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ORGANO GROUP VB CHEMISTRY

IV. VIBRATIONAL STUDY OF SOME TERTIARY SUBSTITUTED ARYL—GROUP VB COMPOUNDS

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Summary

The IR and Raman spectra of a series *para-* and *meta-*substituted aryl—Group VB compounds $(XC_6H_5)_3M$ (X = Cl, F) (M = P, As, Sb, Bi) measured over the spectral range 4000 to 100 cm^{-1}, are reported. The results of a complete vibrational analysis are used to discuss the identification of the products. The shifts of substituent-sensitive vibrations are discussed.

Introduction

In previous papers the synthesis of $(4\text{-}XC_6H_4)_3M$ and $(3\text{-}XC_6H_4)_3M$ compounds (X = Cl, F; M = P [1,2], As [3], Sb [4] and Bi [4]) were described.

In order to obtain the exact phenyl-phosphorus and the X-sensitive frequencies a complete tentative assignment has been made for all the frequencies of the phosphorus compounds. This could be done fairly easily by comparing with a similar complete assignment for the arsine compounds [5]. The assignments reported here are also partly based on earlier work on disubstituted benzene derivatives [6—10]. This exhaustive study of phosphorus and arsenic compounds allowed the assignment of characteristic frequencies in spectra of the antimony and bismuth compounds. In this way the distinction between Cl- or F-substitution and *meta-* or *para-*substitution can be made, and the X-sensitive vibrations can be assigned.

Later these assignments should provide information to locate the ν(P=O), ν(P=S) and ν(P=Se) bands for the oxides, sulfides and selenides of the phosphine derivatives in much the same way as this was done for the substituted phenyl arsine oxides [5].

Results and discussion

The molecules $(4\text{-}XC_6H_4)_3M$ (X = Cl, F; M = P, As, Sb, Bi) can be considered as *para-*disubstituted benzene derivatives. The phenyl groups then belong to the

TABLE 1

COMBINATION TONES AND X-SENSITIVE BANDS FOR MOLECULES $(4\text{-}XC_6H_4)_3M$ (In cm^{-1})

Assignment	M			
	P	As	Sb	Bi
X = F				
1st comb. band	1896	1894	1895	1894
2nd comb. band	1770	1762	1759	1772
3rd comb. band	1645	1636	1638	1636
XS 13 ν(C—F)	1229	1231	1226	1220
XS 1 R.S.V.[a]	1093	1075	1054	1044
XS 6a R.S.V.[a]	812	810	804	804
XS 12 R.S.V.[a]	662	586	572	560
XS 9b β(C—F)	430	421	414	410
XS 7a ν(Ph—M)[b]	403	358	328	324
XS 10b γ(C—X)[b]	310	281	238	198
XS 15 β(Ph—M—Ph)[b]	216	207	193	183
XS 11 γ(C—X)[b]	150		135	
X = Cl				
1st comb. band	1905	1898	1900	1899
2nd comb. band	1787	1785	1780	1791
3rd comb. band	1644	1636	1637	1634
XS 12 R.S.V.[a]	1098	1092	1088	1087
XS 1 R.S.V.[a]	1085	1066	1054	1045
XS 6a R.S.V.[a]	744	728	721	715
XS 20a ν(C—X)	530	507	484	481
XS 7a ν(Ph—M)[b]	419	336	294	284
XS 9b β(C—Cl)[b]	327	322	332	327
XS 10b γ(C—X)[b]	267	256	216	184
XS 15 β(Ph—M—Ph)[b]	186	181	170	162
XS 11 γ(C—X)[b]	136	132	123	126

[a] Radial Skeletal Vibration. [b] From Raman data.

local C_{2v} symmetry class and yield 30 fundamentals divided as follows : A_1 (11) + A_2 (3) + B_1 (6) + B_2 (10). All the frequencies are Raman active and all but the A_2 frequency are infrared active.

Similarly the phenyl group of the molecules $(3\text{-}XC_6H_4)_3M$ (X = Cl, F; M = P, As, Sb, Bi) has local C_s symmetry: the 30 fundamentals now divide over the classes : A' (21) + A'' (9). For these compounds all frequencies are both IR and Raman active. For reasons of simplicity and uniformity, the numbering proposed by Varsanyi [10] for disubstituted benzene derivatives has been adopted. These compounds could alternatively be considered as MX_3 molecules with skeletal C_{3v} symmetry [2,6]. The 4 skeletal fundamentals fall into the classes: A_1 (2) + E (2).

