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A FOURIER TRANSFORM ^{13}C NMR STUDY OF PHENYL-PHOSPHORUS, -ARSENIC, -ANTIMONY AND -BISMUTH DERIVATIVES

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Summary

^{13}C NMR spectra of triphenyl-phosphine, -arsine, -stibine and -bismuthine and related metal carbonyl complexes, chalcogenides and phenyl salts have been recorded and the data are compared with literature data. The substituent effects of electron-donor and electron-acceptor substituents can be related to Hammett—Taft constants (σ_R^o).

Introduction

Substituent effects on the π-electron distribution in benzene derivatives can be related to the Hammett—Taft constants σ_R^o [1]. Most progress in the correlation of NMR data with this parameter has been made in the case of ^{19}F NMR of *para*- and *meta*-substituted fluorobenzenes [2,3]. The ^{13}C shifts of the ring carbon atoms in the corresponding nonfluorinated compounds might, however, be expected to reflect the substituent effects more accurately, since both the *para* and *meta* carbon shifts can be obtained from a single sample. So, we have undertaken the study of the ^{13}C NMR spectra of triphenyl-phosphine, -arsine, -stibine and -bismuthine and some related derivatives (metal carbonyl complexes, chalcogenides and phenyl salts).

Results and discussion

The ^{13}C-{^1H} decoupled spectral data are shown in Table 1. The $J(^{13}C—^{31}P)$ coupling constants are given in brackets. The chemical shifts are calculated in ppm relative to TMS. The observed values are negative since the resonances occur at higher frequencies, i.e. at lower magnetic field. The reproducibility of the chemical shifts was ±0.07 ppm. Where a comparison with shifts reported elsewhere [4,5] is possible, the discrepancies are mostly less than 1 ppm. The resonance of the substituted carbon atom (C_x), if observed, is identified by the absence of NOE * upon decoupling. The assignment of the *para* carbon resonance is based on its relative intensity (1 : 2) compared with the *ortho* and *meta* carbon resonances; in addition, the *para* carbon resonances in phosphorus derivatives show weak or no ^{13}C—^{31}P coupling, as expected. The assignment of the *meta* carbon vs. the *ortho* carbon resonance follows the work of Bodner and Gaul [5]. Their assumption that $^2J(^{13}\text{C}—^{31}\text{P})$ is larger than $^3J(^{13}\text{C}—^{31}\text{P})$ seems to fail however in certain cases.

Assuming the contribution from the inductive effect of a substituent X to both the *para* and *meta* carbon shifts to be the same, the so-callled corrected *para* shift, $\delta_p(^{13}\text{C})—\delta_m(^{13}\text{C})$, has been defined as a measure of the resonance interaction between the benzene ring and its substituent [6]. This parameter clearly resembles the empirical resonance-related parameter $\delta_p(^{19}\text{F})—\delta_m(^{19}\text{F})$ discovered by Taft et al. [7], for the ^{19}F shifts of the fluorobenzene. For ^{13}C, Lauterbur [8] reported a satisfactory correlation between the σ_R° values for X = H, CH_3, OH and OCH_3 and the differences between the *para* and *meta* carbon shifts in the corresponding benzene derivatives. On the basis of the σ_R° values obtained by Taft from reactivities [9] and of the ^{13}C chemical shifts for monosubstituted benzenes given by Maciel and Natterstad [10] we obtain the following relation:

$$\delta_p(^{13}\text{C})—\delta_m(^{13}\text{C}) = -22.06\ \sigma_R^\circ$$

The correlation coefficient is 0.980 and the mean square deviation is 0.36 ppm. Moreover, it should be noted that this relation holds for both electron-donor (—R) and electron-acceptor (+R) substituents, while the analogous relation in the ^{19}F NMR spectroscopy fails for +R substituents because of direct polar conjugation [11]. The σ_R° values calculated by the use of the above equation complete Table 1.

The σ_R° value for triphenylphosphine is almost zero indicating the phenyl-phosphorus π interaction to be negligible. The negative σ_R° values for triphenylarsine, -stibine and -bismuthine shows an electron release by $(p—p)\pi$ conjugation from the Group VB metal towards the phenyl ring. The electrical dipole moment of triphenylbismuthine is about zero [25—27]. An early X-ray diffraction study suggested that the molecule is planar [28], although this was questioned later [29]. Planarity implies sp^2 hybridization on bismuth and the lone pair would then occupy a *p*-orbital. A relatively strong delocalization of the *p*-lone pair electrons on bismuth to the π framework of the ring could then explain the low donor capacity of trivalent bismuth; indeed this compound does not form donor—acceptor complexes with boron halides and the bismuthine pentacarbonyls of Cr, Mo and W [12] are very unstable. The σ_R° value for X = $Bi(C_6H_5)_2$ may be compared with the value for X = I [9].

