TABLE VI
RELATIVE CHEMICAL SHIFTS OF ANALOGOUS ARSENIC,
PHOSPHORUS, AND NITROGEN CHEMICAL ENVIRONMENTS

| Comparison | Source | Fig | Chem shift ratio,[c] arsenic: other atom |
|---|---|---|---|
| As "3p₃/₂" vs. P "2p" | Exptl[a] | 4 | 0.74 |
| As "3p₃/₂" vs. P "2p" | Exptl[b] | 4 | 0.83 |
| As 3p vs. P 2p | SCF | 3 | 0.90 |
| As "3d" vs. P "2p" | Exptl[a] | | 0.74 |
| As "3d" vs. P "2p" | Exptl[b] | | 0.92 |
| As 3d vs. P 2p | SCF | | 0.88 |
| As "3p₃/₂" vs. N "1s" | Exptl[a] | 5 | 0.25 |
| As 3p vs. N 1s | SCF | 3 | 0.40 |
| As "3d" vs. N "1s" | Exptl[a] | | Ca. 0.34 |
| As 3d vs. N 1s | SCF | | 0.39 |

[a] Binding energies corrected using hydrocarbon contaminant as reference material. [b] Directly measured binding energies. [c] Obtained from least-squares treatment of data.

The experimental values reflect the slightly smaller relative shift for arsenic compared to phosphorus

and the much smaller shift for arsenic compared to nitrogen, in accord with the calculated values of Figure 3. A summation of the various chemical shift comparisons is presented in Table VI. This table shows that the variations in orbital energy from the SCF calculations on atoms parallel the experimental findings amazingly well. Note that the best fit between calculation and experiment is found for the direct (unreferenced) experimental data.

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# Substituent Transmission Effects in Some Substituted Triphenylarsines and -stibines Using Nuclear Quadrupole Resonance Spectroscopy

BY T. B. BRILL* AND G. G. LONG

The arsenic, antimony, chlorine, and bromine nqr spectra for a number of ortho-, meta-, and para-substituted triphenylarsines and -stibines have been recorded. The substituents CH₃, CH₃O, CF₃, F, Cl, and Br were investigated along with ($C_6F_5$)₃Sb. There is a notable difference between the triarylarsines and -stibines. The correlation of the arsenic nqr data for the para substituents with Taft's resonance substituent constants suggests that arsenic–ring π interaction exists and is an efficient mechanism of substituent electronic transmission. In the stibine analogs correlation of the nqr data with Hammett's functions is good in all cases except for the CF₃ group. σ–π effects taken together appear more competitive in the stibines.

## Introduction

Trivalent organometalloid compounds of group Va elements, P, As, Sb, and Bi all have a lone pair of electrons which is chemically important. The Lewis basicities of these elements toward metal ions as well as virtually all of their chemical reactions involve this lone pair. Triphenylarsine, -stibine, and -bismuthine lack the basic character of their trialkyl analogs, which suggests some delocalization of the lone pair onto the ring.[1] Arguments both for[2] and against[3] this type of delocalization have been presented based on the uv spectra of the arsine and stibine. These data, however, reflect excited-state effects and may not be directly applicable to the ground state.

There is some evidence that the set of substituent parameters to which experimental data correlate is indicative of the mechanism of transmission of sub-

stituent character to a point of observation.[4] Additional information regarding the nature of pnigogen atom–aryl bonding could possibly be revealed in the arsenic and antimony nqr spectra in substituted aryl systems. Correlation of the ⁷⁵As and ¹²¹,¹²³Sb nqr data with the resonance substituent parameters of Taft, *et al.*,[5] would suggest a definite amount of ring–lone pair interaction. Correlation of data with the more general substitutent constants of Hammett[6] suggests that nqr coupling is sensitive to competitive inductive effects in the σ framework of the molecule and the π resonance effects.

