.r. spectra	calc.	i.r. spectra	calc.	i.r. spectra	calc.
q	A_1	1075	1063	1064	1040	1092	1142	1096	1141	1095	1137
r	A_1	672	660	672	660	674	666	674	664	671	661
t	A_1	280	310	250	250	220	241	216	204	242	247
u	B_1	185	210	—	225	184	223	198	228	213	223
y	B_2	445	470	443	465	453	468	454	468	451	468
x	B_2	165	190	—	162	180	163	175	163	160	163
ν_{M-X}	A_1	230	240	—	165	330	344	257	263	167	174

The infrared spectra of a large number of compounds with the general formula PhHgX, where X = Cl, Br, I, S, OH, O, CO, NO_3, etc. have been described in a review [27]. However, an adequate interpretation of the infrared spectra has been made only for the simplest derivatives PhHgCl, [21,26,27] PhHgBr, PhHgI, [26,27] PhZnI, and PhCdI. [21] The M-sensitive vibrations listed in Table 6 were isolated by analysing the experimental infrared spectra and by calculations on in-plane vibrations.

V. VIBRATION SPECTRA AND STRUCTURES OF PHENYL DERIVATIVES OF GROUP IIIB ELEMENTS

1. Compounds of the Type Ph_3M

It has been established experimentally that Ph_3B, Ph_3Ga, PhIn, and Ph_3Tl are monomeric in solutions and that only Ph_3Al is appreciably associated [20,31]. X-Ray [32] and electron [33] diffraction data indicate a planar trigonal structure of the central MC_3 unit in Ph_3B, Ph_3Ga, and Ph_3In molecules with D_{3h} symmetry and with the symmetry reduced to D_3 for the molecule as a whole owing to the relative positions of the phenyl groups. Ph_3Al crystals contain molecular dimers with symmetrical bridging phenyl groups [34]. These dimers are at least partially retained in solutions [35]. Therefore Ph_3Al presumably has a distorted planar molecular framework and there is probably a transition to C_{3v} or C_3 symmetry. Table 2 shows that the selection rules for the vibration spectra of molecules with D_{3h} and D_3 symmetries indicate that the M-sensitive vibrations (A_1' or A_1) are forbidden in the infrared and are active with marked polarisation in the Raman spectra. Degenerate vibrations (E′ or E) are active both in the infrared and Raman spectra and are depolarised. When the planar skeleton is distorted, i.e. on passing to C_{3v} symmetry, the symmetrical vibrations are no longer forbidden and the class A_1 vibrations should appear in the infrared spectra.

The infrared spectrum of Ph_3B was reported for the first time by Sharp and Sheppard [36] and that of Ph_3Al by Costa and coworkers [37,38], but without a detailed interpretation of the observed frequencies and their assignment. The infrared spectra of crystalline specimens of Ph_3B (Shurvell and Faniran [39,40]) and Ph_3Al (Shurvell [41]) have been measured and the observed bands have been assigned in terms of monosubstituted benzenes (local C_{2v} symmetry).

The present author and his coworkers [31,42,43] investigated the infrared spectra of triphenyl derivatives of boron, aluminium, gallium, and indium from 200 to 3200 cm^{-1} in different states of aggregation. In order to interpret the spectra, specimens enriched in boron-10, boron-11, and deuterium were obtained and calculations were made on the normal vibrations for the Ph–M and C_6D_5–M models. Subsequently the same investigators obtained the Raman spectrum [44] of Ph_3B and carried out calculations for the in-plane molecular vibrations of the class E′, A_1', and A_2' discussed in this section [12,44]; this yielded a complete interpretation of the vibration spectrum and demonstrated unambiguously the planar structure of the BC_3 central unit. Table 7 lists the experimental and calculated wavenumbers of the M-sensitive vibrations of the Ph_3M molecules, where M = B, Al, Ga, or In.

2. Compounds of the Type Ph_2MX

We were unable to find in the literature any direct measurements designed to elucidate structures of this type. Ph_2BCl and Ph_2BBr are known to be monomeric and they have been assigned the C_{2v} or C_2 symmetry with a planar central unit and rings displaced to some extent from this plane. All the vibrations of the C_2 structure are active in the infrared. The analogous aluminium and gallium compounds are dimerised and have M–X...M bridges [45], which leads to a distortion of the plane of the C_2MX central unit. The infrared spectra of compounds of the type Ph_2MX have been by no means fully investigated.

Bellamy and coworkers measured the infrared spectra of a number of compounds containing the Ph_2B group and assigned the intense absorption in the range 1250–1280 cm^{-1} to νPh–B.[46,47] However, fairly complete spectra and their interpretation have been published very recently. Nahm et al.[48] measured the infrared spectra of a series of compounds Ph_2BX, where X = F, Cl, Br, or I, and assigned the principal bands by comparing these spectra with one another and with the literature data[49]. Measurements have been made[12] of the infrared spectra of a number of compounds Ph_2MX (M = B, Al, or Ga; X = Cl or Br) in the range 200–2000 cm^{-1} and they have been interpreted with the aid of calculations of the frequencies and modes of the in-plane vibrations for a model with C_{2v} symmetry. Analysis of the experimental and calculated data indicates a strong interaction between the vibrations of the Ph–M and M–X groups. There is particularly strong mixing of the r and ν_{B-X} vibrations in the Ph_2BX spectrum, t and νAl–X in the Ph_2AlX spectrum, and t, u, and νGa–X vibrations in the Ph_2GaX spectrum. Additional difficulties arise in the interpretation of the spectra of the gallium and aluminium compounds as a result of their dimerisation[45].