Starting from a complete vibrational assignment for all the phosphorus compounds and by comparison with the previously published completely assigned spectra of the corresponding arsines [5], the analysis of spectra of the antimony and bismuth compounds was easily performed. From the complete assignments [17], for reasons of brevity, we discuss only the frequencies which are useful for the identification of the compounds as *p*- or *m*-disubstituted phenyl derivatives (F- or Cl-substituents) or for the discussion of the substituent

TABLE 2

COMBINATION TONES AND X-SENSITIVE BANDS FOR MOLECULES $(3\text{-}XC_6H_4)_3M$ (In cm^{-1})

Assignment	M			
	P	As	Sb	Bi
X = F				
1st comb. band	1945	1935	1938	1932
2nd comb. band	1870	1864	1868	1868
3rd comb. band	1752	1769	1769	1763
4th comb. band	1680	1679	1682	1681
XS 13 ν(C—F)	1212	1212	1207	1205
XS 6b R.S.V.[a]	878	856	846	836
XS 1 R.S.V.[a]	661	661	658	644
XS 6a R.S.V.[a]	511	521	521	521
XS 15 β(C—F)	439	430	422	418
XS 7b ν(Ph—M)	411	314	252	243
XS 10a γ(C—X)[b]	247	247	243	237
XS 9a β(Ph—M—Ph)[b]	226	216	216	200
XS 10b γ(C—X)[b]	176	167	147	143
X = Cl				
1st comb. band	1944	1942	1946	1936
2nd comb. band	1875	1875	1877	1871
3rd comb. band	1762	1763	1757	1754
4th comb. band	1686	1683	1684	1677
XS 1 R.S.V.	1119	1103	1096	1090
XS 6b R.S.V.	765	752	740	731
XS 6a R.S.V.	660	651	645	640
XS 7b ν(C—X)	420	422	424	421
XS 7a ν(Ph—M)	404	308	262	229
XS 15 β(C—Cl)[b]	339	361	339	332
XS 10a γ(C—X)[b]	249	234	229	220
XS 9a β(Ph—M—Ph)[b]	220	211	203	199
XS 10b γ(C—X)[b]	146	138	127	119

[a] Radial Skeletal Vibration. [b] Values taken from Raman spectra.

sensitive (XS) vibrations. Tables 1 and 2 list the relevant material. Comparison of the upper and lower parts of Tables 1 and 2 reveals that the numbering of a given fundamental changes according to whether an F or a Cl atom is the second substituent. This difference arises only from the mass difference of both substituents. For "in-plane" vibrations substituents whose first atom has atomic weight < 25 is "light" (e.g. F). For "out-of-plane" vibrations all polyatomic and monoatomic substituents with atomic weight > 25 are "heavy" (e.g. Cl) [11].

1. Assignments relating to m/p and F/Cl substitution

The absorptions in the 1600—2000 cm^{-1} region are combination bands of the γ(C—H) vibrations which themselves yield absorptions in the frequency range 800—1000 cm^{-1}. These combination tones allow a distinction to be made between *para-* and *meta-*disubstituted phenyl compounds [11]. *Para-*substitution leads to absorptions at about 1900, 1780 and 1640 cm^{-1}. From Table 1 it can be seen that these bands were observed in all the $(4\text{-}XC_6H_4)_3M$ compounds, and that they are remarkably insensitive to the nature of either X or M. On the other hand, *meta*-substitution yields four, instead of three specific combination bands at about 1940, 1870, 1760 and 1680 cm^{-1}. Again the wavenumbers of these bands are found to be nearly independent of the nature of X and M, as is seen from the comparison of the data in Table 2.

The nature of the substituent X can also be determined easily from the spectra. In the compounds $(4\text{-}FC_6H_4)_3M$ the X-sensitive bands XS 13 and XS 9b are characteristic; for $(4\text{-}ClC_6H_4)_3M$ the bands XS 12 and XS 9b. The wavenumbers for these bands are also given in Table 1. The corresponding X-sensitive bands for the compounds $(3\text{-}XC_6H_4)_3M$ are XS 13 and XS 15 for X = F, and XS 1 and XS 15 for X = Cl (Table 2).

