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^1H, ^{13}C, and ^{31}P NMR Study of Primary and Secondary Phenylamines, -phosphines, and -arsines and Their Anions

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Abstract: NMR spectra of the compounds $(C_6H_5)_nXH_{3-n}$ and $(C_6H_5)_nXH_{2-n}Na$ (n = 1, 2; X = N, P, or As) in tetrahydrofuran solution have been recorded and assigned. The results are consistent with the existence of a $p\pi$–$p\pi$ interaction between substituent and phenyl ring in all cases when the substituent is nitrogen but only in the anions when the substituent is phosphorus or arsenic. Equilibria involving ion pairing are throught to be significant in these solutions.

Introduction

The relative acidities of the hydrides and organohydrides of the group 4B and 5B elements have previously been investigated by ^1H NMR spectroscopy in liquid ammonia.[1,2] It was found that alkyl substitution of germane, phosphine, or arsine resulted in decreased acidity for these hydrides. Similarly, phenyl substitution of germane also resulted in the reduction of its acidity. In contrast, aryl substitution of phosphine or arsine has been reported to cause an increase in the acidity of these hydrides in tetrahydrofuran solvent.[3]

It has been suggested[2] that the decrease in acidity of germane upon phenyl substitution may be largely a consequence of preferential solvation of $[GeH_3]^-$ compared to the series $[(C_6H_5)_{3-n}GeH_n]^-$. The theory has been put forward that the increase in the acidities of phosphine and arsine upon aryl substitution may be attributed to a $p\pi$–$p\pi$ interaction which results in delocalization of the negative charge of the anion into the aromatic ring, thereby stabilizing it relative to the conjugate acid. This interaction is thought not to be in effect in the case of phenyl-substituted germanes because the solitary nonbonding pair of electrons in their anions would occupy an orbital of predominantly s character.[4]

We have measured the ^1H, ^{13}C, and, where applicable, ^{31}P NMR spectra of the series of compounds $(C_6H_5)_nXH_{3-n}$ (n = 1, 2) and their respective monosodium salts $(C_6H_5)_nXH_{2-n}Na$, where X = N, P, and As, in order to find substantiating evidence for the theory outlined by Jolly.[4] There have been previous extensive investigations on the effect of substituents on the NMR parameters of monosubstituted benzenes,[5-7] but little systematic work has been done on the NMR of anionic monosubstituted benzenes other than carbanions.[8-10] No direct comparison of the effect of the different solvents, i.e., ammonia and tetrahydrofuran, on the relative acidities of the group 5B phenyl-substituted hydrides has previously been made.

We have confirmed the previously reported[3] relative acidities of phosphine and phenylphosphine in tetrahydrofuran, as well as in ammonia, by the use of ^{31}P NMR. We report here the ^{31}P NMR parameters of PH_2Na in tetrahydrofuran. The effects of concentration and temperature on the ^{31}P and ^{13}C chemical shifts of sodium hydrogen–phenylphosphide have also been examined.

Experimental Section

Preparations. The hydrides which were not commercially available were prepared by standard literature methods.[11-13] Phenylphosphine was prepared by the $LiAlH_4$ reduction of $C_6H_5PCl_2$ in ether. Diphenylphosphine was prepared by the reaction of $(C_6H_5)_2PCl$ with sodium in liquid ammonia followed by hydrolysis. Phenylarsine was prepared by the reduction of $C_6H_5AsO(OH)_2$ with Zn–Hg and concentrated HCl. Diphenylarsine was made by the reaction of triphenylarsine with sodium in liquid ammonia followed by hydrolysis. All of the prepared hydrides were distilled under dynamic vacuum and stored in sealed vessels. Manipulations were carried out either by vacuum-line techniques or in a good glove box under a dry nitrogen atmosphere with care being taken to exclude oxygen since these hydrides are very susceptible to oxidation.

Tetrahydrofuran solutions of the monosodium salts of the above compounds as well as of PH_3 were prepared by the reaction of the appropriate hydride with sodium metal in tetrahydrofuran. In this reaction hydrogen gas is evolved and brightly colored solutions are formed. The colors of the solutions vary from yellow to orange in the order C_6H_5PHNa, $(C_6H_5)_2PNa$, C_6H_5AsHNa, $(C_6H_5)_2AsNa$; these reactions are complete within 2 or 3 h. The reaction of PH_3 with sodium in tetrahydrofuran proceeds at a much slower rate, and in this case hydrogen was still being evolved after 24 h at which point the remaining PH_3 was removed under vacuum. The PH_2Na solution is lemon-yellow in color. In no case was there evidence for the formation of disodium salts in solution.

The monosodium salts of aniline and diphenylamine were prepared by the reaction of these compounds with sodium in liquid ammonia at room temperature in sealed vessels. These reactions were found to be too slow in tetrahydrofuran. The tetrahydrofuran solutions of these salts were only slightly colored. The $(C_6H_5)_2NNa$ solution was pale yellow and the C_6H_5NHNa solution was nearly colorless.