Table 7. Experimental and calculated frequencies (wave-numbers, cm^{-1}) of the M-sensitive vibrations in the spectra of Ph_3M (M = ^{10}B, ^{11}B, Al, Ga, or In).[12,44]

Designation of vibration according to Whiffen (Ref.5)	Vibration symmetry (D_{3h})	Ph_3B			Ph_3Al		Ph_3Ga		Ph_3In	
		i.r. spectra	Raman spectra	calc. (D_{3h})	i.r. spectra	calc. (D_{3h})	i.r. spectra	calc. (D_{3h})	i.r. spectra	calc. (D_{3h})
q	E′	^{10}B 1248 ^{11}B 1235	1240 m(d)	1269 1250	1085 —	1075 —	1080	1069	1070	1065
	A_1'		1145 (s(p)	1160	—	1105	—	1072	—	1070
r	E′	^{10}B 895 ^{11}B 880	— —	910 895	— 670	— 710	— 665	690	673	685
	A_1'		690 s(p)	700	—	703	—	700		702
t	E′	^{10}B 650 ^{11}B 635	— —	630 625	— 425	— 452	— 315	335	270	260
	A_1'	—	255 m(p)	250	—	230	215	215	—	210
u	E′	^{10}B 408 ^{11}B 400	— —	425	332	310	—	250	248	240
	A_2'	—	—	300	—	220	225	207	195	185
y	E″,A_2''	—	—	—	460	—	440 445 453		446	—

Deacon and Green[50] investigated the infrared spectra of Ph_2TlBr in the range 200–3650 cm^{-1} and Srivastava et al.[51] extended this study to a series of compounds Ph_2TlX (X = Cl, CN, CNO, NCS, N_3, NO_2, etc.). The differences in the assignments by these two groups of investigators concern mainly two infrared bands. Deacon and Green[50] assigned a weak band near 1063 cm^{-1} to the q-vibration and a band near 230 cm^{-1} to the u-vibrations, while Srivastava assigned an intense band at 1020 cm^{-1} to the q-vibration and interpreted the 230 cm^{-1} band as a second component of the u-vibration.

The experimental and calculated wave-numbers of the M-sensitive vibrations of compounds with the general formula Ph_2MX are compiled in Table 8.

3. Compounds of the Type $PhMX_2$

The planar structure of the $PhBCl_2$ molecule was demonstrated by electron diffraction[52] and this is probably also true of the Br and I derivatives. If this is so, they have the C_{2v} symmetry and their infrared spectra should show all the vibrations except A_2.

The compounds $PhAlX_2$ and $PhGaX_2$ are associated into cyclic dimers with bridging M–X–M bonds, which should lead to a distortion of the geometry of an individual molecule and to changes in the vibration spectra[45].

The vibration spectra of boron derivatives have been investigated in greatest detail. Thus Butcher and Gerrard[53] measured the infrared spectra of $PhBCl_2$ and $PhBBr_2$ in the range 400–4000 cm^{-1} and assigned the principal bands. An intense 1215–1236 cm^{-1} band was assigned to Ph–B stretching vibrations and bands in the range 850–960 cm^{-1} were assigned to the symmetric and antisymmetric vibrations of the group BX_2.

Greenwood and Wright[54] supplemented these investigations by a study of the infrared spectra of $PhBF_2$. They noted an appreciable increase of the wave-number of the Ph–B stretching vibrations (1292, 1300 cm^{-1}) and detected the vibrations of the BF_2 group in the range 1340–1380 cm^{-1}. The increase of νPh–B was explained by the partial double bond character of Ph–B owing to the delocalisation of the ring π electrons and the P_π non-bonding electron of fluorine via the vacant p orbital of the boron atom. Lockhart[55,56] measured the infrared and Raman spectra of the $PhB^{35}Cl_2$, $PhB^{35}Cl^{37}Cl$, $PhBBr_2$, and PhBBrCl over a wide range (20–1650 cm^{-1}) and carried

Table 8. Experimental (infrared) and calculated frequencies (wave-numbers, cm^{-1}) of the M-sensitive vibrations of compounds of the type Ph_2MX (M = B, Al, or Ga; X = F, Cl, Br, or I).

Designation of vibration according to Whiffen (Ref.5)	Vibration symmetry (C_{2v})	Ph_2BF	Ph_2BCl (Ref.12)		Ph_2BBr (Ref.12)		Ph_2BI	Ph_2AlCl (Ref.12)		Ph_2AlBr (Ref.12)		Ph_2GaCl (Ref.12)		Ph_2GaBr (Ref.12)		Ph_2TlCl	Ph_2TlBr
		i.r. spectra (Ref.48)	i.r. spectra	calc.	i.r. spectra	calc.	i.r. spectra (Ref.48)	i.r. spectra	calc.	i.r. spectra	calc.	i.r. spectra	calc.	i.r. spectra	calc.	i.r. spectra (Ref.52)	i.r. spectra (Ref.55)
q	B_1	1375 m.	1250 s.	1285	1260 s.	1280	1260 s.	1095 s.	1090	1095 s.	1085	1090 s.	1072	1090 s.	1072	1015	1063
	A_1	1338 m.	1185 s.	1168	1167 s.	1165	1166 s.	1085 s.	1080	1085 s.	1075	1070 s.	1069	1070 s.	1069		
r	B_1		896 m.	915	892 m.	910	887 m.	675 s.	715	675 s.	715	675 s.	700	670 s.	700		668
	A_1		663 m.	685		675			700		700		690		690		
t	B_1	671 w.	630 m.	635	647 s.	630	633 m.	490 s.	505	450 s	500	335 m.	360	320 m.	355	255	253
	A_1	582 w.	580 m.		580 s.		571 m.		260		230	255 w.	250	245 w.	220	240	
u	B_1		308 w.	308		300			250		245	230 w.	220	210 w.	220		231
				300					230		210		205		195		
y	B_2		600					450 s.		455 s.		453 s.		445 s.		452	450
			545							445 s.		448 s.				438	
ν_{MX}	A_1	1348	910 s.	905	837 s.		811 s.	490 s.	480	450 s.	460	335 m.	340	295 m.	310		

Table 9. Experimental and calculated frequencies (wave-numbers, cm^{-1}) of the M-sensitive vibrations of molecules of the type $PhMX_2$ (M = B, Al, or Ga; X = F, Cl, Br, or I).