2. *X-sensitive vibrations of para-substituted derivatives*

(a) Fluorine-substituted compounds

XS 13, ν(C—F) and XS 9, β(C—F). These are clearly C—F vibrations as they are practically not influenced by a change of M.

XS 1, R.S.V. This frequency is accepted to be characteristic of the heavy substituent in *p*-disubstituted benzene derivatives where one of the substituents is light (F) and the other is heavy (M). It was the subject of many discussions. Horner et al. [12] and Sheldon [13] assigned it to a specific metal—phenyl vibration. Also, Petit [14] assignes this frequency to a C—As stretching or a specific metal—phenyl vibration. Kross et al. [15] however found a linear relationship between the frequency of this band and the square of the electronegativity of the substituent atom. This was taken as evidence that normal mode 1 is an X-sensitive vibration of the phenyl ring. Table 1 shows that the frequency of XS 1 decreases with decreasing electronegativity of the M atom, and so we ascribe it to a skeletal vibration of the phenyl ring perturbed by the M atom.

XS 6a. It is assumed that this "in-plane" ring deformation is determined by the light substituent. The frequency ranges only from 812 to 804 cm^{-1}, the light substituent being always F.

XS 12 R.S.V. The frequency of this mode is found between 560—602 cm^{-1}. For a light and a heavy substituent the reported interval ranges from 481 to 680 cm^{-1} [10]. It is clear that in our case the observed frequency interval is determined by the lighter substituent (F), but is shifted also by the heavier substituent.

XS 7a. This vibration could be either the second ν(C—X) or the Ph—M stretching frequency. As this frequency is clearly determined by the M atom, as indicated by the frequency shift 403—324 cm^{-1}, we assign it to the ν(Ph—M) stretching. In $(C_6H_5)_3P$ Shobatake [6] assignes to ν(Ph—P) the frequencies 428 and 398 cm^{-1} $(E + A1)$.

XS 10b and 11. The frequency of the C—X "out-of-plane" 10b mode is generally higher than that of the second C—X "out-of-plane" mode 11, when at least one of the substituents is heavy. The frequency range we find for 10b is 310—198 cm^{-1}. For XS 11 we observe a range 150—137 cm^{-1}. The XS 10b mode is obviously strongly influenced by the M atom.

XS 15 β(Ph—M). Shobatake [6] found for the β(Ph—M) in the molecules $(C_6H_5)_3M$ respectively: $(C_6H_5)_3P$ 209 cm^{-1}, $(C_6H_5)_3As$ 192 cm^{-1}, $(C_6H_5)_3Sb$ 161 cm^{-1} and $(C_6H_5)_3Bi$ 157 cm^{-1}. The frequency region observed here is 216—183

cm^{-1}. The expected frequency decrease as a function of M is observed. Our values are slightly higher than those of Shobatake and this is probably a result of the influence of the F-substituent on the C—M bond.

(b) Chlorine-substituted compounds

XS 12 and XS 1 R.S.V. These are respectively assigned in the frequency range 1098—1087 cm^{-1} and 1085—1045 cm^{-1}. For two heavy substituents normal mode 12 is assumed to be characteristic of the lighter substituent, and normal mode 1 of the heavier substituent [10]. This is in good agreement with our assignment in both the Cl- and the F-substituted compounds.

XS 6a, α(C—C—C) is found in the frequency range 944—715 cm^{-1}. The mass difference between fluorine and chlorine produces a shift of circa 100 cm^{-1} in the $(4\text{-}ClC_6H_4)_3M$ (M = P, As, Sb, Bi) in comparison with the $(4\text{-}FC_6H_4)_3M$ compounds.

XS 20a. This fundamental is one of the ν(C—X) vibrations and is assigned in the frequency region 530—481 cm^{-1}. The small shifts observed indicate that this normal mode is sensitive to the chlorine substituent. The frequency range is, however, too great for XS 20a to be a pure C—Cl stretching vibration.

XS 7a. The second ν(C—X) vibration falls in the region 186—162 cm^{-1}. Its assignment as the ν(Ph—M) vibration was discussed in detail in section 2(a).

XS 10b, 15 and 11. The assignment and the discussions of these XS vibrations are similar to these for the fluorine-substituted compounds in section 2(a).

