

hand, the vibrational correlation diagram proposed by these authors, which is significant for weak to medium strength hydrogen bonding, becomes meaningless at the proton sharing point beyond which the system has to be described rather as an  $\text{BH}^+$  oscillator perturbed by an anion  $\text{A}^-$  than as a  $\text{AH}$  vibrator. This statement

is clearly proved in the  $\text{HI-NH}_3\text{-C}_2\text{H}_4$  and  $\text{HI-N(CH}_3)_3\text{-C}_2\text{H}_4$  cases.

Registry No. HI, 10034-85-2;  $\text{NH}_3$ , 7664-41-7;  $\text{N(CH}_3)_3$ , 75-50-3; Ar, 7440-37-1;  $\text{O}_2$ , 7782-44-7;  $\text{N}_2$ , 7727-37-9;  $\text{C}_2\text{H}_4$ , 74-85-1.

## $^{13}\text{C}$ NMR of Arylgermanes and Arylgermyl Anions. Main-Group Elements as Anionic $\pi$ -Donor Substituents. 2<sup>1</sup>

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**Abstract:**  $^{13}\text{C}$  NMR spectra of the compounds  $(\text{C}_6\text{H}_5)_n\text{GeH}_{4-n}$  and  $(\text{C}_6\text{H}_5)_n\text{GeH}_{3-n}\text{Na}$  ( $n = 1, 2, 3$ ) as well as  $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{GeM}$  ( $\text{M} = \text{H, Na}$ ) have been recorded and assigned. Comparison of the chemical shifts with those of analogous group 5B compounds demonstrates that the extent of delocalization of the negative charge of the germyl anions into the aromatic rings is significantly less than that found in the anions of phenyl-substituted phosphines and arsines. The distribution of  $\pi$  electrons in monosubstituted benzenes whose substituents are anionic centers appears to be the result of the balance between mesomeric effects and a polarization dependent upon the degree to which the negative charge is localized on the substituent atom. The magnitudes of these effects depend somewhat on the extent and nature of solute-solvent interaction, ion pairing, and association in the solutions of these salts which in turn are a function of the polarity of the solvent.

It has been demonstrated<sup>2</sup> that, in the absence of significant neighbour anisotropy effects, carbon-13 chemical shifts of  $\text{sp}^2$ -hybridized carbon atoms in planar conjugated systems are proportional to the  $\pi$ -electron densities. The theoretical rationale for such observations has been presented by Karplus and Pople.<sup>3</sup> In the case of monosubstituted benzenes it is apparent that only the para and perhaps the meta carbon atoms are sufficiently distant from the substituent so that such a proportionality may be generally valid.<sup>4</sup> Data and arguments have been presented<sup>5</sup> which indicate that the  $^{13}\text{C}$  chemical shift of the para carbon atom in monosubstituted benzenes is linearly related to the total  $\pi$ -electron density at that position. It was also suggested that the difference between para carbon chemical shift and that of the meta carbon is linearly related to the  $\pi$ -electron density at the para carbon atom due to resonance with the substituent on the ring. The validity of this latter conclusion may be somewhat difficult to establish unambiguously. However we note that monosubstituted benzenes, with positively charged substituents, appear to give rise to the largest shifts to low-field strength for a meta carbon resonance.<sup>4</sup> Consistent with this it is also observed that monosubstituted benzenes possessing negatively charged substituents, such as those considered in this paper, are among the very few compounds which display a significant shift of the meta carbon resonance to higher field strength from that of benzene. This suggests that the chemical shift of the meta carbon resonance is predominantly influenced by electrostatic field effects which undoubtedly affect the para carbon in an analogous way. Calculations<sup>6</sup> show that energetically the inductive effects of meta and para substituents are of comparable magnitude. It seems, therefore, that the simple difference  $(\delta_p - \delta_m)_{^{13}\text{C}}$  may well be the best indicator of the degree of resonance delocalization of charge from the substituent into

the ring of a monosubstituted benzene.

Using these arguments, it has been shown<sup>1</sup> that phenyl-substituted phosphines and arsines display little, if any, resonance between the nonbonded pair of electrons on the group 5B atom and the benzene ring, whereas the corresponding anions (e.g.,  $\text{C}_6\text{H}_5\text{PH}^-$ ) exhibit considerable resonance. This resonance in the anions is undoubtedly the main reason that phenyl substitution of phosphine or arsine increases the acidity of the remaining protons.<sup>7</sup> It has been observed, however, that phenyl substitution of germane decreases the acidity of the remaining protons.<sup>8</sup> This difference in the behavior of germanes, compared to that of arsines, has been rationalized by Jolly.<sup>9</sup> His argument is that the single nonbonding pair of electrons in, for example,  $\text{C}_6\text{H}_5\text{GeH}_2^-$  would have predominantly s-orbital character and thus could undergo little delocalization into the benzene ring. On the other hand,  $\text{C}_6\text{H}_5\text{AsH}^-$  has two nonbonded electron pairs which would have appreciable p-orbital character and therefore some delocalization could occur.