Designation of vibration according to Whiffen (Ref.5)	Vibration symmetry (C_{2v})	$PhBF_2$	$PhBCl_2$ (Ref.58)		$PhBBr_2$ (Ref.58)		$PhBI_2$	$PhAlCl_2$ (Ref.58)		$PhAlBr_2$ (Ref.58)		$PhGaCl_2$ (Ref.58)		$PhGaBr_2$ (Ref.58)	
		i.r. spectra (Ref.54)	i.r. spectra	calc.	i.r. spectra	calc.	i.r. spectra (Ref. 48)	i.r. spectra	calc.	i.r. spectra	calc.	i.r. spectra	calc.	i.r. spectra	calc.
q	A_1	1292	1225	1210	1220	1205	1208	1095	1080	1090	1080	1090	1073	1085	1073
r	A_1	—	895	880	880	865	—	675	700	670	700	674	690	670	690
t	A_1	559	632 380	650 ** 355	622	635	585	475 350	482 (460)* 295 (360)	405	432 (405) 220	390	397 (392)	315 300	320(312)
u	B_1	—	330	320	255	270	—	255	260	210	185	228	270	240	210
y	B_2	643	550 475	542 490	525 450	525 472	—	—	—	—	—	—	—	—	—
ν_{M-X}	B_1	1382	915	905	850	827	717	475	495 (465)	405	422 (395)	390	400 (380)	315 300	335 (315)
	A_1	1344	632 380	650 ** 355	622 270	635 240	691	475 350	482 (460) 295 (360)	405	432 (405) 220	390 315	397 (392) 290 (300)	315 300 250	320 218(237)

*The wave-numbers calculated for the model with tetrahedral CMX angles are given in brackets.

**According to the calculation two moles contribute, making the vibrations $t_{A_1} + \nu^{A_1}_{M-X}$.

out a complete assignment of the observed bands. The differences between the band assignments in the $PhBCl_2$ and $PhBr_2$ spectra by the two groups of investigators[53,55] concern mainly the position of the νS band of BX_2.

Nahm et al.[48] studied the infrared spectra (250–4000 cm^{-1}) of a series of compounds $PhBX_2$, where X = F, Cl, Br, or I, and Lee[57] described the infrared spectrum of $PhTlX_2$.

The present author and his coworkers[58] investigated experimentally (infrared spectra) and theoretically (calculation of the frequencies and modes of the normal vibrations) a series of compounds of the type $PhMX_2$ (where M = B, Al, or Ga; X = Cl or Br). Analysis of the results enabled the authors to refine the band assignments in the spectra of boron derivatives and to follow the variation of the frequencies and modes of the M-sensitive vibrations on replacement of M and X.

Stephenson and Coburu[98] discussed certain questions of the structure of the compounds and their dimers on the basis of calculations for planar and tetrahedral conformations of the gallium and aluminium derivatives and a comparison of the infrared spectra with the available[59-64] infrared and Raman spectra of the dimers $(AlX_3)_2$ and $(GaX_3)_2$.[59-64] Table 9 lists the experimental and calculated wave-numbers of the M-sensitive vibrations of a series of compounds of the type $PhMX_2$.

VI. VIBRATION SPECTRA AND STRUCTURES OF PHENYL DERIVATIVES OF GROUP IVB ELEMENTS

Numerous studies have been made on the vibration spectra of compounds of the type $PH_4 - nMX_n$ (where M = C, Si, Ge, Sn, or Pb; X = Cl, Br, or I; n = 0, 1, 2, 3, or 4), but here too there are contradictions in the interpretation and many of the investigations do not include the long-wavelength part of the spectrum, which is particularly important for heavy elements.

1. Compounds of the type Ph_4M

X-Ray diffraction studies showed that crystalline Ph_4C,[65] Ph_4Si,[66] Ph_4Ge,[67] and Ph_4Sn[68] have a central C_4M unit with a tetrahedral structure (T_d symmetry) with the overall molecular symmetry reduced to S_4 when the disposition of the phenyl groups is taken into account. Such decrease of symmetry from T_d to S_4 should be reflected in the infrared spectra primarily by a lifting of the prohibition of symmetrical class A_1 vibrations in the infrared. However, the majority of studies on the vibration spectra of the compounds Ph_4M dealt with individual parts of the spectrum[69-74] and the bands observed in the infrared and Raman spectra were interpreted by comparison with the spectra of aliphatic compounds of the same elements[75] or of halogenobenzenes, i.e. in terms of the monosubstituted benzene approximation with C_{2v} symmetry without taking into account the vibrations of the central unit of the molecule and the interaction of different phenyl groups[76].

In later studies by Smith[77,78], Poller and coworkers[79,80], and other investigators[81-83] the vibration spectra of Ph_4M were considered from the standpoint of the overall molecular symmetry and the possible splitting of the M-sensitive vibrations. The present author and his coworkers[84] calculated the wave-numbers and modes of the in-plane vibrations of the Ph_2M fragment with a CMC angle of 109° and M = C, Si, Ge, Sn, or Pb, which largely confirmed the assignments of the M-sensitive vibrations in the above investigations[78-83] and showed the necessity to take into account the overall molecular symmetry.

Table 10 presents the experimental wave-numbers of the M-sensitive vibrations for Ph_4M molecules and the values calculated for the Ph_2M fragment.

2. Compounds of the Type Ph_3MX

We were unable to find in the literature any direct data concerning the compounds of the type Ph_3MX. The central unit most probably has a tetrahedral structure with C_{3v} or C_3 molecular symmetry. In this case both components of the M-sensitive vibrations (A and E) should be active in the infrared and Raman spectra. The differences in the spectra on passing from C_{3v} to C_3 symmetry are probably small.

A number of workers investigated the vibration spectra of Ph_3MX, where M = C, Si, Ge, Sn, or Pb; X = H, D, Cl, Br, etc., but, as for Ph_4M molecules, most of the investigations dealt only with individual sections of the spectrum and the assignments were made by analogy with monosubstituted benzenes (C_{2v} symmetry).