## Experimental Section

**Syntheses.**—The syntheses and properties of most of the compounds mentioned in this study have been previously reported and are summarized in Table I. The triphenylstibine, purchased from M and T Chemicals, Inc., Rahway, N. J., was recrystallized from ethanol. The other compounds were made by one of the following two general methods as described in previous preparations of these compounds: (A) reaction of an aryl Grignard reagent with either AsCl₃ or SbCl₃; (B) the reac-

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(1) W. C. Davies and H. W. Addis, *J. Chem. Soc.*, 1622 (1937); M. E. Peach and T. C. Waddington, *ibid.*, 1238 (1961); R. J. Gillespie and E. A. Robinson, *Advan. Inorg. Chem. Radiochem.*, 1, 385 (1959).
(2) H. Jaffe, *J. Chem. Phys.*, 22, 1430 (1954); C. N. R. Rao, J. Ramachandran, and A. Balasubramanian, *Can. J. Chem.*, 39, 171 (1961).
(3) W. R. Cullen and R. M. Hochstrasser, *J. Mol. Spectrosc.*, 5, 118 (1960); W. R. Cullen, B. R. Green, and R. M. Hochstrasser, *J. Inorg. Nucl. Chem.*, 27, 641 (1965).

(4) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 2, 232 (1964).
(5) R. W. Taft, *J. Phys. Chem.*, 64, 1805 (1960), and references therein.
(6) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1970.

TABLE I

ANALYTICAL DATA FOR SUBSTITUTED TRIPHENYLARSINES AND -STIBINES

| Compound | Method of synthesis | % metal Calcd | % metal Found | % C Calcd | % C Found | % H Calcd | % H Found | Mp, °C | Lit. mp, °C |
|---|---|---|---|---|---|---|---|---|---|
| $(p\text{-}CH_3C_6H_4)_3As$ | A | 21.51 | 21.89 | | | | | 148–149 | 146,[a,b] 147–148[c] |
| $(p\text{-}BrC_6H_4)_3As$ | B | 13.80 | 13.77 | 39.82 | 39.87 | 2.23 | 2.30 | 139 | 93–95[d] |
| $(p\text{-}ClC_6H_4)_3As$ | A | 18.29 | 18.16 | | | | | 104–107 | 105.4[e] |
| $(p\text{-}CH_3C_6H_4)_3As$ | A | 18.90 | 18.73 | | | | | 159–161 | 158,[f] 157–159[g] |
| $(m\text{-}BrC_6H_4)_3As$ | B | 13.80 | 13.68 | | | | | 65–66 | |
| $(m\text{-}CH_3C_6H_4)_3As$ | A | 21.51 | 22.09 | 72.41 | 72.74 | 6.08 | 6.05 | 95 | 95–96,[h] 96[a] |
| $(m\text{-}ClC_6H_4)_3As$ | B | 18.29 | 17.98 | 52.78 | 52.32 | 2.96 | 3.19 | 72.5–74.5 | 73.3[e] |
| $(o\text{-}BrC_6H_4)_3As$ | B | 13.80 | 13.82 | | | | | 177 | |
| $(o\text{-}CH_3C_6H_4)_3As$ | A | 21.51 | 21.29 | 72.41 | 72.06 | 6.08 | 6.12 | 108–109 | 98,[i] 108–110[c] |
| $(p\text{-}CH_3C_6H_4)_3Sb$ | A | 30.81 | 30.86 | 63.83 | 63.29 | 5.36 | 5.19 | 126 | 122,[k] 127–128,[j] 127[l] |
| $(p\text{-}CF_3C_6H_4)_3Sb$ | A | | | 45.28 | 44.93 | 2.17 | 2.13 | 130–132 | |
| $(p\text{-}FC_6H_4)_3Sb$ | A | 29.85 | 29.28 | 53.11 | 53.02 | 2.97 | 2.78 | 83–84.5 | |
| $(p\text{-}ClC_6H_4)_3Sb$ | A | 26.63 | 26.50 | | | | | 110–111 | 99.5–100.5,[n] 110.5–111[m] |
| $(m\text{-}CH_3C_6H_4)_3Sb$ | B | 30.81 | 31.13 | | | | | 67.5–68 | 67–68,[o] 72[m] |
| $(o\text{-}CH_3C_6H_4)_3Sb$ | A | 30.81 | 31.10 | | | | | 105–106 | 112,[o] 102[m] |
| $(C_6F_5)_3Sb$ | A | | | | | | | 74.5 | 74[p] |