All of the solutions were filtered and sealed in NMR tubes under vacuum at −196 °C. The solutions all appear to be stable for long periods of time at room temperature. We did observe a small amount of dark sediment in some samples after a few days, but the amount of this sediment did not increase after storage for several months at room temperature and no changes in the NMR spectra were noted. The sediment is perhaps finely divided sodium or insoluble salts which eluded filtration. It has been noted previously that tetrahydrofuran solutions of lithium diorganophosphides showed appreciable reaction with the solvent only after prolonged heating.[14]

NMR Spectroscopy. Samples for ^1H NMR were prepared by sealing the tetrahydrofuran solutions, ammonia solutions, or neat liquids under vacuum at −196 °C in 5-mm- or 4-mm-o.d. NMR tubes. When 4-mm tubes were used, these were inserted concentrically into 5-mm tubes containing the lock compound. Samples for ^{13}C and ^{31}P NMR were similarly sealed in 8-mm-o.d. tubes which were inserted concentrically into 10-mm-o.d. tubes containing the lock compound.

^1H NMR spectra were recorded at both 90 and 80 MHz using respectively a Varian EM-390 spectrometer and a Bruker WP-80 Fourier-transform spectrometer. When the latter was used, the spectra were ^2H-locked to acetone-d_6 and were accumulated in 8K of memory. These

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Table I. ^{1}H Chemical Shifts[a] (ppm)

	1 (X-H)	2,6 (ortho)	3,5 (meta)	4 (para)
1. $C_6H_5NH_2$	4.23 (br)	6.52	6.98	6.52
2. $C_6H_5PH_2$	3.90	7.43	7.21	7.21
3. $C_6H_5AsH_2$	*b*	7.47	7.20	7.21
4. C_6H_5NHNa	2.75	6.20	6.65	5.77
5. C_6H_5PHNa	2.23	7.16	6.58	6.29
6. C_6H_5AsHNa	1.18	7.36	6.59	6.43
7. $(C_6H_5)_2PH$	(5.29)[c]	7.04	7.16	6.78
8. $(C_6H_5)_2NH$	5.17	7.43	7.24	7.21
9. $(C_6H_5)_2AsH$	4.89	7.44	7.19	7.18
10. $(C_6H_5)_2NNa$		6.92	6.92	6.25
11. $(C_6H_5)_2PNa$		7.48	6.79	6.52
12. $(C_7H_5)_2AsNa$		7.59	6.80	6.63
13. $C_6H_5GeH_3$[d]	4.29	7.49	7.29	7.32
14. $C_6H_5GeH_2Na$[e]	3.30	7.51	6.78	6.73

[a] Unless otherwise indicated, chemical shifts (±0.01 ppm) are for THF solutions, ~1 M; measured relative to neat external Me_4Si and corrected empirically to the value relative to internal Me_4Si; the benzene resonance occurs at 7.31 ppm relative to internal Me_4Si in THF. [b] Peak obscured by solvent signal (3.4 → 3.7 ppm). [c] Peak not observable because of broadening in THF solvent; the value given was measured in $CDCl_3$ relative to benzene (benzene assigned 7.31 ppm). [d] Chemical shifts from ref 15; measured in CCl_4 solution (1 M) relative to benzene (benzene assigned 7.31 ppm). [e] Chemical shifts from ref 15; measured in NH_3 solution (1 M) relative to benzene (benzene assigned 7.31 ppm).

spectra were recorded at spectral widths of 1200 Hz (0.293 Hz/data point; pulse repetition time 3.408 s) and a pulse width of 3.5 μs. Chemical shifts were measured relative to neat tetramethylsilane as an external reference.

^{13}C NMR spectra were recorded at 20.115 MHz using the abovementioned Bruker WP-80 spectrometer and were ^{2}H-locked to D_2O. These spectra were accumulated in 8K of memory using a spectral width of 6000 Hz (1.47 Hz/data point; pulse repetition time 0.68 s) and a pulse width of 1.5 μs. The spectra were broadband decoupled in the ^{1}H region except in selective decoupling experiments in order to assign the ^{13}C resonances and in an off-resonance experiment in order to detect the C_1 resonance of phenylphosphine. Chemical shifts were measured relative to neat tetramethylsilane as an external reference.

^{31}P NMR spectra were recorded using a Bruker WH-90 Fourier-transform multinuclear spectrometer. The spectra were ^{2}H-locked to acetone-d_6 or D_2O and were accumulated in 8K of memory. Spectra were obtained at 36.43 MHz using spectral widths of from 8 to 25 kHz (1 to 6 Hz/data point; pulse repetition time 1.02 to 0.16 s) and a pulse width of 5 μs. Spectra were recorded both proton coupled and broadband decoupled. Chemical shifts were measured relative to external 85% H_3PO_4.

Results

The interpretation of NMR data from one compound to another is often fraught with difficulty, not the least of which is the effect of the solvent on the chemical shifts being compared. In cases where comparisons are being made in different solvents having differing polarities, care must be taken that the effects observed are not just due to solvent interactions. This is particularly true in cases where there is a possibility of hydrogen bonding in one solvent but not in the other. These effects can be allowed for in part by making measurements at a series of concentrations and extrapolating to infinite dilution. We have chosen to work with dilute solutions of approximately 1 M concentration in the same solvent, namely, tetrahydrofuran (THF). In this way we hope to systematize the hydrogen-bonded and other interactions that will affect the electron distribution in the phenyl rings and to make, where possible, only internal comparisons of chemical shifts.