The infrared spectra of a number of compounds containing the Ph_3C group have been measured[69,85-87] and two bands, at 1185 and 1280 cm^{-1}, have been assigned to the C_6H_5-C stretching vibrations; these vibrations were found to depend little on the substituent X. On the basis of the $^{12}C \rightarrow {}^{13}C$ isotopic shift, Weston et al.[88] assigned only one infrared band to the stretching vibration, this is near 1192, 1202, and 1211 cm^{-1} for Ph_3CH, Ph_3COH, and Ph_3CCl respectively.

Table 10. Experimental and calculated frequencies (wave-numbers, cm^{-1}) of the M-sensitive vibrations in the spectra of Ph_4M (M = C, Si, Ge, Sn, or Pb).

Designation of vibration	Vibration symmetry (S_4)	Ph_4C		Ph_4Si		Ph_4Ge		Ph_4Sn		Ph_4Pb	
		expt. (Ref. 87)	calc.* (Ref. 81)	expt. (Ref. 78)	calc.* (Ref. 84)	expt. (Ref. 81)	calc.* (Ref. 84)	expt. (Refs. 78,82)	calc.* (Ref. 84)	expt. (Refs. 82,83)	calc.* (Ref. 84)
q	E	1260	1220	1108	1105	1033	1086	1075	1085	1060	1080
	A	1190	1205	1100	1085	1030	1070	1062	1069	1063	1065
r	E	—	860	710	716	675	690	682	688	668	683
	A	—	820	700	700	655	673	—	671	645	665
t	E	635	590	435	425	332	305	268	260	225	226
	A	240	253	235	228	222	217	214	210	200	193
u	E	332	350	261	228	232	319	225	275	181	240
	B	292	180	223	215	214	204		195		187
y	E	527	—	520	—	480	—	460	—	450	—
	B	492		510		465		448		440	
x	E	200	—	185	—	187	—	193	—	147	—
	B			170		168		152			

*The calculation was performed for the Ph_2M model with the angle $\alpha = 109°$.

Kriegsmann and Schowtka[71] assigned the 490–515 cm^{-1} bands in the spectra of Ph_3SiX (where X = H, F, Cl, or OH) to $\nu Ph-Si$ (ν_{as}) and Smith assigned the 420–445 cm^{-1} and 330 cm^{-1} bands to t_E- and t_A-vibrations respectively[72].

Later Smith[77] made a detailed study of the infrared and Raman spectra of Ph_3SiX and the Si-sensitive vibrations listed in Table 11 were taken from his communication. The infrared spectra of compounds of the type PhGeX in the range 200–2500 cm^{-1} were reported by Cross and Glockling[89] and by Mackay et al.[90], while Durig et al.[91] extended the infrared range to 33 cm^{-1} and investigated the Raman spectrum; on this basis, they assigned the Ge-sensitive bands (the A and E components).

The vibration spectra of Ph_3SnX were studied by a number of workers[70,73-75,79-83,85-92]. Kriegsmann measured the infrared and Raman spectra of Ph_3SnX (where X = OH, Cl, Br, or I).[75,93,94]. Harrah and Ryan[95] interpreted the spectra of a number of aromatic organotin compounds and extended the measurements to 200 cm^{-1}.

Poller made a detailed study of the $Ph_{4-n}SnX_n$ (where X = Cl or Br; n = 1, 2, 3, or 4) spectra[79] and his assignments have been confirmed by other workers[80,92,96].

Clark et al.[83] investigated the infrared and Raman spectra of Ph_3PbX (where X = F, Cl, Br, or I) and assigned the observed bands. From the shift of certain Pb-sensitive bands in different states of aggregation, the authors deduced that the compounds are monomeric in benzene solutions and associated in crystals.

3. Compounds of the Type Ph_2MX_2

There are almost no experimental data concerning the structure of compounds of this type. Keidel and Bauer[85] suggest that Ph_2SiCl_2 has C_2 symmetry. The M-sensitive vibrations should then be split into A and B components active in the infrared and Raman spectra. A more complex crystalline structure, consisting of planar Cl_2PbCl_2 cells containing equivalent Pb–Cl bonds with the phenyl groups at right angles to the axis of the ring and bonds approximately perpendicular to the plane of the ring, has been described for Ph_2PbCl_2.[87]

Table 11. Experimental frequencies (wave-numbers, cm^{-1}) of the M-sensitive vibrations in the spectra of Ph_3MCl and Ph_2MCl_2 (M = C, Si, Ge, Sn, or Pb).

Designation of vibration according to Whiffen (Ref.5)	Vibration symmetry (C_{3v})	Ph_3MCl					Vibration symmetry (C_{2v})	Ph_2MCl_2			
		C (Ref. 88)	Si (Ref. 77)	Ge (Ref. 91)	Sn (Ref. 79)	Pb (Ref. 83)		Si (Ref. 77)	Ge (Ref. 90)	Sn (Ref. 80)	Pb (Ref. 83)
q	E	1210	1117	1094	—	1058	B_1	1120	1095	—	1052
	A_1		1102				A_1	1102	1088	—	
r	E	845	716	678	—	687	B_1	717	680	—	652
	A_1	818	700	665	—	—	A_1	697	671	—	
t	E	635	434	329	270	235,225	B_1	444	332	275	236
	A_1	(263)	306	273	240	200	A_1	318	270	230	195
u	E	311	250	250	217	175	B_1	283	—	—	167
	A_1		240	232	210		A_1	245	270	—	—
y	E	503	504	469	450	448	B_2	480	453	—	—
	A_1			460	442	441			420	444	445
						438					
ν_{M-X}	A_1	746	552	375	335	290	B_1	576	398	365	—
		735					A_1	548		356	

The vibration spectra of Ph_2CH_2, Ph_2SiX_2 (X = H, CH_3, F, Cl, or OH,[71,72,77,78,90] Ph_2GeX_2 (X = Cl or Br),[90] Ph_2SnX_2 (X = Cl, Br, or I),[73,80,90] and Ph_2PbX_2 (X = Cl, Br, or I)[84] have been investigated experimentally[78,97]. The M-sensitive vibrations of these compounds are listed in Table 11.