[a] A. Michaelis, *Justus Liebigs Ann. Chem.*, **321**, 141 (1901). [b] F. Sachs and H. Kantorowicz, *Chem. Ber.*, **41**, 2767 (1908). [c] D. S. Tarbell and J. R. Baughm, Jr., *J. Amer. Chem. Soc.*, **67**, 41 (1945). [d] J. R. Vaughn, Jr., and D. S. Tarbell, *ibid.*, **67**, 144 (1945). [e] R. F. deKetelaere, F. T. Delbeke, and G. P. van der Kelen, *J. Organometal. Chem.*, **28**, 217 (1971). [f] A. Michaelis and L. Weitz, *Chem. Ber.*, **20**, 48 (1886). [g] F. F. Blicke and E. L. Cataline, *J. Amer. Chem. Soc.*, **60**, 419 (1938). [h] G. B. Deacon and R. A. Jones, *Aust. J. Chem.*, **16**, 499 (1963). [i] G. J. Burrows and E. E. Turner, *J. Chem. Soc.*, **117**, 1373 (1920). [j] P. Pfeiffer, *Chem. Ber.*, **37**, 4620 (1904). [k] M. S. Malinovskii and S. P. Olifirenko, *Zh. Obshch. Khim.*, **19**, 1402 (1950). [l] T. V. Talalaeva and K. A. Kocheshkov, *J. Gen. Chem. USSR*, **16**, 777 (1946). [m] V. P. Glush Kova, T. V. Talalaeva, Z. P. Tazmanova, G. S. Zhdanov, and K. A. Kocheshkov, *Sb. Statei Obshch. Khim.*, **2**, 992 (1953); *Chem. Abstr.*, **49**, 6859 (1955). [n] J. I. Harris, S. T. Bowden, and W. J. Jones, *J. Chem. Soc.*, 1568 (1947). [o] A. Michaelis and U. Genzken, *Justus Liebigs Ann. Chem.*, **242**, 164 (1887). [p] M. Fild, O. Glemser, and G. Cristoph, *Angew. Chem.*, **76**, 953 (1964).

tion of $AsCl_3$ or $SbCl_3$ with an aryldiazonium tetrafluoroborate suspended in ethyl acetate followed by reduction with zinc. C and H analyses were performed by Galbraith Laboratories, Knoxville, Tenn. All of the compounds are white crystalline solids.

**Nqr Spectra.**—The nqr data in this paper were recorded using a system which has been described before.[7] Due to the uncertainty of ascertaining the center line of the resonance multiplet, the error in the frequencies is about 0.03 MHz.

## Results and Discussion

In nqr spectroscopy, the coupling between the quadrupole moment of the nucleus, $Q$, and the largest component of the electric field gradient tensor, $q_{zz}$, is detected in the solid state.[8] For antimony both the nqr coupling constant, $e^2Qq/h$, and the electric field gradient asymmetry parameter, $\eta$, are obtainable. Arsenic, chlorine, and bromine all have spin $^3/_2$ nuclei so that $\eta$ cannot be determined routinely from their spectra. However, for small values of $\eta$, $e^2Qq/h$ will be approximately twice the resonance frequency for spin $^3/_2$.[8] $e^2Qq/h$ is very sensitive to small changes in $\sigma$ and $\pi$ bonding at the atom containing the quadrupolar nucleus. The microsymmetry about arsenic and antimony in these systems is $C_3$ so that ideally $\eta$ will be zero. The fact that small values of $\eta$ are found in the antimony compounds suggests that packing forces cause minor distortions in the molecules and that very small lattice contributions to the electric field gradient do exist. An additional complicating factor is the Sternheimer antishielding effect.[9] For example, along the series arsenic–antimony–bismuth, the valence electrons of the atom become more polarizable by extramolecular forces. These distortions can lead to anomalous electric field gradient effects which are exceptionally difficult to interpret.[9] The nqr data for bis-

muth will be quite confused in the presence of extensive antishielding.