^{1}H NMR. The ^{1}H chemical shift data for the compounds studied together with literature data[15] for phenylgermane and its conjugate sodium salt are summarized in Table I. Figure 1 shows schematically the chemical shifts relative to benzene. In order to obtain these data the aromatic region of each ^{1}H spectrum was simulated using the iterative program NUMARIT[16] and the generated spectrum was compared with the experimental spectrum until an acceptable fit was obtained. In several cases the degree of resolution and the small relative chemical shifts did not allow a reliable evaluation of the ^{1}H–^{1}H coupling constants, and in these cases come of the smaller coupling constants were assigned reasonable fixed values in order to determine the chemical shifts. In general, the root mean square (rms) deviation between the calculated and the assigned experimental line positions was 0.2 Hz or less. The coupling constants are in the normal ranges for substituted benzenes, but the variations in coupling constants from compound to compound are of comparable magnitude to their standard deviations.

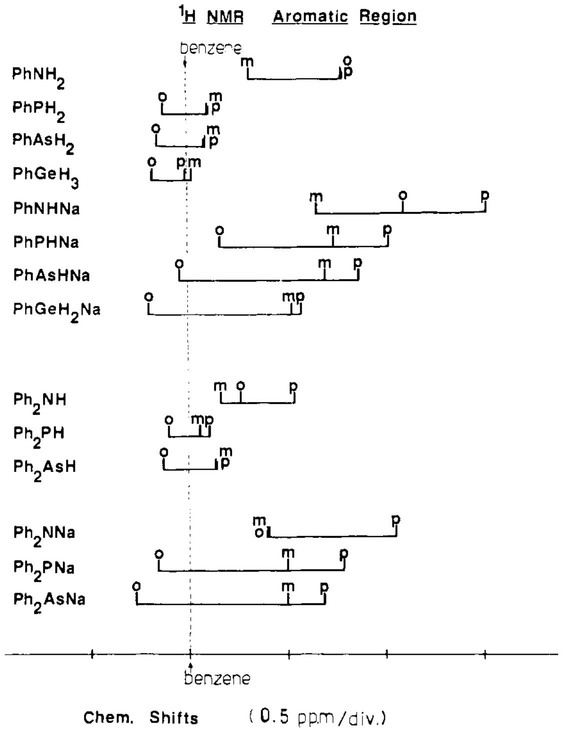

Figure 1. Schematic diagram of phenyl–proton chemical shifts: Ph = phenyl; o = ortho; m = meta; p = para.

The ^{1}H chemcial shifts for aniline (5% in CCl_4) have been reported previously[6] as −0.76 ppm (ortho), −0.20 ppm (meta), and −0.63 ppm (para), relative to benzene; shifts to higher field strength are defined as negative. In THF solution (~1 M) the chemical shifts are slightly different (ortho, −0.78 ppm; meta, −0.32 ppm; para, −0.78 ppm), indicating that solvent effects are significant. The meta and para proton resonances are shifted upfield so that the ortho and para resonances coincide in this solvent. It is also observed that in THF solvent the N–H peak of aniline is quite broad and that of diphenylamine is so broadened that it is not observable in this solvent. In solvents such as chloroform or carbon tetrachloride these same peaks are sharp. This broadening effect is undoubtedly due to the presence of the nuclear quadrupole moment on nitrogen and upon the different relaxation rates in the various solvents.

^{13}C NMR. The ^{13}C chemical shifts are listed in Table II, and are shown schematically in Figure 2. Because of their relative intensities, it was comparatively easy to assign the resonances of the para and the substituted carbons. Assignment of the ortho and meta carbon resonances were made after selective proton-decoupling experiments. For the ^{13}C spectrum of aniline, as a 5% solution in CCl_4, deuterium substitution has been used[6] to arrive at the following chemical shifts (ppm): C_1, 19.2; C_2, −12.4; C_3, 1.3; C_4, −9.5, all relative to benzene as zero chemical shift.

In THF solution we find that the para carbon resonance is shifted to higher field than that of the ortho carbon, the values

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Table II. ^{13}C Chemical Shifts[a] (ppm)

	δ_{C_1}(subst)	δ_{C_2}(ortho)	δ_{C_3}(meta)	δ_{C_4}(para)	($\delta_{C_4} - \delta_{C_3}$)
1. $C_6H_5NH_2$	149.22	117.55	129.71	115.21	−14.50
2. $C_6H_5PH_2$	129.16	135.45	129.19	128.80	−0.39
3. $C_6H_5AsH_2$	130.20	136.36	129.34	128.54	−0.80
4. C_6H_5NHNa	167.16	115.54	129.78	106.50	−23.28
5. C_6H_5PHNa	159.98	130.18	127.15	117.28	−9.87
6. C_6H_5AsHNa	157.70	133.22	127.05	118.53	−8.52
7. $(C_6H_5)_2NH$	144.93	118.13	129.84	120.87	−8.97
8. $(C_6H_5)_2PH$	135.85	134.64	129.23	129.05	−0.18
9. $(C_6H_5)_2AsH$	137.46	135.26	129.42	128.83	−0.59
10. $(C_6H_5)_2NNa$	159.49	118.98	129.71	113.33	−16.38
11. $(C_6H_5)_2PNa$	155.45	130.81	127.79	120.21	−7.58
12. $(C_6H_5)_2AsNa$	156.37	133.35	127.50	120.68	−6.82

[a] Chemical shifts (±0.04 ppm) are relative to neat external Me_4Si; all solutions are approximately 1 M in THF; the benzene resonance occurs at 128.91 ppm.