4. Compounds of the Type $PhMX_3$

It has been shown by electron diffraction that $PhMX_3$ molecules have a CMX_3 tetrahedral framework and the C_{3v} symmetry has been assigned to them[23]. Calculation of the normal vibration modes for molecules of the type $PhMX_2$, where M is a Group IIIB element, showed that the M-sensitive vibrations do not have the character of individual group vibration and include to a greater or lesser extent the vibrations of all the atoms of the central unit[58]. However, in analysing the vibration spectra of $PhMX_3$, most workers consider separately the vibrations of the Ph–M (C_{2v} symmetry) and MX_3 (C_{3v} symmetry) groups and observe the non-split q-, r-, t-, u- and x-vibrations of monosubstituted benzene and the symmetrical and degenerate vibrations of the MX_3 groups.

The vibration spectra of $PhCH_3$, its deuteriated analogues, and $PhCCl_3$ have been investigated in detail by a number of workers[98-100] and have been fully interpreted from an analysis using experimental infrared, Raman spectroscopic, and calculated data.

The infrared and Raman spectra of $PhSiX_3$, where X = F, Cl, or H, have been studied[71]. Smith extended the investigation of the infrared spectra of these compounds initially to 250 cm^{-1} [72,77] and later to 50 cm^{-1}.[73]

Durig et al.[101] supplemented these studies by investigating the Raman spectra of $PhSiCl_3$. The same

workers[78,101] and also Jakoubkova and Hetflejs[102] made a detailed study of the vibration spectra of $PhGeCl_3$; Durig and Sink[103] obtained and analysed in detail the infrared and Raman spectra of $PhGeCl_3$. The infrared spectra of $PhSnCl_3$ have been investigated up to 400 cm^{-1} [70,73] and subsequently the range was extended to 50 cm^{-1} (Smith[78]) and the Raman spectra were also studied[101].

Table 12. Experimental frequencies (wave-numbers, cm^{-1}) of the M-sensitive vibrations in the spectra of $PhMCl_3$ (M = C, Si, Ge, Sn, or Pb).

Designation of vibration according to Whiffen (Ref.5)	$PhCCl_3$ (Ref.98)		$PhSiCl_3$		$PhGeCl_3$		$PhSnCl_3$		$PhPbCl_3$
	i.r. spectra	Raman spectra	i.r. spectra (Ref.78)	Raman spectra (Ref.101)	i.r. spectra (Ref. 78)	Raman spectra (Ref. 101)	i.r. spectra (Ref. 78)	Raman spectra (Ref.101)	i.r. spectra (Ref. 83)
q	1188	1184	1118	1122	1088	1085	1067	1067	1052
r	627	630	714	719	674	677	662	660	652
t	308	307	346		290		250		240
u		246	284	248	255	214	218	184	170
y	507	506	460		454		439		445
ν_{M-XE}	790	788	584		429		377		—
ν_{M-XA}				518		407		363	—

Table 12 lists the wave-numbers assigned to the M-sensitive vibrations.

VII. VIBRATION SPECTRA AND STRUCTURES OF PHENYL DERIVATIVES OF GROUP VB ELEMENTS

A pyramidal structure is characteristic of Group VB elements in the tervalent state. The angle between the bonds at the vertices of the pyramid depends on the nature of the group joined to the element. In aromatic derivatives the CMC angle is reduced from 116° ± 2° in Ph_3N (Sasaki et al.[104]) to 103° in Ph_3P (Daly[105]) and 96° in Ph_3As (Gullen and Hochstrasser[106]), which has been attributed to different degrees of conjugation. The overall symmetry of molecules of this type depends on the structure of the groups combined with the elements.

1. Compounds of the Type Ph_3M

As stated above molecules of this type are pyramidal and, for the same phenyl substituents, the central MC_3 unit should have C_{3v} symmetry. However, it has been shown[104,105] that the overall symmetry of such molecules is reduced to C_3 owing to the rotation of the planes of the rings. Such molecular symmetry should lead to the activity of the class A and E vibrations to which all M-sensitive vibrations belong, both in the infrared and Raman spectrum, and in the latter the class A vibrations should be polarised.

Despite the large-scale employment of aromatic nitrogen derivatives in the chemistry of dyes and in photochemical research, the vibration spectra or even the simplest derivative Ph_3N have been studied very incompletely. As a rule, only the positions of individual bands have been determined in the spectra of tertiary aromatic amines.

Thus, having analysed the infrared spectra of a large number of tertiary aromatic amines, Bellamy[107], Ritschl[108], and Katritzky and Jones[109] assigned the intense bands in the range 1210–1340 cm^{-1} to νPh–N stretching vibrations and noted that the positions of the bands depend on the electron-accepting properties of the ring substituents.

Colthup[110] assigned the medium-intensity band near 1275 cm^{-1} in the infrared spectrum of Ph_3N to νPh–N. Since account must be taken of the possibility of the splitting of the M-sensitive vibrations of the Ph_3N molecule, the infrared band discovered by Colthup should probably be assigned to the E component of the *q*-vibration. However, the q_A-component has never been observed, although it should be active in the infrared for C_{3v} or C_3 symmetry. Colthup's studies on the infrared and Raman spectra with polarisation and also calculations on the A and E class vibrations of Ph_3N made it possible to assign to the q_E- and q_A-vibrations an intense infrared and depolarised Raman band near 1280 cm^{-1} and a weak infrared band and intense and highly polarised Raman line near 1175 cm^{-1}.[44] These data indicate a small deviation of the central Ph–N bonds from the plane and suggest the possibility of D_3 symmetry for the Ph_3N molecule.

Table 13. Experimental and calculated frequencies (wave-numbers, cm^{-1}) of the M-sensitive vibrations in the spectra of Ph_3M (M = N, P, As, Sb, or Bi).