**Triphenylarsines.**—Table II shows the shift in the

TABLE II

ARSENIC AND HALOGEN NQR FREQUENCIES (MHz) AT 300°K[a]

| Compound | $^{75}As$ | $^{35}Cl$ | $^{81}Br$ |
|---|---|---|---|
| $(C_6H_5)_3As$ | 97.05[b] | | |
| $(p\text{-}CH_3C_6H_4)_3As$ | 97.63 (10) | | |
| $(p\text{-}BrC_6H_4)_3As$ | 98.21 (10) | | 223.7 (2) |
| $(p\text{-}ClC_6H_4)_3As$ | 98.27 (8) | 34.18 (4) | |
| | | 34.23 (4) | |
| | | 34.41 (4) | |
| $(p\text{-}CH_3OC_6H_4)_3As$ | 99.93 (3) | | |
| $(m\text{-}BrC_6H_4)_3As$ | 97.75 (25) | | 222.0 (8) |
| $(m\text{-}CH_3C_6H_4)_3As$ | 98.49 (8) | | |
| $(m\text{-}ClC_6H_4)_3As$ | 99.28 (10) | 34.20 (4) | |
| | | 34.25 (4) | |
| $(o\text{-}BrC_6H_4)_3As$ | 99.98 (6) | | |
| $(o\text{-}CH_3C_6H_5)_3As$ | 100.9 (3) | | |

[a] Parenthetical numbers are signal-to-noise ratios. [b] An average of four closely spaced resonance frequencies as reported in ref 11.

$^{75}As$ resonance frequency due to ortho, meta, and para substitution of the phenyl rings. Triphenylarsine has been shown to have very complex packing in the crystal lattice,[10] and this fact is confirmed by the multitude of closely spaced resonances observed by Barnes and Bray.[11] In all cases studied the frequency in the substituted compound is increased over that of the parent compound, $(C_6H_5)_3As$, but the difference is only 3–4% of the overall effect. The geometry and electronic character of the molecule are, therefore, not markedly changed by ring substitution. There is no correlation between $\nu(^{75}As)$ and the general substituent parameters presented by Hammett[6] or the $\sigma_I$ of Taft.[12] However, plotting $\nu(^{75}As)$ of the para-substituted ar-

(7) T. B. Brill and G. G. Long, *J. Phys. Chem.*, **75**, 1898 (1971).

(8) T. P. Das and E. L. Hahn, *Solid State Phys., Suppl.*, **No. 1** (1958).

(9) R. M. Sternheimer and H. M. Foley, *Phys. Rev.*, **102**, 731 (1956), and references therein.

(10) J. Trotter, *Can. J. Chem.*, **40**, 1878 (1962).

(11) R. G. Barnes and P. J. Bray, *J. Chem. Phys.*, **23**, 407, 1177 (1955).

(12) R. W. Taft, Jr., and I. C. Lewis, *J. Amer. Chem. Soc.*, **81**, 5343 (1959).