Table III. ^{31}P NMR Parameters[a]

	$\delta_{^{31}P}$	$J_{^{31}P'H}$	$J_{^{31}PCC'H}$	$J_{^{31}P^{13}C}$[g]	$J_{^{31}PC^{13}C}$[g]	$J_{^{31}PCC^{13}C}$[g]
PH_2Na[b]	−303.4 (1)	147 (3)[e]				
PH_2K[c]	−256	134				
PH_3[b]	−245.4 (1)	189 (3)[e]				
PH_3[c]	−240	182				
$C_6H_5PH_2$[b]	−125.7 (1)	198.7 (2)[f]	6.9 (6)[e]	8.8 (8)	16.2 (8)	5.9 (8)
$C_6H_5PH_2$[c]	−122	196				
C_6H_5PHNa[b]	−120.9 (1)	162.8 (2)[f]	5.4 (1)[f]	44.1 (8)	16.2 (8)	5.9 (8)
C_6H_5PHNa[d]	−98.4 (1)	152 (3)[e]				
$(C_6H_5)_2PH$[b]	−41.3 (1)	215.4 (2)[f]	6.6 (8)[e]	11.7 (8)	16.2 (8)	5.9 (8)
$(C_6H_5)_2PH$[c]	−41.1	214				
$(C_6H_5)_2PNa$[b]	−22.5 (1)		6.0 (1)[f]	44.1 (8)	17.7 (8)	4.4 (8)
$(C_6H_5)_2PNa$[c]	−24.4					

[a] Chemical shifts are measured relative to external 85% H_3PO_4; negative values indicate shifts to higher field strength; the estimated error in the last digit is given in parentheses. [b] This work; approximately 1 M in THF solution. [c] Mark, V.; Dugan, C. H.; Crutchfield, M. M.; Van Wazer, J. R. *Top. Phosphorus Chem.* **1967**, *5*, 227 ff. [d] This work; approximately 1 M in NH_3 solution. [e] Coupling as measured by ^{31}P NMR. [f] Coupling as measured by ^{1}H NMR. [g] Couplings measured by ^{13}C NMR.

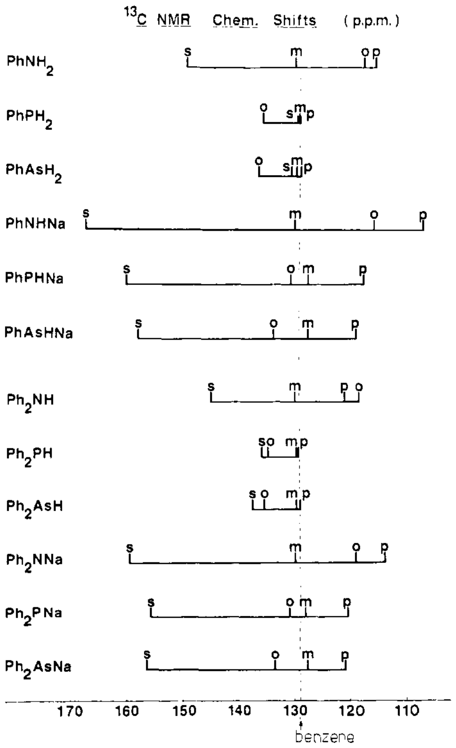

Figure 2. Schematic diagram of phenyl-^{13}C chemical shifts; s = substituted carbon; other abbreviations as for Figure 1.

relative to benzene being 20.2 (C_1), −11.5 (C_2), 0.71 (C_3), and −13.8 ppm (C_4). This shift is analogous to that observed for the para proton in agreement with the suggestion that the change of solvent actually affects the electron distribution in the ring,

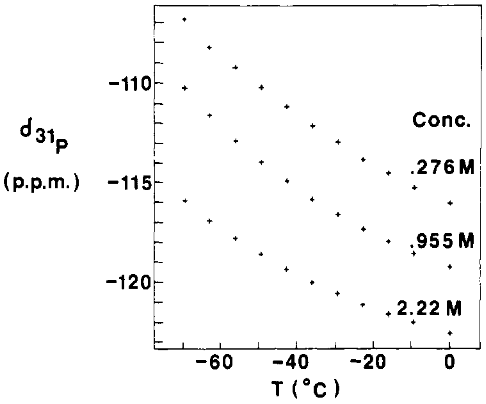

Figure 3. Plot of ^{31}P chemical shift of C_6H_5PHNa in tetrahydrofuran solution at three different concentrations vs. temperature.

probably via interactions such as hydrogen bonding between the solvent and the substituent NH_2 protons.