3. *X-sensitive vibrations of meta-substituted derivatives*

(a) Fluorine-substituted compounds

XS 13 and XS 15. Both modes are seen to undergo little shift on changing M, and therefore can be safely assigned to C—F vibrational modes.

XS 6b. In *meta*-disubstituted benzene in which at least one substituent is heavy, the accepted frequency range of vibration 6b is 700—900 cm^{-1} [10]. The frequency of this mode is found above 800 cm^{-1} only when one of the substituents is light. Fluorine is counted as a light substituent and therefore we situate normal mode 6b in the frequency region 878—836 cm^{-1}.

XS 1. The frequency interval of R.S.V. 1 is reported as 661—644 cm^{-1}. Several authors note coupling between normal mode 1 and the C—X stretching mode of the light substituent; on the other hand mode 6b discussed above couples with the ν(C—X) of the heavier substituent. A comparison of the values for XS 6b and XS 1 (Table 2) shows that mode 6b shifts more than mode 1 and this is accepted as evidence for the coupling.

XS 6a. The frequency is found constant at 621 cm^{-1} and is clearly determined by the lighter substituent. This constant frequency also indicates that in these *meta*-fluorine substituted aryl—Group VB compounds no significant electron shifts occur.

XS 7b. This assignment in the region 411—243 cm^{-1} is based upon the assignment and the discussion for this normal mode in *para*-substituted aryl—Group VB compounds in the section 2.

XS 10a and XS 10b. In the case of mixed substitution the frequency values are found in between those for the identically substituted derivatives [10]. The normal mode 10a should then be found closely to the vibration 10a of *meta*-difluoro benzene, namely 248 cm^{-1} [16], and so the frequency region assigned for XS 10a for the *meta*-fluoro substituted compounds is 247—237 cm^{-1}. XS 10b is found in the region 176—143 cm^{-1}. No values for normal mode 10b of *m*-$C_6H_4[(C_6H_5)_2P]_2$ could be found.

XS 9a. As for XS 7b this assignment is based upon earlier assignments for $(4\text{-}FC_6H_4)_3M$ (M = P, As, Bi, Sb) compounds in section 2.

(b) Chlorine-substituted compounds

XS 1. The absorption frequencies assigned to this mode fall in the accepted frequency region for two heavy substituents. In the $(3\text{-}FC_6H_4)_3M$ compounds (F = light substituent) XS 1 was assigned near 660 cm^{-1}. Normal mode 1 in the $(3\text{-}ClC_6H_4)_3M$ compounds is characteristic for chlorine substitution on the phenyl ring.

XS 6b, R.S.V. 6a is found in the region 765—731 cm^{-1}. As discussed for XS 6b in the Introduction vibration 6b only appears above 800 cm^{-1} when one of the substituents is light. Chlorine is regarded as a heavy substituent, and therefore a shift to lower wavenumbers is found.

XS 7a and XS 7b. The frequency of the fundamental 7b > 7a. Normal mode 7b is found near 420 cm^{-1} and is determined in the measured compounds by the chlorine atom. The stretching vibration Ph—M 7a is assigned in the region 404—229 cm^{-1}.

XS 15. The in plane-ring substituent deformation β(C—Cl) is found near 340 cm^{-1}, except in $(3\text{-}ClC_6H_4)_3As$. Probably a coupling between 7a—ν(Ph—As) and β(C—Cl) could explain this value.

XS 10a and XS 10b. As reported in section 3(a) the frequency of vibration 10a > 10b. Normal mode 10a shifts from 249 to 220 cm^{-1} and 10b from 146 to 119 cm^{-1}. The C—X "out-of-plane" 10a is determined by the chlorine atom, while 10b is influenced by the M atom.

XS 9b, β(Ph—M) is found between 220 and 199 cm^{-1}. Changing M has no significant influence on the frequency of this vibration.

Experimental

The experimental conditions for recording the IR and Raman spectra and the spectrometers used have been described in a previous paper [5].

Each compound was investigated by both IR and Raman spectroscopy. Spectra of the solids (IR, Raman) and of CCl_4 solutions (IR) and of $CHCl_3$ solutions (Raman) were taken. In some instances Raman depolarisation measurements helped a correct assignment.

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