TABLE III
ANTIMONY AND HALOGEN NQR DATA[a] (MHz) FOR TRICOORDINATE ANTIMONY(III) COMPOUNDS AT 300°K

| Compound | $^{121}$Sb | | $^{123}$Sb | | $e^2Qq/h(^{121}$Sb$)$ | $\eta$(Sb) | $\nu(^{35}$Cl$)$ |
| | $^5/_2 \leftrightarrow {}^3/_2$ | $^3/_2 \leftrightarrow {}^1/_2$ | $^5/_2 \leftrightarrow {}^3/_2$ | $^3/_2 \leftrightarrow {}^1/_2$ | | | |
|---|---|---|---|---|---|---|---|
| $(C_6H_5)_3$Sb[b] | 150.2 (20) | 71.51 (20) | 90.91 (15)[c] | 46.54 (20) | 501.0 | 0.09 | |
| | 153.1 (20) | 76.57 (20) | 92.83 (15)[c] | 46.70 (20) | 510.4 | 0.03 | |
| $(p\text{-}CH_3C_6H_4)_3$Sb | 151.1 (3) | 75.64 (4) | 91.67 (2) | 45.90 (5) | 503.8 | 0.03 | |
| $(p\text{-}CF_3C_6H_4)_3$Sb | 152.2 (3) | 76.09 (5) | . . . | 46.26 (3) | 507.3 | 0.00 | |
| $(p\text{-}FC_6H_4)_3$Sb | 152.2 (3) | 76.22 (4) | . . . | 46.37 (4) | 507.5 | 0.04 | |
| $(p\text{-}ClC_6H_4)_3$Sb | 153.4 (7) | 76.94 (7) | . . . | 46.32 (4) | 511.6 | 0.05 | 34.10 (4) |
| | | | | | | | 34.25 (4) |
| | | | | | | | 34.39 (4) |
| $(m\text{-}CH_3C_6H_4)_3$Sb | 152.2 (4) | 76.17 (6) | . . . | 46.23 (6) | 507.4 | 0.03 | |
| $(o\text{-}CH_3C_6H_4)_3$Sb | 157.0 (7) | 78.77 (6) | . . . . | 47.76 (4) | 523.6 | 0.05 | |
| $(C_6F_5)_3$Sb | 163.7 (25) | 82.04 (20) | 99.41 (6)[c] | 49.96 (20) | 545.9 | 0.04 | |

[a] Parenthetical numbers are signal-to-noise ratios.   [b] In agreement with the results first reported in ref 11.   [c] $^7/_2 \leftrightarrow {}^5/_2$ transition also observed.

sines against $\sigma_R{}^0$ resonance parameters, which Taft and his coworkers[5] derived from $^{19}$F chemical shifts in substituted fluorobenzenes, gives a linear correlation (Figure 1). For the substituents studied, $\sigma_R{}^0$ values
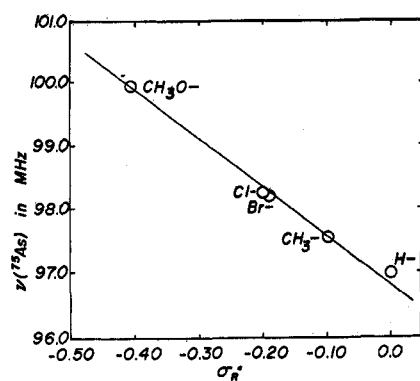


Figure 1.—The correlation of arsenic nqr frequencies and Taft's resonance substituent parameters in para-substituted triphenylarsines. The fact that the correlation is almost quantitative may be fortuitous in view of the few compounds which could be studied.

are negative indicating electron transfer from the substituent to the ring. There are several plausible arguments which will account for this correlation, and in view of the variable factors such as small hybridization changes at arsenic and possible bond length and angle variations, it is exceptionally difficult to demonstrate the source with certainty.

The data do suggest that the most efficient means of transmission of substituent electronic character to the arsenic atom is through the $\pi$ system in these compounds. This does not imply that $\sigma$-inductive effects are nonexistent but simply that the quantities to which nqr coupling at the arsenic atom is sensitive feel the principal influence *via* the $\pi$ network.[18]

In the very simplest description the ring might be taken as a bulk unit with no separate consideration of $\sigma$ and $\pi$ AsC bonding. As the ring electron density increases, it becomes less electronegative and the per cent p character in the AsC bond decreases.[14] The resonance frequency should then increase as is observed.[15]

(13) Hereinafter, the $p_z$ orbital on the pnigogen atom will be taken to be coincident with the $C_3$ axis. The other three hybrids contain a high proportion of the $p_x$ and $p_y$ orbitals and are predominantly $\sigma$ bonding with the phenyl rings.

(14) H. A. Bent, *J. Chem. Educ.*, **37**, 616 (1960).

(15) T. B. Brill and G. G. Long, *Inorg. Chem.*, **9**, 1980 (1970).

Considering the $\pi$ system in more detail, two possible mechanisms of $\pi$ interaction between the ring and the arsenic atom are possible

$$\pi(\text{p-p}) \quad C_6H_5 \overset{..}{\longleftarrow} \overset{..}{A}s$$

$$\pi(\text{p-d}) \quad C_6H_5 \overset{..}{\longrightarrow} \overset{..}{A}s$$
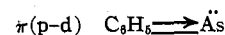
Although it is presently not possible to distinguish between these two mechanisms by nqr alone, $\pi$(p-p) bonding will account for the nqr data in the para-substituted arsines. Since electron density is transferred to the ring from the substituent, an increase in the $p_z$ orbital population of arsenic might be expected. Such an increase will yield a slightly higher resonance frequency.[15]

The three meta-substituted arsines do not appear to correlate with any substituent constant possibly because of small variations in molecular geometry.