It would be expected that if indeed the monoanions of phenyl-substituted germanes exhibit little or no conjugation between the nonbonded electron pair on germanium and the phenyl rings, then, in the  $^{13}\text{C}$  NMR spectra of these anions, the para carbon resonances would not be greatly shifted to higher field strength than the meta carbon resonances. We now present  $^{13}\text{C}$  NMR data for a series of aryl-substituted germanes and their monosodium salts which demonstrate that mesomeric effects in these anions are considerably less than in the analogous arsine and phosphine anions.<sup>1</sup>

Olah and Hunadi<sup>10</sup> have reported the  $^{13}\text{C}$  NMR parameters for several tertiary phenyl-substituted silyl anions and have concluded, on the basis of the smaller shifts to higher field strength of the para carbon resonances in these anions compared to those of analogous carbanions, that conjugation between the phenyl ring and substituent is much reduced in the silyl anions. Their results indicate to us that primary and secondary phenylsilyl anions would display much less conjugation between phenyl ring and substituent

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Table I. <sup>13</sup>C Chemical Shifts (ppm) of Silanes, Germanes, Arsiners, and Their Anions<sup>a</sup>

	δ <sub>C<sub>1</sub></sub> (ipso)	δ <sub>C<sub>2</sub></sub> (ortho)	δ <sub>C<sub>3</sub></sub> (meta)	δ <sub>C<sub>4</sub></sub> (para)	δ <sub>Me</sub>	(δ <sub>C<sub>4</sub></sub> - δ <sub>C<sub>3</sub></sub> )
C <sub>6</sub> H <sub>5</sub> SiH <sub>3</sub> <sup>b</sup>	128.39	136.51	128.83	130.58		1.75
C <sub>6</sub> H <sub>5</sub> SiH <sub>3</sub> <sup>c</sup>	127.97	135.83	128.10	129.78		1.58
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SiH <sub>2</sub> <sup>d</sup>	131.90	136.29	128.68	130.36		1.68
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SiH <sub>2</sub> <sup>c</sup>	131.41	135.63	128.08	129.82		1.74
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiH <sup>e</sup>	133.7	136.1	128.4	130.1		1.7
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiH	133.30	135.78	128.03	129.78		1.75
(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> Si <sup>f</sup>	134.27	136.44	127.90	129.61		1.71
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiLi <sup>g</sup>	145.0	136.1	127.5	128.4		0.9
C <sub>6</sub> H <sub>5</sub> GeH <sub>3</sub> <sup>b</sup>	131.60	136.06	129.04	129.70		0.66
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeH <sub>2</sub> <sup>b</sup>	134.65	135.84	129.11	129.83		0.72
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeH <sup>b</sup>	136.36	135.78	129.05	129.82		0.77
(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> Ge <sup>h</sup>	141.5	136.3	128.2	129.0		0.8
( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> GeH <sup>b</sup>	133.06	135.69	129.70	139.35	21.35	(0.9) <sup>i</sup>
C <sub>6</sub> H <sub>5</sub> GeH <sub>2</sub> Na <sup>j</sup>	163.28	139.61	127.69	124.11		-3.58
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeHNa <sup>j</sup>	164.39	137.79	126.85	123.49		-3.36
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeNa <sup>j</sup>	165.31	137.31	126.93	123.85		-3.08
( <i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> GeNa <sup>j</sup>	161.29	137.30	127.65	132.33	21.20	(-4.1) <sup>i</sup>
C <sub>6</sub> H <sub>5</sub> AsH <sub>3</sub> <sup>k</sup>	130.20	136.36	129.34	128.54		-0.80
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> AsH <sup>k</sup>	137.46	135.26	129.42	128.83		-0.59
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> As <sup>b</sup>	140.69	134.46	129.40	129.19		-0.21
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> As <sup>l</sup>	139.58	133.65	128.59	128.37		-0.22
C <sub>6</sub> H <sub>5</sub> AsHNa <sup>k</sup>	157.70	133.22	127.05	118.53		-8.52
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> AsNa <sup>k</sup>	156.37	133.35	127.50	120.68		-6.82