Designation of vibration according to Whiffen (Ref.5)	Vibration symmetry (C_3)	Ph_3N (Ref.44)			Ph_3P (Ref.111)		Ph_3As (Ref.111)		Ph_3Sb (Ref.111)		Ph_3Bi (Ref.111)	
		expt.		calc. (D_{3h})	expt.							
		i.r. spectra	Raman spectra		i.r spectra	Raman spectra	i.r spectra	Raman spectra	i.r. spectra	Raman spectra	i.r. spectra	Raman spectra
q	E	1280	1280 m(d)	1265	1090 m		1075 m.		1065 m.		1061 m.	
	A		1175 s(p)	1175	1104 w.	1098 s(p)	1082 w.	1086 m(p)		1068 m(p)	1055 m.	1060 w.
r	E	890		890	690 s.	703 m.	668 m.		655 w.		645 w.	650 s.
	A		717 s(p)	720		684 m.		670 s(p)		657 (p)		
t	E	620		630	420 m.	412 m.	310 m.	317 m.	276 m.	276 w.	225 s.	223 m.
	A		290 m(p)	253	255 m.	253 s(p)	242 w.	241 s(p)		224 m(p)	216 m.	210 s.
u	E	435 w.	417 m(d)	465	270 w.	274 w.	233 w.					
	A	325 w.	335 m(d)	365	214 w.	215 w.	192 m.	197 s.	255 s.	259 w.	235 m. 199	236 200
y	E, A	515 503			513 s. 500 s. 490 s.	502 m.	473 m. 468 s.		462 m. 450 s. 446 m.	460 w.	450 s. 435 m.	
x	E, A	242	250		196 186	202 191	192 m. 184 w.	197 s.	179 160	178 168	166 146	166

In recent years a number of studies have been made on the vibration spectra of triphenyl compounds of phosphorus[76,95,105,111–123], arsenic[76,95,111,117,119,123–127], antimony[76,95,111,123,128], and bismuth[76,95,111]. However, despite a fairly large number of investigations and the availability of data not only for infrared but also for Raman spectra with polarisation, the observed bands were as a rule assigned to specific vibrations in terms of the monosubstituted benzene approximation. The possible splittings of the M-sensitive vibrations were discussed only in later studies by Green and coworkers[118,125,126]. Table 13 lists the M-sensitive bands.

It is noteworthy that, in contrast to Ph_3N, in the infrared spectrum of which the A components of the M-sensitive vibrations are inactive (approximate D_3 symmetry), both components are as a rule observed in the infrared spectra

of the compounds Ph_3M, where M = P, As, or Sb. This can be traced particularly clearly for the components of the *t*-vibrations.

2. Compounds of the Type Ph_2MX

It has been shown by electron diffraction that aliphatic derivatives of Group VB elements of the type $(CH_3)_2MX$ have C_s symmetry [23]. Similar conclusions have been reached concerning the structure of aromatic derivatives on the basis of polarisation data for Raman spectra. In the case of C_s symmetry all the vibrations should be observed in the infrared and Raman spectra and therefore the infrared spectra should show both components of the M-sensitive vibrations.

Bellamy [107] and Katritzky and Jones [109] assigned to the Ph–N vibrations the intense infrared bands of Ph_2NH and Ph_2NCH_3 in the range 1280–1350 cm^{-1}, increasing to 1370 cm^{-1} in Ph_2ND as a result of interaction with N–D deformation vibrations [129].

Bearing in mind the smallness of the deviation from planarity of the C_3N central unit in Ph_3N, we calculated the wave-numbers and modes of the vibrations of the planar Ph_2NCH_3 model (C_{2v} symmetry). [130] The principal bands were assigned by comparison of the infrared spectra of Ph_3N and Ph_2NCH_3 and calculations on the vibrations of these molecules.

The vibration spectra of Ph_2PH, [115,131] Ph_2AsH, [131] Ph_2PCl, [122,132] Ph_2AsCl, Ph_2AsBr, [127] and Ph_2AsCH_3 [125,126] were investigated in a number of studies. Analysis of the infrared and Raman spectra of most of these compounds made it possible to separate the M-sensitive vibrations, which are listed in Table 14.

Table 14. Experimental frequencies (wave-numbers, cm^{-1}) of the M-sensitive vibrations in the spectra of Ph_2MX and $PhMX_2$.

Designation of vibration according to Whiffen (Ref.5)	Vibration symmetry (C_s)	Ph_2NCH_3	Ph_2PCl		Ph_2AsCl		$PhN(CH_3)_2$	$PhPCl_2$		$PhAsCl_2$	
		i.r. spectra (Ref. 130)	i.r. spectra (Ref. 132)	Raman spectra (Ref.132)	i.r. spectra (Ref. 127)	Raman spectra (Ref.127)	i.r. spectra (Ref. 130)	i.r. spectra (Ref. 132)	Raman spectra (Ref.132)	i.r. spectra (Ref. 132)	Raman spectra (Ref.132)
q	A″	1282 s.	1096 s.		1075		1230 s.	1085 s.	1087 w(p)	1076	1077
	A′	1250 s.		1099 w(p)		1082					
r	A″	865 s.	700 s.		668		810 w.	699 s.	698 w(p)	672	677
	A′	785 m.		693 w(p)		672					
t	A″	593 m.	404 s.		312	320	525 w.				
	A′	567 s.		285 w(p)	301	302			290 m(p)	307	312
u	A″					248	465 w.				254
	A′					218					227
y	A″	510 m.	462 m.		473 460	479 465	515 m.	460 s	460 m(d)	460	465
νM–X	A′ (A′, A″)	953 m.	593 s. 462 m.		372	372	1060 m. 945 m.	500 s. 460 s.	500 m(p) 460 m(d)	368 390	369 393

3. Compounds of the Type $PhMX_2$

It has been shown by electron diffraction that in the vapour phase $PhNH_2$ has the C_s symmetry and therefore the N-sensitive vibrations are active in both infrared and Raman spectra. Bellamy [107] and Katritzky and Jones [109] assigned to νPh–N a band in the range 1250–1340 cm^{-1} in the infrared spectra of a large series of primary aromatic amines. Ritschl and Kunkel [133] studied the infrared spectra of 18 *para*- and *meta*-substituted dimethylanilines and assigned the 1340 cm^{-1} band to the Ph–N vibrations and the 1057 and 943 cm^{-1} bands to the ν_{as} and ν_s vibrations of the CH_3–N group. On the basis of the $^{14}N \rightarrow {}^{15}N$ isotopic shift, Tsuboi assigned the 1276 cm^{-1} infrared band of $Ph^{15}NH_2$ to the stretching vibration of the Ph–N group. [134]

According to Evans's data [135], this band should be regarded as due to the *q*-vibration. The remaining N-sensitive vibrations have been much less studied. The infrared and Raman spectra of $PhPH_2$, [121,131] $PhAsH_2$, [131] $PhPCl_2$, [122,132] $PhAsCl_2$, [127,132] $PhAsBr_2$, [127] and $PhAs(CH_3)_2$, [125,126] have been studied in a number of investigations. Table 14 lists the vibrations assigned to the PhM and MX_2 groups.