In the case of phenylphosphine the substituted carbon resonance was obscured by the resonance of the meta and para carbons, and its position was located by recording a partially proton-decoupled spectrum. The meta and para ^{13}C resonances of phenylphosphine occur as three approximately equal-intensity and equally spaced (~5 Hz) peaks in the ^{1}H-decoupled spectrum. These arise from a ^{31}P-coupled doublet to the meta carbon and a singlet from the para carbon. It is not immediately obvious how these three lines should be assigned. However, since the coupling constant from ^{31}P to ^{13}C meta is usually about 5 Hz and the meta carbon shift is usually close to 129 ppm, we have chosen that assignment as being most likely.

Changing the concentration of C_6H_5PHNa in THF caused only minor changes in its ^{13}C chemical shifts, the largest observed shift being −1.6 ppm for the substituted carbon as the concentration was changed from 0.28 to 2.22 M.

^{31}P NMR. The ^{31}P NMR data for phosphine, the phenyl-substituted phosphines, and their respective anions are summarized in Table III, along with the ^{31}P–^{13}C coupling constants derived from the ^{13}C spectra. Figure 3 shows the effect of temperature and concentration of the ^{31}P chemical shift of C_6H_5PHNa in THF solution. Significant variation in chemical shift is observed with changes of either temperature or concentration. The coupling constants J_{P-H}, on the other hand, did not vary significantly with concentration over the range studied. However, changing the solvent from THF to liquid ammonia resulted in a decrease in J_{P-H} of 10 Hz.

Solutions containing equal amounts of PH_3 and $C_6H_5PH_2$ and 1 equiv of base in either THF or liquid ammonia gave ^{31}P NMR spectra which showed the samples to contain predominantly C_6H_5PHNa and PH_3. This confirms the earlier observation[3] that phenylphosphine is a stronger acid than phosphine.

Discussion

^{1}H Data. The interpretation of the chemical shift changes that occur for the protons attached to the group 5 element is relatively straightforward. Successive replacement of hydrogens in the XH_3 compounds by phenyl groups results in a shift of the X–H resonance to lower field strength. This is to be expected since the phenyl group withdraws electron density from X, either inductively or by resonance, and hence deshields the remaining protons. In addition there is the deshielding effect of the ring current associated with the phenyl ring. The effective shielding that the phenyl group exerts on the remaining protons of a substituted hydride has previously been shown to be dependent on the electronegativity of the substituted element,[17] and therefore the relative values for this shielding, from one compound to the next, may depend primarily upon the inductive effect of the phenyl group. When these hydrides are deprotonated, there is an upfield shift of the resonances of the remaining X–H protons of 1–2 ppm due to the increased shielding from the negative charge on the X atom. It is interesting to note that the magnitude of this upfield shift increases as group 5 is descended. This may reflect either the differences in electronegativities of the group 5 elements or the varying abilities of the anions to form ion pairs with the cation Na^+. Also to be considered is the ability of the group 5 element to donate electron density, via a π interaction to the phenyl ring. We hestitate to make a comparison with the analogous shift upon deprotonation of phenylgermane because of the use of different solvent systems in this earlier study.[15]

The changes which occur in the chemical shifts of the ring protons of phenylgermane upon ionization have been interpreted to mean that mesomeric effects in the anion are minimal.[15] The fact that the ortho protons resonated to low field of benzene whereas the meta and para protons resonated at much higher field was taken as an indication that the isolated negative charge on the germanium had polarized the π electrons of the aromatic ring. We find the same trends in ^{1}H chemical shifts for the phenylphosphorus and phenylarsenic compounds upon ionization. However, as a result of ^{13}C studies reported here, we now feel that the previous interpretation may need revision.

A definitive interpretation of the ^{1}H chemical shift changes is difficult to achieve because they are relatively small and are more strongly influenced by solvent effects than the ^{13}C chemical shifts. The ortho proton shift will be influenced by inductive, resonance, magnetic anisotropy, and electric field effects as well as dispersive forces resulting from bulky substituents. These effects will be much smaller at the meta position, and presumably only the resonance effect is significant at the para position. In this regard the observed upfield meta proton shift upon deprotonation may indeed reflect a polarization of the aromatic ring possibly coupled with the effect of the electric field[18] produced at the meta proton by the highly polar substituent. A reasonable correlation (Figure 4) between the chemical shifts of the ^{13}C para and ^{1}H para suggests that the differences between the para and meta proton shifts could also be a qualitative indication of an increase in π electron density at the para position. The points for the anions in this graph appear to deviate slightly from the earlier best fit, but this is perhaps a result of the use of a different solvent which will have a more marked effect on the proton NMR than on the ^{13}C NMR. Given below is a similar interpretation of the ^{13}C shifts which we feel is more reliable because the ^{13}C shifts are not as strongly influenced by intermolecular effects as are the ^{1}H shifts. No direct correlations between ^{1}H and ^{13}C chemical shifts of monosubstituted benzenes other than the one shown in Figure 4 are to be found.

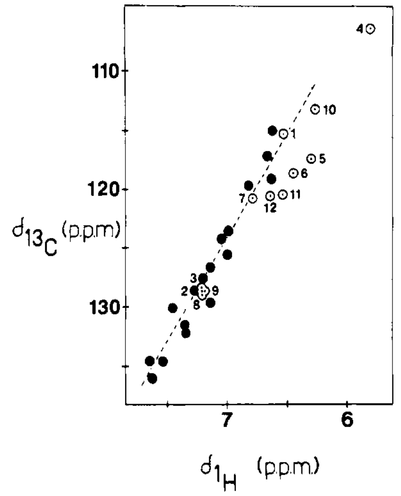

Figure 4. Plot of para-^{13}C vs. para-^{1}H chemical shifts of monosubstituted benzenes; the numbered points correspond to the compounds as numbered in Tables I and II. (●) Taken from ref 30; (⊙) this work; dashed line represents the best straight line fit to these data.