<sup>a</sup> Unless indicated otherwise solutions are approximately 1 M; chemical shifts are relative to neat (CH<sub>3</sub>)<sub>4</sub>Si, external; (±0.06 ppm). <sup>b</sup> Solutions in tetrahydrofuran; benzene resonance occurs at 128.91 ppm. <sup>c</sup> Reference 15; 20–40% in CDCl<sub>3</sub>; CHCl<sub>3</sub> internal reference assigned 77.20 ppm. <sup>d</sup> Neat liquid. <sup>e</sup> Reference 10; tetrahydrofuran solution; relative to internal (CH<sub>3</sub>)<sub>4</sub>Si. <sup>f</sup> Reference 15; 2% in CDCl<sub>3</sub>; referenced as for footnote b. <sup>g</sup> Reference 10; tetrahydrofuran solution; secondary reference solvent tetrahydrofuran, peaks assigned 26.2 and 78.0 ppm. <sup>h</sup> Saturated solution in CDCl<sub>3</sub>; secondary reference, CDCl<sub>3</sub> assigned 76.9 ppm. <sup>i</sup> Corrected for *p*C<sub>1</sub> (toluene) = 8.9 ppm, δ<sub>C<sub>2</sub></sub> (toluene) = 0.7.<sup>14</sup> <sup>j</sup> Solutions in NH<sub>3</sub>; benzene resonance occurs at 129.04 ppm. <sup>k</sup> As footnotes a and b; ref 1. <sup>l</sup> Reference 16; CDCl<sub>3</sub> solution; secondary reference CDCl<sub>3</sub> assigned 76.98 ppm.

than do the analogous phosphine anions.<sup>1</sup> Unfortunately reaction of phenyl- or diphenylsilanes with alkali metals generally results in formation of more highly phenylated species.<sup>11</sup>

**Experimental Section**

**Preparations.** Phenylgermane, diphenylgermane, and triphenylgermane as well as phenylsilane were prepared by lithium aluminum hydride reduction of the respective chlorides in diethyl ether. Diphenylsilane and tri-*p*-tolylgermane were prepared earlier by Dr. I. Drummond of this department by analogous methods.<sup>12,13</sup> The hydrides were purified prior to use by trap to trap distillation for the monophenyl derivatives, vacuum distillation for the diphenyl derivatives, and recrystallization from methanol for the triphenyl- and tri-*p*-tolylgermanes. Tetraphenylgermane (Alfa) was recrystallized from toluene. Phenylphosphine and monosodium phenylphosphide were prepared as previously described.<sup>1</sup> Triphenylarsine (Alfa) was used without further purification.

Attempts to prepare solutions of sodium salts of the organogermanes by direct metalation in tetrahydrofuran were unsuccessful. The reactions are slow in this solvent and result in several species being formed. It is possible that the anionic species react with this solvent or alternatively that they are not sufficiently stabilized by solvation to prevent further reaction between the anions and unreacted starting material. Solutions of the monosodium salts of the germanes in liquid ammonia, however, are relatively stable.<sup>8</sup> These solutions were prepared by the addition of the appropriate germane, via a break seal, to a slight excess of either sodium or sodium amide (generated *in situ*) in liquid ammonia. The reactions with sodium amide were somewhat cleaner. The pale yellow solutions of the resulting sodium salts were filtered into NMR tubes which were then sealed at -196 °C under vacuum.

The neutral germanes themselves have low solubility in liquid ammonia therefore NMR samples of these compounds were prepared in tetrahydrofuran solution.

<sup>13</sup>C NMR. All NMR samples were prepared as approximately 1 M solutions in sealed 8-mm o.d. tubes. These tubes were inserted concentrically into 10-mm o.d. NMR tubes containing the lock compound. All spectra were recorded at 20.115 MHz using a Bruker WP-80 Fourier transform spectrometer and were <sup>2</sup>H locked to D<sub>2</sub>O. The spectra were accumulated in 8K of memory using a spectra width of 6000 Hz (1.47 Hz/data point; pulse repetition time 0.68 s) and a pulse width of 1.8 μs. The spectra were broad-band decoupled in the <sup>1</sup>H region. Chemical