The resonance parameter is positive for all the tetravalent phosphorus derivatives under study meaning that a delocalization of π charge occurs from the phenyl group to the vacant, low energy $3d_\pi$ orbitals of phosphorus. The phosphonium salts exhibit the largest π delocalization, undoubtedly because of the formal positive charge on phosphorus in these compounds.

Comparing the σ_R° values for the compounds 24, 25 and 26 with the σ_R **

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* NOE = Nuclear Overhauser enhancement.

** In ref. 3 these values were incorrectly labeled σ_R°; see also ref. 2b.

TABLE 1

^{13}C COUPLING SHIFTS (ppm RELATIVE TO TMS) AND ^{13}C—^{31}P COUPLING CONSTANTS (Hz) (IN BRACKETS) FOR PHENYL-GROUP VB COMPOUNDS

Compound		$-\delta(C_o)$	$-\delta(C_m)$	$-\delta(C_p)$	σ_R^0
1	$P(C_6H_5)_2$ [a]	134.15 (19.5)	128.89 (7.0)	129.07	0.00_8
2	$As(C_6H_5)_2$ [b]	134.57	129.49	129.27	-0.01_0
3	$Sb(C_6H_5)_2$ [c]	137.13	129.80	129.49	-0.01_4
4	$Bi(C_6H_5)_2$	138.33	131.26	128.52	-0.12_3
5	$P(C_6H_5)_2Mn(CO)_4Cl$	133.94 (10.0)	129.17 (9.8)	131.38 (2.4)	0.09_9
6	$P(C_6H_5)_2Mn(CO)_4Br$	134.08 (9.8)	129.18 (9.8)	131.39 (2.7)	0.09_9
7	$As(C_6H_5)_2Mn(CO)_4Br$ [a]	133.63	129.66	131.16	0.06_8
8	$Sb(C_6H_5)_2Mn(CO)_4Br$	131.12	130.11	131.34	0.05_5
9	$P(C_6H_5)_2Mn_2(CO)_8P(C_6H_5)_3$	133.66 (10.0)	128.88 (9.8)	131.10 (0.9)	0.10_1
10	$P(C_6H_5)_2Cr(CO)_5$ [k]	132.73 (11.5)	128.54 (9.5)	130.08	0.06_9
11	$P(C_6H_5)_2Mo(CO)_5$ [e]	133.05 (12.7)	128.83 (9.2)	130.33 (2.2)	0.06_8
12	$As(C_6H_5)_2Mo(CO)_5$ [f]	132.71	129.27	130.20	0.04_2
13	$Sb(C_6H_5)_2Mo(CO)_5$	135.19	129.53	130.28	0.03_4
14	$P(C_6H_5)_2W(CO)_5$ [g]	133.22 (12.1)	128.85 (9.9)	130.57 (2.3)	0.07_7
15	$As(C_6H_5)_2W(CO)_5$ [h]	132.64	129.28	130.43	0.05_2
16	$Sb(C_6H_5)_2W(CO)_5$ [i]	135.23	129.71	130.59	0.04_0
17	$P(C_6H_5)_2Fe(CO)_4$	133.47 (10.5)	128.87 (10.5)	131.08 (2.9)	0.09_9
18	$As(C_6H_5)_2Fe(CO)_4$	132.67	130.15	131.43	0.06_8
19	$Sb(C_6H_5)_2Fe(CO)_4$ [j]	135.37	130.15	131.43	0.05_8
20	$P(C_6H_5)_2CO(CO)_3SnCl_3$	133.20 (10.5)	129.75 (10.9)	132.63 (3.1)	0.13_0
21	$As(C_6H_5)_2Co(CO)_3SnCl_3$	132.29	130.13	132.12	0.09_0
22	$Sb(C_6H_5)_2Co(CO)_3SnCl_3$	134.77	130.17	132.25	0.07_6
23	$P(C_6H_5)_2Ni(CO)_3$ [k]	133.12 (13.6)	128.56 (9.3)	129.82	0.05_7
24	$P(O)(C_6H_5)_2$	132.22 (10.1)	128.64 (12.1)	132.00	0.15_1
25	$P(S)(C_6H_5)_2$	132.43 (10.7)	128.67 (12.6)	131.68 (3.1)	0.13_5
26	$P(Se)(C_6H_5)_2$	132.88 (10.9)	128.73 (12.7)	131.73 (3.2)	0.13_5
27	$^{+}P(C_6H_5)_3I^-$	134.46 (10.9)	130.97 (12.9)	135.87 (3.1)	0.2_2
28	$^{+}As(C_6H_5)_3I^-$	132.91	131.72	135.03	0.14_9