^{13}C Data. It has generally been accepted that the paramagnetic contribution to the shielding (σ_p of a ^{13}C atom is dominant over the diamagnetic contribution (σ_d) as well as other contributions from neighboring atoms. In general, ^{13}C chemical shifts do not correlate well with charge density except in cases where there is a similarity of environment for the ^{13}C nuclei being considered such that the charge density at the nucleus is the dominant effect determining the relative chemical shifts. In these latter cases the apparent dependancy of chemical shift upon charge density arises from the $\langle r^{-3}\rangle_{2p}$ dependancy of σ_p. That is, a withdrawal of electrons would cause a shrinking of the 2p orbital, thus giving rise to an increase of σ_p which would correspond to a low-field shift in the ^{13}C NMR.[5] Karplus and Pople[19] have derived an approximate expression for the chemical shift of an "aromatic" ^{13}C nucleus, that is, a nucleus contained in an aromatic ring which is trigonally bonded to two other carbon atoms and one hydrogen atom. This expression states that the chemical shift depends approximately linearly on the local π-electron density on the ^{13}C nucleus in question, the free valence of that atom, and the polarity of the C–H σ bond.

Substituted Carbon Atom (C_1). The substituted carbon atom of the monosubstituted benzene ring shows the largest variation of chemical shift relative to benzene. Spiesecke and Schneider[6] have found that after making an empirical correction for substituent anisotropy there is an apparent correlation between the chemical shift of the C_1 atom and the electronegativity of the substituent. The more electronegative substituents give rise to C_1 resonances at lower field. It is of interest to note that in all of the compounds studied in this work deprotonation of the substituent resulted in large shifts to lower field for the C_1 atom. These shifts are clearly in the opposite direction to those expected from a decrease in the electronegativities of the substituents. Similarly, low-field shifts have been observed for the C_1 atoms of the phenoxide ion,[7] the benzene thiolate anion,[20] and the phenylmethyl carbanion.[10] It seems that this is a general phe-

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nomenon for monosubstituted benzenes in which the substituent is an anionic center. It has been shown[21] that the interaction between the π-donor substituent, as well as resulting in a net transfer of electron density from the substituent to the ring, also results in a polarization of the ring which reduces the π electron density at the substituted carbon atom. This, no doubt, is the main reason for the downfield shifts of the resonances of the substituted carbon atoms of the anions. There may also be contributions from intermolecular dispersion forces[22] and the magnetic anisotropy of the substituent. It is interesting to note that the chemical shifts of the substituted carbon atoms of phenylphosphine and phenylarsine are close to that of benzene. This is consistent with the expected absence of a pπ–pπ interaction between the ring and substituent in these neutral molecules.

Ortho Carbon Atom (C_2). The various effects which contribute to the chemical shift of the substituted carbon atom are also expected to influence the shielding of the ortho carbon atom. It may be noted that the ^{13}C chemical shifts for the ortho as well as the meta positions have not been found to correlate well with other parameters such as substituent reactivity parameters nor with the respective ^1H chemical shifts. In general, it may be noted that for the group 5B phenyl hydrides deprotonation has a comparatively small effect on the ortho ^{13}C chemical shift presumably because of a calcellation of the various effects.

In every case except one the ortho carbon resonance shifts to higher field upon deprotonation (see Table II). It is quite possible that this is an indication of a mesomeric effect corresponding to increased π electron density at the ortho position. The one exception is that of diphenylamine where presumably the strong steric interaction of the two rings prevents planarity and therefore significantly reduces the resonance effect, thus allowing other effects to dominate the shielding of the ortho carbon atom.

Meta Carbon Atom (C_3). The chemical shifts of the meta carbon atoms in the compounds studied do not vary greatly from those of benzene. This is consistent with all previous ^{13}C work on monosubstituted benzenes.[5] It is thought that substituent anisotropy, inductive effects, and steric interactions do not extend as far as the meta carbon atom.[6] Also, there should be little contribution from resonance effects at this position. The effect of the electric field imposed by the highly polar substituents may be most significant in rationalizing the meta shift in the anions since other effects are expected to be small. In this regard it should be noted that, whereas the meta ^{13}C resonances of aniline and diphenylamine show no appreciable shift upon deprotonation, the analogous phosphorus and arsenic compounds all display a small upfield shift of the meta carbon resonance of 1–2 ppm.

In general, because the changes in the meta shift are small and because no significant correlations with other parameters have been observed, a detailed interpretation of the observed meta shifts in monosubstituted benzenes has not been attempted. The most significant use of the meta shift has been as a small correction to the para shift[7] when correlating the latter with parameters related to the π electron density at the para position, such as Taft's $\sigma_R{}^0$.[23] The reason given for this is that the weak effects which influence the meta shift might also influence the para shift proportionately, but the para shift will also have a large contribution from the resonance effect.