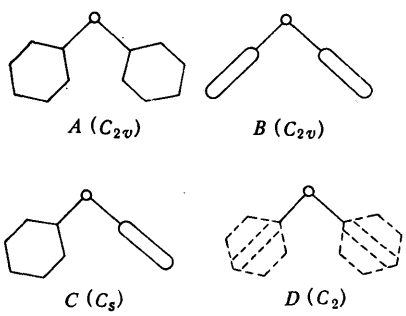
Analysis of the vibration spectra has confirmed the C_s symmetry of the molecules investigated [121,131,132,135]. The barrier to rotation of the C–N bond in the $PhNH_2$ molecule (3.54 kcal $mole^{-1}$) and the barrier to inversion at the nitrogen atom (4.5 kcal $mole^{-1}$) have been estimated [135].

VIII. VIBRATION SPECTRA AND STRUCTURES OF PHENYL DERIVATIVES OF GROUP VIB ELEMENTS

Aromatic derivatives of Group VIB elements in the crystalline state have an R–M–R central unit with a bent structure ($\alpha < 180°$) and the planes of the benzene rings are rotated relative to one another by an angle φ. The angles depend on the central atom M and are $\alpha = 123° \pm 2°$ for $(p\text{-}Br\text{-}C_6H_4)_2O$, [23] $\alpha = 109°$ and $\varphi = 56°$ for $(p\text{-}CH_3C_6H_4)_2S$, [138] $\alpha = 106°$ and $\varphi = 55°$ for $(p\text{-}CH_3C_6H_4)_2Se$, [139] and $\alpha = 101°$ and $\varphi = 62°$ for $(p\text{-}CH_3C_6H_4)_2Te$. [140]

Compounds of the Type Ph_2M

When discussing the vibration spectra of molecules of this type, one considers several configurations differing in the disposition of the benzene rings relative to one another and referring to different symmetry species:



As for the phenyl derivatives of the elements of other Groups, some investigators interpret the vibration spectra of the compounds examined in this section in terms of the monosubstituted benzene approximation without taking into account the interactions of two phenyl groups via the M atom [137]. Katon and Feairheller [141] and Green [142] believe that the asymmetric configuration C (C_s symmetry) is the most probable and interpret the vibration

spectra of Ph_2O and Ph_2S from the standpoint of the presence of two non-equivalent weakly interacting rings: the π orbitals of one ring overlap with those of the O or S atoms, while the second ring is not involved in such overlapping. On this basis, different M-sensitive vibrations are assigned to each benzene ring. However, other investigators concluded from a comparison of the polarisabilities and dipole moments [143] and also an analysis of the infrared, Raman, and NMR spectra [147] that the rings in these molecules are fairly mobile and therefore the B and D configurations with equivalent rings are probable for Ph_2M. The present author's calculation on class A_1 and B_1 vibrations of the A and B models of the Ph_2O and Ph_2S molecules [136] permits an interpretation of the bands which have been assigned [142,143] to the M-sensitive vibrations of two non-equivalent rings, being the symmetric and antisymmetric components of these vibrations. However, it has been shown that the contributions of the first and second rings of model C to the M-sensitive vibrations are in fact non-equivalent.

The vibration spectra of the phenyl derivatives of selenium and tellurium have been hardly investigated. Fritz and Keller [137] measured the infrared spectra of a number of O, S, Se, and Te derivatives in the range 250 to 3500 cm^{-1}, but the spectra are quoted almost without interpretation. The authors assigned bands near 455 to 487 cm^{-1} to Ph–Te vibrations.

Table 15. Experimental and calculated frequencies (wave-numbers, cm^{-1}) of the M-sensitive vibrations in the spectra of Ph_2M (M = O, S, Se, or Te).

Designation of vibration according to Whiffen (Ref.5)	Vibration symmetry (C_2)	Ph_2O			Ph_2S			Ph_2Se		Ph_2Te	
		i.r. spectra (Ref.6)	Raman spectra (Ref.6)	calc. for 120° (Ref.136)	i.r. spectra (Ref.7)	Raman spectra (Ref.7)	calc. for 110° (Ref.136)	i.r. spectra (Ref.137)	calc. for 105° (Ref.107)	i.r. spectra (Ref.137)	calc. for 100° (Ref.136)
q	B	1236 s.	1240 w.	1238	1083 s.	1093 s.	1075	1064 m.	1070	1063 w.	1069
	A	1198 m.	1200 m(p)	1205	1085 s.	1095 s(p)	1097	1085 m.	1085		1082
r	B	866 s.	868 w.	850	688 s.	696 s.	690	665 s.	672	662 s.	670
	A	798 s.	800 m(p)	785	700 w.	696 s(p)	700	687 s.	685		685
t	B	563 w.	568 m.	550	412 w.	412 w.	402	318 m.	305	255 s.	255
	A	314 w.	315 m(p)	290	270 w.	270 m(p)	280		266	202 w.	208
u	B	498 s.	508 w.	535	412 w.	412 w(d)	403		230	274 w.	266
	A	412 w.	418 w(p)	422 290	214	213 m(d)	220		220	188 s. 146 w.	218
x	B										
y	B	498 s. 480 s. 478 s	485 w.		519 s. 466 s.			479 s. 456 s.		460 s. 445 s.	

