

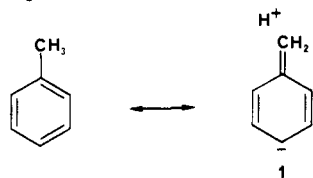
Neutral Hyperconjugation

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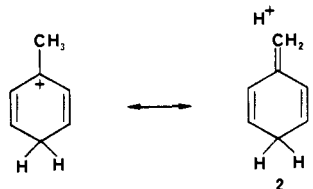
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Abstract: Structural evidence for hyperconjugation in the neutral ground state has been obtained from one-bond, carbon-carbon coupling constants. Hyperconjugation in $X-C_6H_4-CH_2-M(CH_3)_3$ should be enhanced by increased donor properties of M (in the order C, Si, Ge, Sn) and receptor properties of X (in the order MeO, Me, H, CN, NO₂). These expectations are borne out by the changes in the coupling between ¹³CH₂ and the ipso aromatic carbon and the coupling between ¹³CH₂ and M, in agreement with the double-bond, no-bond valence structure $X-C_6H_4=CH_2^+M(CH_3)_3$. The ¹¹⁹Sn-¹³CH₃ coupling provides evidence for a novel type of double hyperconjugation. The chemical shifts of the benzylic, ortho, and para carbons exhibit increased shielding for the same M series, also in accordance with the expectations of neutral hyperconjugation.

"Hyperconjugation" is the misnomer given to the interaction of σ electrons with adjacent π orbitals. Although the more accurate term " σ - π conjugation" and the apt but awkward "double-bond, no-bond resonance" are also in use, hyperconjugation continues to be the most widely accepted. Muller and Mulliken² distinguished between hyperconjugation in neutral systems, which they termed "ordinary" or "sacrificial" hyperconjugation, and hyperconjugation in cations (and sometimes in radicals), which they termed "strong" or "isovalent" hyperconjugation. Neutral hyperconjugation is illustrated by the interaction of the methyl group in toluene with the π electrons (1). Charged



hyperconjugation is illustrated by the interaction of the methyl group in the Weyland intermediate (protonated toluene) with the π electrons (2). The descriptor "sacrificial" referred to the loss



of certain π interactions in 1 and the introduction of a dipolar resonance structure.

The Baker-Nathan effect invoked neutral hyperconjugation and alternating aromatic bond lengths to explain substituent effects in S_N2 reactions of benzylic systems.³ Calculations and work in the gas phase, however, demonstrated that the original Baker-Nathan observations were the result of solvent effects rather than substrate structure.⁴ Other authors presented evidence that bond length effects, e.g., the shortened C-C single bond in propene, were the result of the s character of the saturated carbon rather than of neutral hyperconjugation.⁵⁻⁷ These results have led one recent textbook to conclude that "the evidence is against hyperconjugation in the ground states of neutral molecules".⁸

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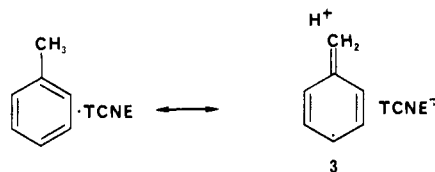
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The situation is quite different for positively charged systems, in which electron demand is considerably enhanced. The higher stability of tertiary carbocations (Me_3C^+) over less substituted cations (CH_3^+) is best explained in terms of charged hyperconjugation, as in 2. Hyperconjugation, however, finally achieved widespread acceptance when new observations were made on systems with strong electron donors, in particular, silicon and tin. These are the atoms that receive positive charge in valence structures analogous to 2. Higher polarizability and lower electronegativity than H or C vastly increase the ability of these atoms to serve as electron donors. The early work of Eaborn,⁹ Pitt,¹⁰ Traylor,¹¹ and Davis¹² studied donor atoms such as Si, Ge, Sn, Pb, and Hg and demonstrated the importance of hyperconjugation in electrophilic aromatic substitution (as in 2), cation-generating solvolysis reactions, ionization potentials, reduction potentials, and electronic spectra (charge-transfer bands in particular from species such as 3). Traylor summarized the factors



that influence the importance of hyperconjugation.¹³ Today's studies of the β effect of silicon and its congeners are all descendants of these early demonstrations of the importance of the donation of electrons from metal-carbon (or rather metalloid-carbon) σ bonds to electron-deficient π acceptors.¹⁴ Such hyperconjugative interactions are now well accepted.