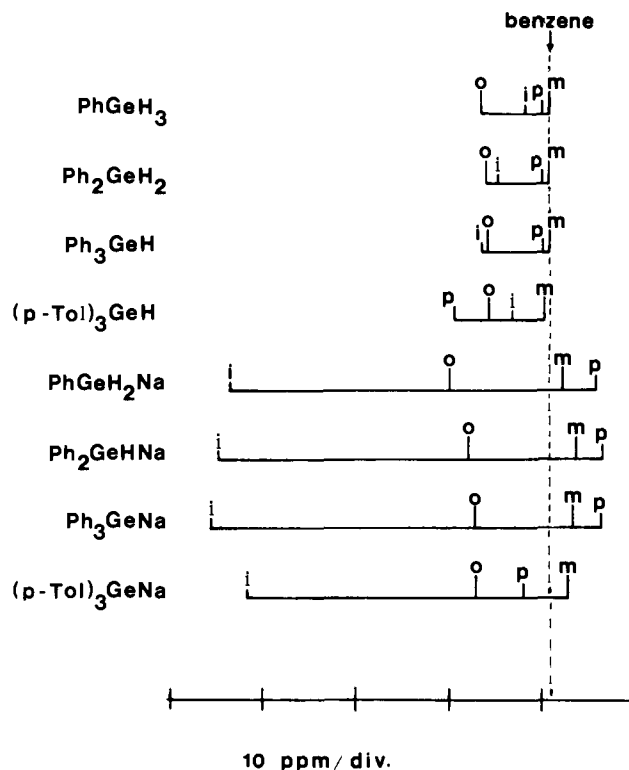


Figure 1. Schematic diagram showing the <sup>13</sup>C chemical shifts of the ring carbon atom resonances for arylgermanes and their monoanions relative to that of benzene: i = ipso (substituted) carbon, o = ortho, m = meta, p = para.

shifts were measured relative to neat tetramethylsilane as an external reference. The spectra were recorded at ambient temperature.

**Results**

The <sup>13</sup>C NMR shifts of the arylgermanes and their monosodium salts are listed in Table I and are shown schematically relative to the chemical shift of benzene in Figure 1. The resonances have

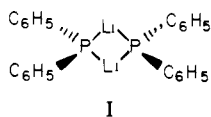
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been assigned on the basis of their relative intensities and upon the fact that meta carbon resonances are characteristically close to that of benzene.<sup>14</sup> The assignment of the resonances of the distributed benzenes ( $p\text{-CH}_3\text{-C}_6\text{H}_4$ )<sub>3</sub>GeH and ( $p\text{-CH}_3\text{-C}_6\text{H}_4$ )<sub>3</sub>GeNa are based also on the known additivity of substituent chemical shifts in disubstituted benzenes.<sup>14</sup> The observed chemical shifts for these compounds agree closely with those obtained by combining the appropriate values for (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeH and (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeNa with those of toluene.

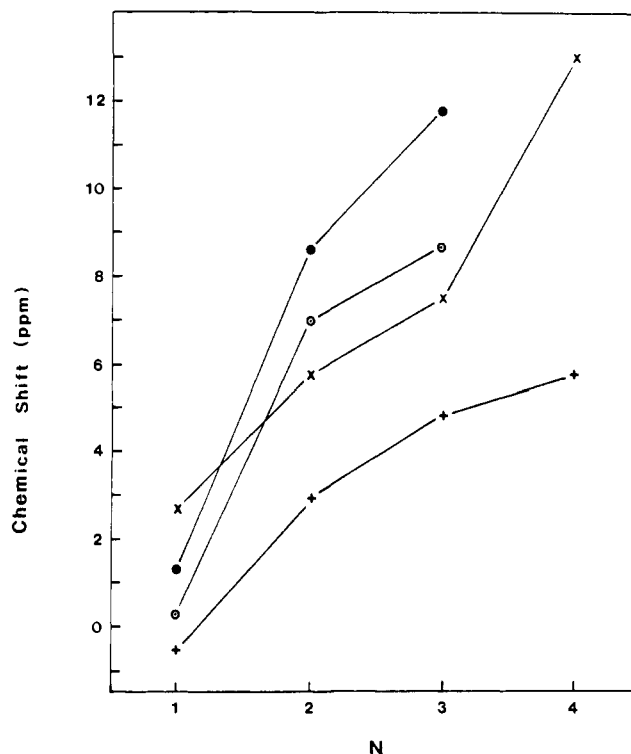
Ideally it is desirable to compare chemical shifts obtained from dilute solutions in a common noninteracting solvent. These conditions could not be fully realized in this work because the germyl anions require a solvent of considerable polarity, namely, NH<sub>3</sub>, to yield stable solutions, whereas the neutral hydrides do not have appreciable solubility in ammonia. Previous <sup>13</sup>C NMR studies of analogous anions have been carried out mostly in tetrahydrofuran solvent.<sup>1,2,10</sup> The diamagnetic correction between various solvents is not significant in comparison to the magnitude of the relative <sup>13</sup>C chemical shifts being considered. Solute-solvent interactions do not appear to be important for the neutral germanes and silanes because of their nonpolar character.