Para Carbon Atom (C_4). It has been concluded previously[6,7] that the para carbon is sufficiently removed from the substituent so that its chemical shift will be affected only by mesomeric effects. Reasoning from the expression for the chemical shift of an "aromatic" carbon atom given by Karplus and Pople[19] and by correlating experimental data, Maciel and Natterstad[7] have concluded that the chemical shift of the para carbon in monosubstituted benzenes, is proportional to the total π-electron density at the para position, and that the "corrected" para shift ($\delta_{^{13}C\ para} - \delta_{^{13}C\ meta}$) is proportional to the π-electron density at the para carbon resulting from resonance with the ring substituent, particularly for substituents that are π-electron donors. While their conclusions were based upon data for compounds containing mainly uncharged substituents, we note that the phenoxide anion was included in one of their plots and did not show any significant deviation from the observed trend. We also note that the ^{13}C data for the anions studied in this work do not deviate greatly from the correlation shown in Figure 4 and that, as noted before, the meta ^{13}C resonances do not vary greatly from that of benzene. For these reasons we feel that there are no unusual effects occurring to influence the chemical shift of the para carbon in the anions other than resonance with the substituent. Therefore, the conclusions of Maciel and Natterstad,[7] referred to above, may be extended to include anionic π-electron-donating substituents such as those studied here. Table II includes the values of the parameter ($\delta_{^{13}C\ para} - \delta_{^{13}C\ meta}$) for these compounds.

From these data we conclude that, while aniline and diphenylamine display considerable resonance delocalization, there is effectively no such resonance effect in the neutral phosphorus and arsenic analogues. Deprotonation of these compounds results in an increase in the π-electron density at the para carbon for aniline and diphenylamine. In the case of the phenylphosphines and -arsines deprotonation results in a significant resonance effect which was not present in the neutral molecules.

While it may be possible that a polarization of the phenyl ring could account for the significant upfield shifts of the para ^{13}C resonance, as was previously suggested for the ^1H chemical shifts of $C_6H_5GeH_2Na$,[15] there appears to be no precedent for such a large effect in the ^{13}C NMR. Also if such a polarization were in effect it could be expected that the meta ^{13}C resonance would also be shifted markedly upfield. This is not the case. While indeed there may be *small* contributions from such a polarization, which could account for the small upfield shifts of the meta carbon of the phenylphosphorus and -arsenic anions, we conclude that a considerable resonance delocalization of negative charge into the phenyl ring must be invoked in order to explain the much larger upfield shifts of the para carbon resonance.

We hope to investigate the ^{13}C NMR spectra of the analogous group 4B anions, where it has been suggested, on the basis of their reduced acidity, that there is not a significant resonance delocalization of negative charge into the aromatic ring. A preliminary experiment in this regard corroborates this view. The ^{13}C NMR spectrum of a species thought to be $(C_6H_5)_2SiHNa$ in THF displays almost no change in the relative positions of the para and meta ^{13}C resonances from those of the neutral hydride. The substituted carbon resonance does show the expected downfield shift as has generally been noted for anionic species; however, this shift is not as great as in the group 5B compounds.

^{31}P NMR. The observed ^{31}P chemical shifts are in reasonable agreement with previously published data (see Table III). The most notable feature is that deprotonation of PH_3 results in a large upfield shift of 58 ppm, while deprotonation of phenylphosphine results in a downfield shift of 5 ppm and deprotonation of diphenylphosphine an even larger downfield shift of 19 ppm. The latter shift is consistent with the observed shifts for lithium diphenylphosphide,[14] but we note that the chemical shift for PH_2Na is at significantly higher field than the previously reported value for PH_2K.[24] The downfield shift of the phenyl and diphenylphosphines upon deprotonation might be attributed to a pπ–pπ interaction with the phenyl groups as has been previously suggested[14] and which is in accord with our interpretation of the ^{13}C data.

It is of interest to note that solvent plays a significant role in the ^{31}P chemical shift of C_6H_5PHNa. The ^{31}P chemical shift of this compound in liquid ammonia is about 22 ppm to lower field than for the same compound in tetrahydrofuran whereas the parent hydride $C_6H_5PH_2$ has the same chemical shift in both solvents. Presumably the ^{31}P chemical shift is sensitive to the degree of solvation of the salt. In this regard it is shown that the ^{31}P shift varied with both temperature and concentration (Figure 3). While

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we do not have sufficient data to fully describe the equilibria that exist in solution, it would seem that these equilibria are more involved than the simple equilibrium proposed to exist between solvent-separated and contact ion pairs for analogous carbanions (e.g., $(C_6H_5)_3CNa$).[8,10,25]

The one-bond ^{31}P–^{13}C coupling constants for both phenylphosphine and diphenylphosphine (Table III) increase by a factor of 4 upon deprotonation of these hydrides. It is, however, quite possible that these couplings are negative since it has been suggested that a large separation in energy between valence s and p electrons may result in a negative one-bond coupling constant.[26] It is important to note that ^{31}P couplings frequently undergo a change of sign, and therefore a correlation with s character of the bonds is not possible until the signs are determined.