Although the early Baker-Nathan observations proved not to be due to neutral hyperconjugation, in the 1970s spectroscopic evidence began to accumulate supporting such a phenomenon in ground states, particularly by ¹⁹F,^{9,15,16} ¹³C NMR,¹⁶⁻¹⁸ ¹H NMR,¹⁸ and infrared¹⁹ spectroscopies. For example, the para carbon in

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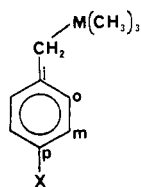
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the series $C_6H_5CH_2M(CH_3)_3$ was observed to resonate at 123.90, 123.84, 123.15, and 123.21, respectively, for $M = Si, Ge, Sn,$ and Pb , supporting a donor order of $Pb \sim Sn > Ge \sim Si$, but these shielding variations are quite small. Most convincing was the comparison between the ^{19}F chemical shift for $p-F-C_6H_4-CH_2Si(CH_3)_3$, in which the freely rotating C-Si bond permits optimal overlap with the aromatic π bonds, and that of 5-fluoroindane, in which the saturated five-membered ring constrains the C-Si bond to a position orthogonal to the π bonds and hence nonoverlapping.¹⁵ The ^{19}F chemical shifts clearly indicate neutral hyperconjugation in the freely rotating system and parallel the more impressive changes associated with charged hyperconjugation in the charge-transfer bands of the analogous tin systems studied by Traylor.¹¹ Neutral hyperconjugation also has been used to interpret rotational barriers between aryl and alkyl groups.²⁰

Despite this evidence for neutral hyperconjugation, the phenomenon is not fully accepted because it lacks a true structural basis.⁸ Are there ground-state structural perturbations that are caused by hyperconjugation? When the electron donor is hydrogen or carbon, as in **1**, there are convincing alternative explanations for any structural changes.⁵⁻⁷ To date, no study has examined structural aspects of systems with donors such as tin that are extremely effective in charged hyperconjugation. Chemical shifts are subject to many perturbations and would not be so reliable as hard structural parameters such as bond lengths. We felt that one-bond carbon-carbon coupling constants can serve in lieu of such structural parameters. The magnitude of $^1J(^{13}C-^{13}C)$ within a homologous series is directly proportional to the bond order.^{21,22} Studies have attempted to relate $^1J(^{13}C-^{13}C)$ in aryl-substituted methyl benzoates with π bond orders.²³ We hypothesized that changes in bond orders from neutral hyperconjugation should be reflected in one-bond carbon-carbon couplings. Consequently, our strategy has been to modulate neutral hyperconjugation by preparing a series of substrates with variation of both the electron donor (recipient of the positive charge through hyperconjugation) and the electron acceptor (recipient of the negative charge) and to measure all relevant one-bond couplings. We report these experiments herein.

Results

We chose the aromatic ring as the π component (the acceptor) and Group IV (14) atoms as the σ component (the donor), as in structure **4**. This arrangement permits modulation of both the donor (by changing the atom M) and the acceptor (by changing the para substituent X).



M: C, Si, Ge, Sn

X: NO_2 , CN, H, Me, MeO

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For $X = H, Me,$ and MeO , substrates were prepared for all M atoms. For $X = CN$, only $M = Si$ and Sn were prepared, and for $X = NO_2$ only $M = C$ was prepared. The preparations used a variety of straightforward procedures, which are described under Experimental Section.

For each substrate, ^{13}C chemical shift data were obtained at 75 MHz (Table I). The key structural parameter is the one-bond $^{13}C-^{13}C$ coupling constant. Values may be measured for three distinct aromatic C-C bonds, for the bond between the ring and