Of most importance is the effect of the different solvents on the chemical shifts of the anions when comparisons are made between different species. The choice of solvent will influence the degree of either association or of the solvation of ion pairs. For example, the differences in <sup>13</sup>C chemical shifts for (triphenylsilyl)lithium in tetrahydrofuran<sup>10</sup> and (triphenylgermyl)sodium in liquid ammonia most likely reflect the differences in solvation of the salts in these solvents. The species studied in liquid ammonia will have a much higher proportion of solvent separated ion pairs, whereas the species dissolved in the less polar tetrahydrofuran will be more highly associated. The effect of this is that in ammonia the species exhibit more ionic character, and the <sup>13</sup>C NMR spectra will show larger chemical shifts as a result of enhanced resonance and polarization effects. Changing the counterion (i.e., Li<sup>+</sup> or Na<sup>+</sup>) most likely also affects the ion-pairing equilibria.

A measure of the magnitude of the effect of a change of solvent may be obtained by considering the <sup>13</sup>C NMR of monosodium phenylphosphide in tetrahydrofuran<sup>1</sup> and in liquid ammonia. In tetrahydrofuran the difference between the meta and para <sup>13</sup>C chemical shifts is -9.87 ppm<sup>1</sup>, whereas when the solvent is changed to ammonia, the para carbon resonance shifts to higher field strength while the meta carbon resonance remains at about the same position resulting in a difference of -12.62 ppm. This indicates that, for C<sub>6</sub>H<sub>5</sub>PHNa in ammonia solution, resonance delocalization into the phenyl ring is enhanced presumably because there is a larger effective negative charge associated with the anion as a result of solvent separation of ion pairs. In ether solvents, on the other hand, ion pairs may in fact be highly associated as evidenced by the <sup>7</sup>Li and <sup>31</sup>P NMR study<sup>17</sup> of (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PLi wherein this species is found to adopt the dimeric, Li-bridged structure (I) in diethyl ether solution.



Previously<sup>1</sup> we have referred to the <sup>13</sup>C NMR spectrum of a species thought to be (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiHNa in tetrahydrofuran. This sample was prepared by the brief interaction between sodium and (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiH<sub>2</sub> in liquid ammonia at low temperature followed by evaporation of the NH<sub>3</sub> and dissolution of the residue in tetrahydrofuran. At this point the initially green solution, attributed to radical anion formation, quickly faded to yellow as gas was



**Figure 2.** Graph of the chemical shift (relative to that of benzene) of the ipso carbon atom resonance of phenyl-substituted hydrides vs. the degree of phenyl substitution (N): O, phosphines; ●, arsines; †, silanes; ×, germanes.

evolved. Gas evolution continued at a slower rate for several days. The resulting solution yielded a <sup>13</sup>C NMR spectrum which was assigned to a phenyl group as follows:  $\delta_{C_1}$  146.2,  $\delta_{C_2}$  136.4,  $\delta_{C_3}$  127.5,  $\delta_{C_4}$  127.9. It is known that direct metalation of diphenylsilane in ether solvents results in disproportionation and the formation of more highly phenylated species,<sup>11</sup> and therefore it is quite possible that these NMR parameters correspond not to (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiHNa but to (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiNa. The chemical shifts are quite comparable with those found for (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiLi ( $\delta_{C_1}$  145.0,  $\delta_{C_2}$  136.1,  $\delta_{C_3}$  127.5,  $\delta_{C_4}$  128.4).<sup>10</sup> Inability to reproduce the exact conditions which gave rise to the above mentioned sample and the occurrence of other species (e.g., (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>Si) has discouraged further pursuit of this matter.

## Discussion

The effect of a substituent on the distribution of electrons in a phenyl ring may be divided into two main categories, namely, redistribution of the phenyl group electrons as a result of the polarity of the substituent (inductive and field effects) and effects arising from the transfer of charge from the substituent as in mesomeric or resonance effects.<sup>6</sup> Although these two main classifications may be further subdivided, for the interpretation of solution <sup>13</sup>C NMR chemical shifts it is difficult to separate even these two general categories from solvent effects and other effects not directly related to the electron densities in the phenyl ring. A consideration of trends in the relative chemical shifts of the individual phenyl ring carbon atoms, however, may lead to a qualitative assessment of the nature of the perturbations that the substituents impose on the electron distributions in the rings.