McWhinnie and coworkers [145] assigned the 255 and 202 cm^{-1} bands in the infrared and Raman spectra of Ph_2Te_2 to the asymmetric and symmetrical Ph–Te vibrations respectively. The present authors' calculations of the wave-numbers and modes of the in-plane normal vibrations of the Ph_2Se and Ph_2Te molecules [18], using experimental spectra [137] and structural data [139,140], make it possible to assign the bands in Table 15 to the Se- and Te-sensitive vibrations.

Analysis of the experimental and calculated data for the vibration spectra of aromatic derivatives of the elements permits certain general conclusions.

1. For the vibration spectra to yield sufficiently complete information concerning the structure of aromatic derivatives of the elements, the influence of the nature of the element, and of the degree of complex formation, it is necessary to take into account the overall molecular symmetry and the possible interaction of the substituents via the atom of the element. The monosubstituted benzene approximation employed in the majority of investigations is inadequate for polyvalent elements.

2. Calculations on the vibrations of the phenyl derivatives of Group I–VI elements have established a general relation governing the dependence of the force constants K_{Ph-M} on the position of the element in the Periodic System (Table 16).

Table 16. The force constants K_{Ph-M} for Ph_nM (in units of 10^6 cm^{-1}).

Li 1.2	Be 6.7	B 6.5	C 6.5	N 7.5	O 7.5	F 9.0
	Mg 3.2	Al 3.7	Si 4.3	P 4.12	S 4.1	Cl 5.8
	Zn 3.7	Ga 3.82	Ge 3.8	As	Se 3.7	Br 4.8
	Cd 3.5	In 3.6	Sn 3.65	Sb	Te 3.55	I 3.9
	Hg 3.7	Tl	Pb 3.5	Bi		

Note. The K_{Ph-M} were obtained for derivatives of Group I, III, and V elements [12,44], Group II and VI elements [18], Group IV elements (Ph_2M model with $\angle CMC = 109°$), [84] and Group VII elements [3] using a conversion factor of 1.56.

The principal, most significant change in K_{Ph-M} is its decrease within each Group on passing from elements of the Second Period to those of the Third, Fourth, etc. Periods, K_{Ph-M} decreasing most markedly on passing from elements of the Second Period to those of the Third Period.

Analysis of the published data on the force constants K_{C-M} for methyl derivatives of the same elements reveals a qualitatively similar behaviour [137]. This leads to the conclusion that the main factor influencing the value of K_{C-M} is probably the efficiency of the overlapping of the orbitals forming the C–M σ bond which depends significantly on the relative dimensions (principal quantum number) and geometry (hybridisation) of the orbitals of the valence electrons linking the atoms.

3. The Ph–M stretching vibration of the compounds considered here is not characteristic only of the C–M bond and involves to a greater or lesser extent several complex vibrations of the entire molecule (the q-, r-, and t-vibrations according to Whiffen [5]). When several phenyl groups are attached to a polyvalent atom M, each such vibration is split into components, whose number, activity, and the degree of splitting depend on the nature of the element and molecular structure.

4. Analysis of the calculated modes of the q-, r-, and t-vibrations shows that the contribution of ν_{Ph-M} to each of the three vibrations is non-equivalent and depends

mainly on the force constant K_{Ph-M}. When the C–M bond is very rigid ($K_{Ph-M} > 5 \times 10^6$ cm^{-2}), the q- and r-vibrations are most sensitive to the stretching of this bond and to structural changes in the molecule. Under these conditions, the t-vibration hardly includes ν_{Ph-M} and therefore carries little information about the central framework of the molecule. Table 16 shows that derivatives of elements in the Second Period should be regarded as of the same type and that in this case ν_{Ph-M} contributes most to the q- and r-vibrations.

When $K_{Ph-M} < 5 \times 10^6$ cm^{-2}, which is characteristic of derivatives of elements in the Third, Fourth, Fifth, etc. Periods, the contribution of ν_{Ph-M} to the q- and r-vibrations diminishes significantly and these vibrations, having been displaced towards longer wavelengths to 1050–1070 cm^{-1} and 670–700 cm^{-1} respectively, become relatively insensitive to the nature of the element and the rigidity of the C–M bond. On the other hand, ν_{Ph-M} contributes most to the t-vibration in the spectra of such molecules, and for large masses of M (Hg, Tl, Pb, Te, etc.) and low force constants K_{Ph-M} [around $(3.5-3.6) \times 10^6$ cm^{-2}] the t-vibration becomes a virtually pure ν_{Ph-M} vibration.

5. Within each Group of the Periodic System, the force constant K_{Ph-M} varies in the opposite sense to the mass of the element, i.e. K_{Ph-M} as a rule decreases appreciably with increase of the mass of M. Hence follows the rule, discovered by Whiffen, of the dominant contribution of ν_{Ph-M} to the q-vibration of "light" elements and to the t-vibration of "heavy" elements. However, calculation of the vibration modes shows that, when for any reason K_{Ph-M} decreases appreciably in derivatives of a "light" element or increases in derivatives of a "heavy" element, Whiffen's rule ceases to hold. Thus, for the "lightest" of the elements discussed in this review (lithium), as a result of the sharp decrease of K_{Ph-Li} (1.2×10^6 cm^{-2}) due to the polarisation of the C–Li bond and "electron-deficient" binding the experimental and calculated data fail to show an isotopic shift on replacement of lithium-7 by lithium-6 and there is a decreased contribution of ν_{Ph-Li} to the q- and r-vibrations, an appreciable isotopic shift, and a significant contribution of ν_{Ph-Li} to the t-vibration.

6. It is noteworthy that within each Period K_{Ph-M} varies slightly as a function of the electronic nature of the elements belonging to different Groups of the Periodic System, but these changes are comparatively small (with the exception of lithium in the Second Period) and do not lead to the breakdown of Whiffen's rule. If in addition account is taken of the relatively small change of the mass of the elements within the same Period, the possibility of finding the absorption regions of the q-, r-, and t-vibrations for derivatives of any element from the known spectra of the derivatives of another element in the same Period becomes understandable. However, this interpretation fails to take into account molecular structure and is therefore rough and qualitative.

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