[a] $\delta(C_x)$ —137.73 ppm, $^1J(^{13}C—^{31}P)$ 11.4 Hz. [b] $\delta(C_x)$ —140.62 ppm. [c] $\delta(C_x)$ —139.99 ppm. [d] $\delta(C_x)$ —134.08 ppm. [e] $\delta(C_x)$ —135.81 ppm, $^1J(^{13}C—^{31}P)$ 35.2 Hz. [f] $\delta(C_x)$ —135.06 ppm. [g] $\delta(C_x)$ —135.52 ppm, $^1J(^{13}C—^{31}P)$ 41.1 Hz. [h] $\delta(C_x)$ —136.31 ppm. [i] $\delta(C_x)$ —132.14 ppm. [j] $\delta(C_x)$ —130.95 ppm. [k] Data from ref. 5.

constants obtained by De Ketelaere [3] from fluorine resonance data, good agreement is found. So the conclusions concerning the bonding in phosphine chalcogenides as drawn from the σ_R sequence are supported. The relatively large σ_R^0 values for the chalcogenides, as compared with those for the metal carbonyls, are in accordance with the high electronegativities of the chalcogen atoms O, S and Se.

TABLE 2

CHANGES IN σ_R° IN GOING FROM A TRIPLY- TO A QUADRUPLY-COORDINATED DERIVATIVE OF P, As AND Sb

	$LMn(CO)_4Br$	$LMo(CO)_5$	$LW(CO)_5$	$LFe(CO)_4$	$LCo(CO)_3SnCl_3$
$(C_6H_5)_3P$	0.09_1	0.06_0	0.06_9	0.09_1	0.12_2
$(C_6H_5)_3As$	0.07_8	0.05_2	0.06_2	0.07_8	0.10_0
$(C_6H_5)_3Sb$	0.06_9	0.04_8	0.05_4	0.07_2	0.09_0

For the metal carbonyl complexes the σ_R° parameters yield the sequence: $[Ni(CO)_3] < [Cr(CO)_5]$, $[Mo(CO)_5] < [W(CO)_5] < [Mn(CO)_4X]$, $[Fe(CO)_4]$, $[Mn_2(CO)_8P(C_6H_5)_3] < [Co(CO)_3SnCl_3]$, indicating that the net positive charge on phosphorus increases in this order. This can be taken as an indication of the increasing σ-withdrawing power of the metal carbonyl moiety on going from $[Ni(CO)_3]$ to $[Co(CO)_3SnCl_3]$. Strictly speaking the decrease of the positive charge on phosphorus in going from $[Co(CO)_3SnCl_3]$ to $[Ni(CO)_3]$ could also be considered a consequence of increasing metal-to-phosphorus π back-bonding in this order. Little importance has to be attached, however, to the latter hypothesis since π bonding is generally thought to be negligible in Ni—L linkages [13].