**Ipsocarbon.** The chemical shifts of the neutral phenyl-substituted germanes are closely comparable to those found for the silanes as well as the arsines (Table I) and phosphines.<sup>1</sup> In fact the only resonance whose chemical shift varies greatly, with either change of main-group element or degree of phenyl substitution, is that of the ipso (substituted) carbon. In all cases the ipso carbon resonance shifts to lower field strength upon increased phenyl substitution (Figure 2). This may be attributed to the inductive influence of, and/or the magnetic anisotropy, associated with the ring current, of each additional phenyl group. The small dif-

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ferences in the ipso carbon chemical shifts of the monophenyl derivatives no doubt reflect the small differences in size and electronegativity of these main-group atoms, P, As, Si, and Ge. These properties of the substituent group will affect the magnitude of the inductive and magnetic anisotropic effects on the ipso chemical shift.

As has been found<sup>1,2,5,10,18</sup> for other monosubstituted benzenes, in which the substituent atom is an anionic center, the ipso  $^{13}\text{C}$  resonance for each of the arylgermyl anions is shifted drastically to lower field strength from the chemical shift exhibited in the neutral hydride. This low-field shift may be attributed to a polarization of the phenyl ring resulting in decreased electron density at the ipso carbon. Such polarization has been shown to proceed from the interaction of a  $\pi$ -donor substituent with the ring.<sup>19</sup> However, a polarization also resulting in a decrease of electron density at the ipso carbon atom could be caused by a localized negative charge residing on the substituent atom<sup>12</sup> (i.e., the field effect of a highly polar substituent). Substantiating evidence of this latter effect lies in the observation that while, for example, the triphenylsilyl anion<sup>10</sup> displays considerably less delocalization of negative charge into the phenyl ring than does the analogous carbanion,<sup>2</sup> as evidenced by the chemical shifts of the para carbon resonances, yet the ipso carbon resonance of  $(\text{C}_6\text{H}_5)_3\text{Si}^-$  displays a larger shift to lower field strength relative to the neutral hydride than does that of  $(\text{C}_6\text{H}_5)_3\text{C}^-$ . Triphenylgermane experiences an even larger shift of ipso carbon resonance to lower field strength upon deprotonation. This might be attributed largely to the choice of solvent,  $\text{NH}_3$ , which favors solvent separation of ion pairs, thus increasing the effective negative charge of the anion.

**Ortho Carbon.** The proximity of the ortho carbon atom to the large substituents in these compounds subjects its chemical shift to a variety of competing influences, which are not well understood. Comparison of the neutral germanes and silanes with the analogous arsines and phosphines shows that both the group 4B and 5B compounds exhibit similar ortho carbon chemical shifts, 5.5–7.5 ppm to lower field strength relative to that of benzene. These shifts may be greatly influenced by intramolecular dispersion forces<sup>20</sup> arising from the nonbonded contact between the ortho carbon atom and the substituent. Unlike the phosphines and arsines the germanes and silanes do not show a significant shift of the ortho carbon resonance to higher field strength with increasing substitution (Figure 3). This difference might be related to more severe crowding of the phenyl groups in the group 5B compounds because of the large stereochemical influence of the nonbonding pair of electrons.

Deprotonation of the arylgermanes results, in all cases, in a slight shift to lower field strength for the ortho  $^{13}\text{C}$  resonances. In contrast to this, deprotonation of phenyl- or diphenylarsines or phenyl- or diphenylphosphines causes a small upfield shift of the ortho  $^{13}\text{C}$  resonance.<sup>1</sup> This is consistent with the expected lower degree of  $p\pi-p\pi$  donation of electrons into the phenyl ring for the germlyl anions relative to the group 5B anions.

**Meta Carbon.** The chemical shift of the meta carbon is always the least affected by substituents in monosubstituted benzenes. In the neutral germanes the meta carbon resonance is very close to that of benzene and is independent of the degree of phenyl substitution. The upfield shift of the meta  $^{13}\text{C}$  resonance upon deprotonation of any of the arylgermanes is analogous to that observed for the anions of phenylarsines and -phosphines.<sup>1</sup> This is thought to arise from the polarizing field effect of the negatively charged substituent atom.

