N.M.R. Studies of Phenyl-substituted Group 4 Anions. Ion-pairing and Charge Delocalization *vs.* π-Polarization Effects

Erwin Buncel,*[a] T. Krishnan Venkatachalam,[a] Ulf Edlund,*[b] and Bertil Eliasson[b]

[a] *Department of Chemistry, Queen's University, Kingston, K7L 3N6, Canada*
[b] *Department of Organic Chemistry, Umeå University, S-901 87 Umeå, Sweden*

The n.m.r. chemical shifts of phenyl-substituted silyl, germyl, stannyl, and plumbyl anions show that the remote phenyl carbon positions are mainly affected by π-polarizing effects and that conjugative effects are unimportant in these anionic systems.

The role of charge delocalization in silyl and other group 4 anions has received considerable attention.[1—6] An early proposal, based on electronic absorption spectra of phenyl-substituted silyl-lithiums, claiming that π-interactions (pπ–pπ, or pπ–dπ) must be practically zero,[3] has recently been brought into question on the basis of results from n.m.r. spectroscopy. The chemical shift data suggest that π-interactions are reduced compared to the carbanion analogues but are nevertheless significant. The main support for this notion derives from the apparent ^{13}C n.m.r. chemical shifts of the *para* carbons on decreasing the number of phenyl substituents in the silyl anions.[2] Increased shielding of the *para* carbon was observed, which was especially noticeable on going from the triphenyl to the diphenylmethyl group 4 anion, in accord with an increase in delocalization of charge per phenyl group. Another study, with germyl anions, led to the somewhat unexpected conclusion that the extent of delocalization of charge increased relative to that found in silyl species.[1]

Ion-pairing has also been invoked in the structural description of group 4 anions.[4] The proton chemical shift data of the *meta* and *para* positions of triphenyl anions showed a trend that was opposite to the expected relative order of π-bonding of the group 4 elements. This inverse order, *i.e.* $Si < Ge < Sn < Pb$, could be accounted for if there is an increase in lithium–group 4 atom association on going from Pb to Si. However, the relatively small overall changes in the ^{1}H n.m.r. shifts (*ca.* 0.1 p.p.m.) along the series Si → Pb render this interpretation somewhat uncertain.

In an attempt to clarify some of these apparent anomalies, we have performed a ^{13}C n.m.r. spectroscopic study of a series of phenyl-substituted group 4 anions. The group 4 anions were generated in the appropriate ether by cleavage of the metal–metal bond of the hexaphenyl, diphenyltetramethyl, or tetraphenyldimethyl compounds by Li or K metal. The reaction was performed in an ultrasonic bath at 0 °C. After 3—4 h, *ca.* 3 ml of the solution was transferred to argon-flushed tubes and the n.m.r. spectra recorded.

The ^{13}C n.m.r. chemical shifts of some phenyl-substituted silyl anions are listed in Table 1. The shielding values of the silyl-lithiums agree with those published by Olah *et al.* except for the data reported for Ph_3SiLi.[2] In contrast to the previous data, the chemical shifts of Ph_3SiLi given in Table 1 are close to the values obtained for mono- and di-phenyl substituted silyl anions. This would be expected if π-interactions are suppressed. The shift data reported here for Ph_3SiLi are also in better agreement with the values measured for the corresponding potassium salt. Additional support is given by ^{1}H and ^{7}Li shifts which after susceptibility corrections are close to the shieldings earlier reported for this silyl anion.[4,7] The Ph_3SiLi is known to undergo coupling reactions readily and we could, by further reaction in more polar media, obtain a ^{13}C n.m.r. spectrum identical to that reported earlier.[2] The chemical shifts reported here indicate that the importance of π-interaction in these anions, and the earlier proposal of an increased π-interaction in germyl compared to silyl anions has to be revised. The *ca.* 2 p.p.m. shielding observed for the *para* carbon on changing from triphenyl to phenyldimethyl substitution is of a magnitude that could well be accounted for by other substituent electronic effects.[8]

Table 1. ^{13}C n.m.r. chemical shifts of some group 4 anions.[a]