Table 2 summarizes the changes in the resonance parameter in going from tri-

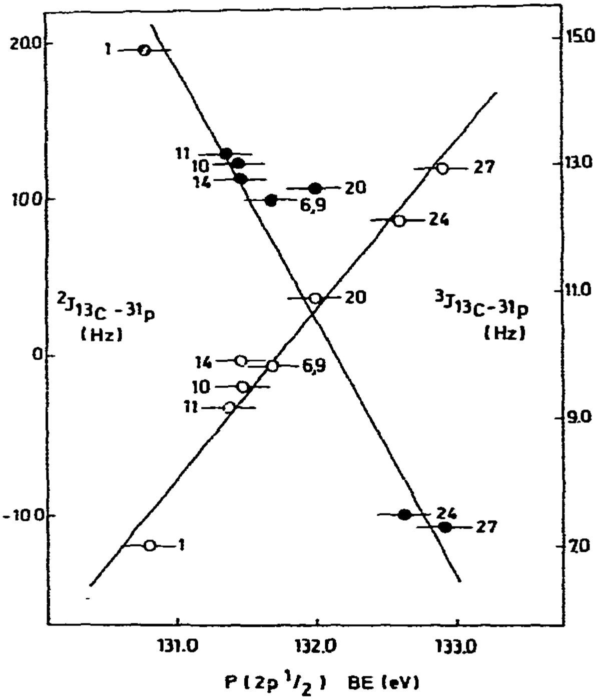

Fig. 1. Plots of $^2J(^{13}C—^{31}P)$ (—●—) and $^3J(^{13}C—^{31}P)$ (—○—) versus binding energy (BE) for $P_{2p1/2}$ levels. (The numbers refer to the compounds listed in Table 1 and the ESCA shifts are taken from ref. 16.)

to tetra-coordinated phosphorus, arsenic or antinomy.

$\Delta\sigma_R^\circ = \sigma_R^\circ$ (carbonyl complex) — σ_R° (free ligand)

Assuming $\Delta\sigma_R^\circ$ to be proportional to the stability of the complex under study, this is seen to decrease in the order $L = P(C_6H_5)_3 > As(C_6H_5)_3 > Sb(C_6H_5)_3$ for each metal carbonyl residue considered.

As for the coupling constants, a significant correlation between $J(^{13}C—^{31}P)$ and P_{2p} ESCA shifts is expected since both parameters are sensitive to changes in the orbital hybridisation of the phosphorus atom [14,15]. Plots of $^{2,3}J(^{13}C—^{31}P)$ coupling constants versus $P_{2p_{1/2}}$ binding energies (BE) are shown in Fig. 1. The gradients of these plots are in agreement with the observations made by other investigators that $^2J(^{13}C—^{31}P)$ decreases while $^3J(^{13}C—^{31}P)$ increases upon quaternization of a phosphorus atom [17]. The plot of $^3J(^{13}C—^{31}P)$ against the binding energy for $P_{2p_{1/2}}$ levels suggest the sign of the three-bond coupling constants to be positive for both the triply- and quadruply-coordinated phenyl phosphorus derivatives considered. However, the relationship between $^2J(^{13}C—^{31}P)$ and $P_{2p_{1/2}}$ BE's suggests the two-bond coupling constants to change sign in going from the metal carbonyl complexes to triphenylphosphine oxide and tetraphenylphosphonium iodide. These conclusions are in good agreement with results obtained from selective proton decoupling experiments. Indeed, the $^{2,3}J(^{13}C—^{31}P)$ coupling constants were found to be positive in triphenylphosphine [18] and in its pentacarbonyl complex of molybdenum(V), while the $^2J(^{13}C—^{31}P)$ has been shown to be negative in tetraethylphosphonium bromide [17].

Experimental

The $LXMn(CO)_4$ complexes were obtained by direct reaction between L and halomanganese pentacarbonyl [19]. $[Mn(CO)_4P(C_6H_5)_3]_2$ was obtained by exposure to ultraviolet radiation of an oxygen-free cyclohexane solution of 2.6 mmoles of $Mn_2(CO)_{10}$ and 5.1 mmoles of $P(C_6H_5)_3$ [20]. To form the $LM(CO)_5$ derivatives, M = Cr, Mo, W, a solution of 0.01 mole of $M(CO)_6$ and 0.005 mole of the ligand L in dioxane was refluxed until the infrared absorption associated with the $A_1(2)$ mode of the $LM(CO)_5$ complex stopped growing. The mixture was then cooled and filtered, and the solvent evaporated in vacuo; the residue was recrystallized several times from a chloroform/methanol mixture.

The $LFe(CO)_4$ species were prepared by a combination of photochemical and thermal reactions using $Fe(CO)_5$ both as solvent and reactant [21]. The compounds $LCo(CO)_3SnCl_3$ were synthesized from $[LCo(CO)_3]_2Hg$ with tin(IV) chloride as described by Newman and Manning [22]. The triphenylphosphine chalcogenides were made as previously described [23] and the salts $(C_6H_5)_4P^+I^-$ and $(C_6H_5)_4As^+I^-$ as described by Chatt and Mann [24].

The ^1H decoupled Fourier transform pulsed ^{13}C NMR spectra were recorded with saturated solutions of the compounds in $CDCl_3$ with a Bruker-Physik HFX_5 spectrometer operating at 22.63 MHz. $CDCl_3$ was used to provide an internal deuterium lock.

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