**Para Carbon.** In all the phenyl-substituted neutral germanes as well as in the silanes, arsines<sup>10,15</sup> (Table I), and phosphines,<sup>1,16</sup> the para carbon resonances occur within 2 ppm of that of benzene. Like the meta carbon resonances they show no dependence upon the degree of phenyl substitution. There is a small but notable

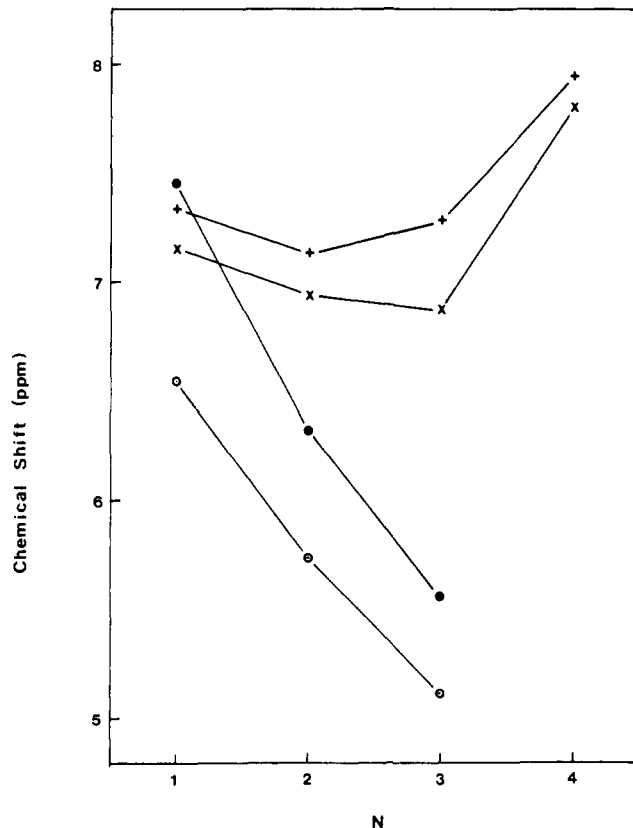


Figure 3. Graph of the chemical shift (relative to that of benzene) of the ortho carbon atom resonance of phenyl-substituted hydrides vs. the degree of phenyl substitution (N) (symbols as for Figure 2).

difference, however, between the group 4B and group 5B compounds in that for the silanes and germanes the para carbon resonance always occurs at lower field strength than the meta carbon resonance, while for the phosphines and arsines the opposite is true. This may be indicative of a weak  $p\pi-p\pi$  interaction between the phosphorous, or arsenic, atoms and the aromatic ring involving a slight delocalization of the formally nonbonding pair of electrons. This effect is very small, however, when compared with that observed for the anions formed by deprotonation of these compounds.<sup>1</sup>

Deprotonation of the arylgermanes causes the para  $^{13}\text{C}$  resonances to shift to higher field strength by 6–7 ppm. This shows that there is an increase in  $\pi$ -electron density at this position. This increase in  $\pi$ -electron density at the para position can be attributed to (i) a resonance delocalization of the negative charge into the phenyl ring and/or (ii) a polarization of the phenyl ring by the highly polar negatively charged substituent. The latter effect also influences the meta  $^{13}\text{C}$  chemical shift, and therefore it has been argued<sup>5</sup> that the difference  $(\delta_p - \delta_m)_{^{13}\text{C}}$  is at least a qualitative measure of the  $\pi$ -electron density at the para position resulting from resonance with the substituent on the ring. The values of  $(\delta_p - \delta_m)_{^{13}\text{C}}$  for the arylgermanes and their anions are included in Table I as are the values for the analogous silanes and arsines. The corresponding values for  $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{GeH}$  and its anion include a correction for the substituent shift caused by the methyl group. A comparison of these values for the arylgermyl anions with those for the anions of the analogous arsines leads us to conclude that, as expected, the germlyl anions exhibit considerably less delocalization of negative charge into the aromatic rings than do the phenyl-substituted arsines. It might be noted, since the  $^{13}\text{C}$  NMR parameters for the phenyl arsines were determined from tetrahydrofuran solutions,<sup>1</sup> that if the more polar solvent  $\text{NH}_3$  had been used for these anions the difference in the resonance effect between these anions and the germlyl anions would be even larger. (See the effect of change of solvent on  $\text{C}_6\text{H}_5\text{PHNa}$ , above.)

Comparison of the NMR parameters for (triphenylgermyl)sodium in  $\text{NH}_3$  with that for (triphenylsilyl)lithium in tetra-

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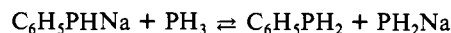
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hydrofuran<sup>10</sup> indicates that both resonance and polarization effects are larger in the former. This is certainly a consequence of the expected higher degree of solvation of ion pairs. It would be expected that in the same solvent with the same counterion,  $(C_6H_5)_3Ge^-$  and  $(C_6H_5)_3Si^-$  would display more comparable <sup>13</sup>C chemical shifts.