	C-1	C-2	C-3	C-4	Others
Ph_3CLi	150.0	124.2	128.1	113.2	90.3
Ph_3SiLi	155.9	137.0	126.9	124.6	
$Ph_2MeSiLi$	160.1	135.4	126.7	123.9	4.8
$PhMe_2SiLi$	166.0	133.8	126.5	122.7	7.5
Ph_3GeLi	159.8	136.9	126.9	124.5	
Ph_3SnLi	166.6	139.2	126.6	124.1	
Ph_3PbLi	191.5	140.2	127.7	123.2	
Ph_3CK	149.1	124.0	129.0	114.3	88.5
Ph_3SiK	158.6	136.9	126.7	123.8	
Ph_2MeSiK	163.2	135.1	126.5	123.0	5.8
$PhMe_2SiK$	170.1	133.6	126.4	121.6	9.1
Ph_3GeK	163.2	137.1	126.7	123.8	
Ph_3SnK	165.8	139.1	126.7	124.2	
Ph_3PbK	190.5	140.1	128.2	123.8	

[a] 0.2—0.3 M in tetrahydrofuran. Samples run in an unlocked mode on a Bruker WM-250 multinuclear n.m.r. instrument, using cyclohexane as reference (δ 27.7).

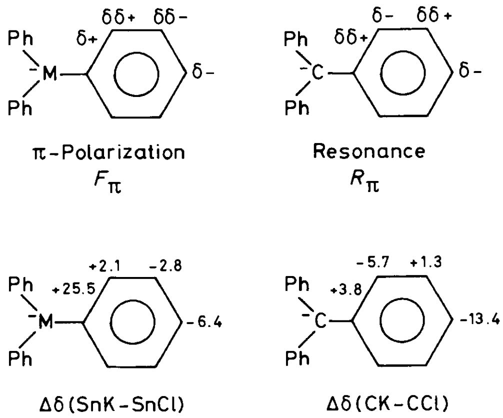

Figure 1

In Table 1, the ^{13}C chemical shifts are also reported for the various Li and K triphenyl group 4 anions. The most striking observation is the nearly constant chemical shifts of the *meta* and *para* carbons found for the series Si → Pb potassium group 4 anions. There is, however, a 5—8 p.p.m. shielding of these positions relative to the corresponding chlorides. This strongly indicates that there is either an insignificant or a constant π–π interaction between the various group 4 atoms and the carbon atoms. The charge pattern obtained relative to the neutral chlorides merely adapts to a π-polarization rather than a conjugative mechanism[8] (Figure 1). In the triphenylmethyl anion system both conjugative and π-inductive effects will be important for the remote carbon shifts: the former mechanism is expected to be the dominant one. We conclude, therefore, that in the series Si → Pb the observed deshielding of the *ipso* position and the shielding of the *para* position is caused by a polarization of the π-cloud due to the negative group 4 element, possibly to some extent modulated by a variable cationic field.

The ^{13}C chemical shifts for C-2, C-3, and C-4 in Ph_3SiLi and Ph_3GeLi are remarkably similar, contrasting with the earlier results.[1,2] Hence, a comparison of these species indicates not only a very similar metal–carbon bonding characteristic but also a comparable metal–lithium interaction. Further inspection of the shift data reveals, however, a deshielding of the *ipso* position and a slight shielding of the *para* position on going to the heavier metals. Such a response could be caused by an increased effective negative charge on the group 4 atom due to a varying cation–anion interaction, and/or a varying cation-induced π-polarization. In a given ion-pair state one expects the difference in π-polarizing ability between Li and K to be most pronounced for the smallest group 4 atom, *i.e.* the lithium cation will more easily polarize the phenyl rings in the silyl system. Hence, with Li^+ the *para* carbon of the triphenylsilyl system will be deshielded relative to that found for the plumbyl anion.

In conclusion, we have shown that the *para* ^{13}C n.m.r. chemical shifts of the phenyl-substituted group 4 anions are rather insensitive to the choice of cation and to the nature of the group 4 atom. The minor shift changes observed for this position by varying the solvent or cation can be accounted for by a change in the π-polarizing power of the negative group 4 atom and/or the effective cation field.

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