The two-bond couplings $J_{^{31}PC^{13}C}$ do not change magnitude upon deprotonation of either phenylphosphine or diphenylphosphine. Previous studies indicate that such couplings are always positive.[27] The three-bond couplings $J_{^{31}PCC^{13}C}$ also do not change upon deprotonation. All of the ^{31}P–^{13}C couplings, except the one-bond couplings in the anions, are of comparable magnitude to the analogous couplings in $(C_6H_5)_3P$.[28]

The one-bond ^{31}P–^{1}H couplings (Table III) are in reasonable agreement with the previously reported values. The significance of the reduction in the one-bond P–H coupling upon deprotonation of phenylphosphine is uncertain as the sign of the coupling was not determined. The three-bond couplings $J_{^{31}PCC^{1}H}$ of $C_6H_5PH_2$ and $(C_6H_5)_2PH$ are consistent with previously reported values.[29]

Conclusions

Earlier conclusions that the ^{13}C para and ^{1}H para chemical shifts of neutral monosubstituted benzenes are linearly related to the π-electron density at the para carbon[6,7] can be extended to include anionic monosubstituted benzenes. The "corrected" ^{13}C para shift $(\delta_{^{13}C\ \mathrm{para}} - \delta_{^{13}C\ \mathrm{meta}})$[7] is a measure of the π-electron density at the para position caused by resonance with the anionic substituent. An analogous correction for the ^{1}H para chemical shift is probably much less reliable because the meta proton shifts appear to have relatively larger contributions from electric field and solvent effects than does that of the meta carbon.

The observed trends in the NMR chemical shifts indicate that there is a significant $p\pi$–$p\pi$ interaction between ring and substituent for the anions of the phenyl-substituted hydrides of phosphorus and arsenic which was not present in the neutral compounds. This resonance interaction in the anions is consistent with the increased acidity of these group 5B hydrides upon phenyl substitution.[3] We would predict that the anions of the phenyl-substituted hydrides of Si, Ge, and Sn would diplay comparatively small upfield shifts for the ^{13}C para resonances relative to the neutral hydrides and small values of $(\delta_{^{13}C\ \mathrm{para}} - \delta_{^{13}C\ \mathrm{meta}})$ in agreement with the reduced acidity of these hydrides upon phenyl substitution. Our observation that $C_6H_5PH_2$ is more acidic than PH_3 to approximately the same degree in both tetrahydrofuran and in liquid ammonia rules out the possibility that the use of different solvents could account for the observed relative acidity differences between the group 4B and group 5B compounds.

Ion-pairing equilibria are in effect in the solutions of the sodium salts as evidenced by the temperature- and concentration-dependent ^{31}P chemical shift of C_6H_5PHNa. These equilibria, however, have only a small effect on the ^{13}C chemical shifts.

Registry No. 1, 62-53-3; **2**, 638-21-1; **3**, 1073-41-2; **4**, 1865-45-8; **5**, 51918-31-1; **6**, 65423-92-9; **7**, 829-85-6; **8**, 122-39-4; **9**, 829-83-4; **10**, 5856-90-6; **11**, 4376-01-6; **12**, 41006-64-8; PH_2Na, 80243-05-6; PH_3, 7803-51-2.

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Comparative Studies of Mo–Mo and W–W Quadruple Bonds by SCF-Xα-SW Calculations and Photoelectron Spectroscopy

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Abstract: The homologous compounds $M_2Cl_4(PR_3)_4$, with M = Mo and W, have been used in a combined theoretical and experimental study to compare the electronic structures of quadruple bonds between molybdenum atoms and between tungsten atoms. The theoretical work was carried out by the SCF-Xα-SW method on the model systems with R = H, but using in all other respects the experimentally measured bond lengths and angles for the compounds with R = CH_3. Relativistic corrections were made for both the molybdenum and tungsten compounds, but were found to be significant only for the tungsten compound. The PMe_3 compounds were used for measurements, made with both He I and He II excitation, of the photoelectron spectra in the gas phase. For both compounds the highest filled orbital is the M–M δ-bonding orbital and the measured ionization energies are 6.44 and 5.81 eV for the Mo and W compounds, respectively. For both compounds the next observed ionizations, at 7.70 eV (Mo) and 7.05, 7.45 eV (W), can be assigned on experimental criteria to the M–M π-bonding orbitals. The spin–orbit splitting of the W–W π peak shows features attributable to mixing of σ, π, and δ components by the spin–orbit coupling operator. These peaks are followed by ionizations assignable to M–P bonding electrons at 8.41 eV (Mo) and 8.36 eV (W). The calculations predict this order correctly for the W compound but reverse the Mo–Mo π and Mo–P ionization energies. The W–W bonding appears to be weaker than the Mo–Mo bonding, and in general the results of this study are consistent with the greater reactivity (i.e., lower chemical stability) of the W–W quadruple bond as compared to the Mo–Mo quadruple bond.

The rapid and extensive development of the chemistry of the quadruply-bonded Mo_2^{4+} unit over the past 16 years has not been matched by comparable fecundity in the chemistry of the W_2^{4+} unit; advances in this chemistry have, instead, been fewer and hard won.[2] Gradually, however, a range of W_2^{4+} compounds matching in composition, though usually not in ease of preparation or stability, those of Mo_2^{4+} compounds is being elaborated. The

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