**Relative Acidities.** The above results are consistent with the postulate<sup>9</sup> that unlike the anions of phenyl-substituted arsines<sup>7</sup> the arylgermyl anions<sup>8</sup> have insufficient resonance stabilization to cause an increase in the acidities of their conjugate acids relative to  $GeH_4$ . Consequently phenyl substitution of germane results in a decreased acidity which has been attributed to the preferential solvation of the smaller anion  $[GeH_3]^-$  relative to the substituted anion  $[C_6H_5GeH_2]^-$ .<sup>8</sup> Further reduction in acidity with increased phenyl substitution may also be attributed to this effect and also to the effect of steric crowding of the bulky phenyl groups.<sup>8</sup>

The group 5B hydrides, on the other hand, appear to show increased acidity upon phenyl substitution,<sup>1,7</sup> and this is consistent with the much larger degree of delocalization of the negative charge of the anions as evidenced by the <sup>13</sup>C chemical shifts of the ring carbon resonances.<sup>1,21</sup> It must be noted, however, that the acidities of phenyl- and diphenylphosphines have been recently remeasured<sup>22</sup> by using  $Me_2SO$  as solvent, and the relative order

of their acid strengths was found to be reversed from that observed in the earlier work.<sup>7</sup> These recent measurements give a difference in acidity of 0.7 pKa unit.<sup>22</sup> In addition we estimate from the <sup>31</sup>P NMR spectrum of the equilibrium mixture, in THF solution, represented by



that phenylphosphine is more acidic than phosphine by only 1 pKa unit. Issleib and Kümmel estimate this difference to be 4.5 pKa units. It would seem, therefore, that the difference between the germanes and the group 5B hydrides is not as great as was previously thought.

It may prove worthwhile to examine the relative acidities of the group 5B hydrides more closely so that values of comparable accuracy to those reported for the germanes<sup>8</sup> may be obtained. It will also be of interest to examine the acidities of group 6B phenyl hydrides such as  $C_6H_5SH$  relative to the parent dihydride for further comparison. The <sup>13</sup>C NMR parameters of  $C_6H_5SNa$ <sup>18</sup> indicate that less resonance delocalization occurs in this salt than was observed for  $C_6H_5PHNa$ .<sup>1</sup>

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**Registry No.**  $C_6H_5SiH_3$ , 694-53-1;  $(C_6H_5)_2SiH_2$ , 775-12-2;  $C_6H_5GeH_3$ , 2875-92-5;  $(C_6H_5)_2GeH_2$ , 1675-58-7;  $(C_6H_5)_3GeH$ , 2816-43-5;  $(C_6H_5)_4Ge$ , 1048-05-1;  $(p-CH_3C_6H_4)_3GeH$ , 3351-47-1;  $C_6H_5GeH_2Na$ , 85649-52-1;  $(C_6H_5)_2GeHNa$ , 85649-53-2;  $(C_6H_5)_3GeNa$ , 34422-60-1;  $(p-CH_3-C_6H_4)_3GeNa$ , 85649-54-3;  $(C_6H_5)_3As$ , 603-32-7.

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## Temperature-Dependent Single vs. Double Ionization in the Mass Spectra of Phthalocyanine and Its Metal(II) Complexes

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**Abstract:** Electron-ionization mass spectra of phthalocyanine and its complexes with Fe, Co, Ni, Cu, and Zn are given as functions of sublimation temperature between 600 and 670 K. Relative ion abundances are independent of residence time in the ion-source region, and no evidence for ion/neutral reaction is found. A novel effect is a decrease in relative abundances of the doubly charged molecular ions as gas temperatures are raised. This does not occur as ionizing energy is raised between 40 and 70 eV and is not a result of increased fragmentation. It is attributed to thermal enhancement of single ionization by vibrationally induced autoionization.

Phthalocyanine and its complexes have become subjects of increased interest because of their utility as pigments, catalysts, semiconductors, and photoconductors and because of the similarity of their structure to that of the naturally occurring porphyrinic substances. These aspects of their importance have been recently reviewed.<sup>1,2</sup>

As mass spectrometric studies have come to include metal coordination complexes,<sup>3,4</sup> several such studies of phthalocyanine

and its complexes have been reported.<sup>5-9</sup> Although disagreeing in certain aspects, these studies showed these compounds to have a very high thermal stability with little tendency of the molecular ions to undergo fragmentation. They showed also an unusually high abundance of doubly charged molecular ions, typically 20% of the total ionization at the routinely used ionizing energies. This is a manifestation of the stability of the aromatic macrocyclic

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