**Triphenylstibines.**—Nqr data for substituted triphenylstibines are shown in Table III. The trends in the $^{121,123}$Sb resonance frequencies of the para-substituted stibines are different from those observed for arsenic. Correlation with $\sigma_R{}^0$ and $\sigma_I$ parameters is very poor and a much better fit is obtained using the general $\sigma$ functions of Hammett[6] (Figure 2). Since the
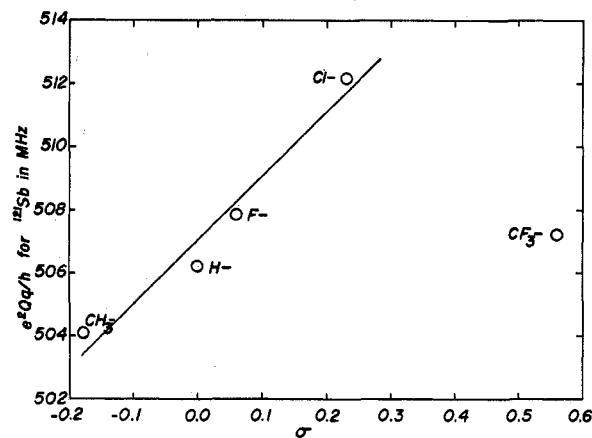


Figure 2.—The correlation of the antimony coupling constants with Hammett's substituent constant in para-substituted triphenylstibines

antimony atom is larger than arsenic, the mismatch of the p and/or d orbitals used in $\pi$ interaction is likely to be greater. The antimony atom may, therefore, not feel $\pi$-system effects with the substituent quite as well

and changes in the $\sigma$ and $\pi$ network could become more competitive. The single point lying drastically off the line is the trifluoromethyl group. $CF_3$ is well known to behave anomalously, however.[16] Sheppard[16] provided evidence that some electron density is returned to the ring *via* through-space effects to counteract the strong electron-withdrawing power of the group.

In connection with pnigogen–ring interaction it is interesting to compare the chlorine resonances in $(p\text{-}ClC_6H_4)_3As$ to those in $(p\text{-}ClC_6H_4)_3Sb$. It has been shown from ir intensities that, within experimental error, $\sigma_R^0$ values for the two groups $(C_6H_5)_2As$ and $(C_6H_5)_2Sb$ are the same.[17] The chlorine resonance frequencies do fall in nearly the same place in both cases indicating that as far as the chlorine atom is concerned, there is little difference between the arsine and stibine. The similarity of the chlorine frequencies in the meta- and para-substituted arsines and stibines suggests that the chlorine atom is not greatly affected by $\pi$ interactions with the ring. A similar observation was made in extensive studies of substituted chlorobenzenes.[18]

In Tables II and III, the ortho-substituted systems yield higher resonance frequencies than their meta and para counterparts. Tris($p$-xylyl)arsine and tris($p$-tolyl)arsine have been studied by X-ray crystallography[19] and permit a comparison to be made regarding the effect on molecular geometry of an ortho substituent relative to a para group. The CAsC angle is the same

(16) M. J. S. Dewar and A. P. Marchand, *J. Amer. Chem. Soc.*, **88**, 354 (1966); R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *ibid.*, **90**, 1757 (1968); W. A. Sheppard, *ibid.*, **87**, 2410 (1965).

(17) J. M. Angelleli, R. T. C. Brownlee, A. R. Katritzky, R. D. Topsom, and L. M. Yakhontov, *ibid.*, **91**, 4500 (1969).

(18) D. Biedenkapp and A. Weiss, *J. Chem. Phys.*, **49**, 3933 (1968); H. O. Hooper and P. J. Bray, *ibid.*, **33**, 334 (1960).

(19) J. Trotter, *Can. J. Chem.*, **41**, 14 (1963); J. Trotter, *Acta Crystallogr.*, **16**, 1187 (1963).

($102°$) for both, the tip of the rings from a position normal to the $C_3$ axis (36, 37°) is effectively the same, and the AsC bond lengths are quite comparable. (1.99, 1.96 Å). The slight increase in the AsC bond lengths of the xylyl compound, if significant, could increase the resonance frequency by decreasing the $p_x$ and $p_y$ orbital populations of arsenic. Through-space effects between the central atom and the ortho group can complicate spectral interpretation, however.

The antimony signals in $(C_6F_5)_3Sb$ are shifted significantly toward higher frequency. The $C_6F_5$ group has been shown to be a strong $\pi$ donor of electron density.[20] In $(C_6F_5)_3P$, the $^{19}F$ nmr spectrum favors $\pi$(p–d) ring–phosphorous bonding.[21] $\pi$(p–d) bonding may also exist in the stibines but it must be kept in mind that a further important consideration at the antimony atom is the strong $\sigma$-withdrawing power of the group. The marked increase in the resonance frequencies is consistent with a decrease in the $p_{x,y}$ orbital population on the antimony atom.

Several substituted triphenylbismuthines have been studied by Petrov, *et al.*[22] The variation in $\nu(^{209}Bi)$ appears not to be governed by any recognizable factors. As pointed out above, the Sternheimer antishielding factor[9] is likely to be an important consideration with the bismuth atom.

(20) M. G. Hogken, R. S. Gay, and W. A. G. Graham, *J. Amer. Chem. Soc.*, **88**, 3457 (1966).

(21) M. Fild, I. Hollenberg and O. Glemser, *Z. Naturforsch. B*, **22**, 253 (1967).

(22) L. N. Petrov, J. A. Kyuntsel, and V. S. Grechiskhin, *Vestn. Leningrad Univ., Fiz. Khim.*, 107 (1969).

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# Solvation Numbers of Group III and Group V Representative Halides in Acetonitrile by Proton Magnetic Resonance

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Proton magnetic resonance spectra of solutions of some group III and group V representative halides in acetonitrile at low temperatures are reported. Under these conditions, separate pmr signals of bulk acetonitrile and acetonitrile molecules in the first coordination sphere of the metal halide solute species can be distinguished. From the relative intensities of these signals the solvation numbers of the metal halides were determined. Variation in the solvation numbers among halides of the same group were observed and are discussed with reference to infrared and conductance measurements previously reported. An apparent solvation number of 1 was observed for boron and gallium trihalides indicating the presence of four-coordinate species, mainly $MX_2(CH_3CN)_2^+$ and $MX_4^-$. The solvation number of 1.5 observed for $AlCl_3$ indicates the presence of six-coordinate $Al(CH_3CN)_6^{3+}$ and four-coordinate $AlCl_4^+$ ions. Among group V metal halides, the pmr data clearly show that $PCl_5$ is not solvated to any extent while $SbCl_5$ has a solvation number close to 1 indicating the presence of six-coordinate species $SbCl_4(CH_3CN)_2^+$ and $SbCl_6^-$. The reduction in the solvation numbers of $GaCl_3$ (0.57) and $SbCl_5$ (0.82) from the expected value of 1 is explained on the basis of contact ion pairing which produces nonsolvated four- or six-coordinate dimeric species of the forms $Ga_2Cl_6$ and $Sb_2Cl_{10}$, respectively.

## Introduction

The results of infrared and conductance measurements of solutions of aluminum trichloride[1] and

boron[2,3] and gallium trihalides[4] in acetonitrile indicated that the halides interact strongly with ace-

(1) C. D. Schmulbach and I. Y. Ahmed, *J. Chem. Soc. A*, 3008 (1968).

(2) I. Y. Ahmed and C. D. Schmulbach, *Inorg. Chem.*, **8**, 1411 (1969).

(3) C. D. Schmulbach and I. Y. Ahmed, *ibid.*, **8**, 1414 (1969).

(4) C. D. Schmulbach and I. Y. Ahmed, *ibid.*, **10**, 1902 (1971).