Table I. Carbon-13 Chemical Shifts of **4**

X	M	$\delta(Me)$	$\delta(M)$	$\delta(CH_2)$	$\delta(p)$	$\delta(m)$	$\delta(o)$	$\delta(i)$	$\delta(X)$
MeO	C	29.2	49.25	31.6	157.7	112.9	131.2	131.7	54.9
	Si	-2.00		25.6	156.5	113.6	128.7	132.2	55.0
	Ge	-2.66		24.9	156.4	113.6	128.3	133.1	55.0
	Sn	-10.3		18.6	155.8	113.7	127.4	134.7	55.0
Me	C	29.4	49.84	31.7	135.0	128.3	130.4	136.6	21.0
	Si	-2.17		26.2	132.8	128.6	127.7	136.9	20.7
	Ge	-2.64		25.6	132.8	128.8	127.4	137.9	20.8
	Sn	-10.2		19.5	132.1	129.0	126.7	139.5	20.8
H	C	29.4	50.3	31.7	125.8	127.6	130.5	139.6	
	Si	-1.94		26.9	123.9	128.0	127.9	140.3	
	Ge	-2.57		26.3	123.8	128.1	127.5	141.2	
	Sn	-10.1		20.1	123.0	128.2	126.8	142.9	
CN	Si	-2.30		28.0	107.2	131.7	128.3	146.9	119.2
	Sn	-10.1		21.3	105.8	131.8	126.8	149.9	119.3
NO_2	C	29.2	49.8	31.9	147.6	122.7	131.0	146.3	

Table II. One-Bond Coupling Constants^a of **4**

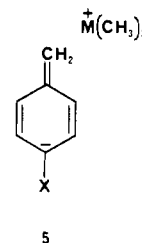
X	M	CH_3-M	CH_2-M	CH_2-C_i	C_i-C_o	C_o-C_m	C_m-C_p
MeO	C	36.0	32.4	36.0	57.0	58.0	67.6
	Si	51.3	46.9	41.5	57.3	58.6	67.6
	Ge			43.2	57.3	58.6	67.6
	Sn	310	294	43.5	57.3	58.7	67.6
Me	C	36.0	32.4	36.0	56.4	56.6	56.9
	Si	51.3	46.5	41.1	56.8	57.2	57.3
	Ge			42.7	56.8	57.2	57.3
	Sn	312	284	43.0	56.8	57.2	57.3
H	C	36.0	32.4	36.0	56.3	56.0	55.9
	Si	51.4	46.1	40.9	56.5	56.8	55.9
	Ge			42.5	56.5	56.8	55.9
	Sn	314	278	42.8	56.5	56.8	55.9
CN	Si	51.8	43.8	40.3	55.9	58.0	60.3
	Sn	321	239	40.4	55.9	58.0	60.8
NO_2	C	35.8	32.3	36.0			

^aThe coupling is $^1J(^{13}C-^{29}Si)$ for silicon and $^1J(^{13}C-^{119}Sn)$ for tin. All other couplings are $^1J(^{13}C-^{13}C)$. Values are given in hertz.

the benzylic carbon and for the bonds between the atom M and both the methylene and methyl carbons (except for the quadrupolar germanium case). These values are presented in Table II.

Discussion

The resonance structure that results from $\sigma-\pi$ overlap in **4** is given by **5**. Thus, hyperconjugation should raise the bond order



5

between the benzylic and ipso carbons (CH_2-C_i) (see **4** for labeling of atoms) and lower the bond order between the donor atom and the benzylic carbon (CH_2-M). In terms of structure, the CH_2-C_i bond length should decrease and the coupling constant increase and the CH_2-M bond length should increase and the coupling constant decrease. Although to date neutral hyperconjugation has not been substantiated by bond length variations, the data in Table II provide the first evidence in terms of coupling constants.

Within each X series (Table II) the CH_2-C_i coupling follows the order $C < Si < Ge < Sn$, from about 36 Hz for C to about 43 Hz for Sn. This is the expected order for increased neutral hyperconjugation. The CH_2-M coupling cannot be followed in a similar fashion because the coupling partner M is changing. The C-C coupling constants within the aromatic ring are essentially

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independent of the changes in M. For example, for X = H each of the aromatic couplings (C_1-C_o , C_o-C_m , C_m-C_p) is invariable from Si to Sn. The difference of 0.2–0.4 Hz between M = C and M = Si, Ge, Sn for each X may indicate a small effect of hyperconjugation (C does not hyperconjugate, the other three do). Although representations such as **5** seem to imply aromatic bond length variation with hyperconjugation, electron donation from the benzylic carbon to the aromatic ring is into nonbonding levels. Thus, contrary to the original Baker–Nathan hypothesis, hyperconjugation does not result in bond length alternation within the aromatic ring, and the present experiments confirm this point. There are variations of the aromatic couplings as X is changed, but these are the well-known direct effects of the X substituents and are about the same from C to Sn.

Structure **5** implies decreased bond order for the CH_2-M bond. This effect also is substantiated by the coupling constants. Although the CH_2-M coupling cannot be compared with variation of M, the trend with variation of X is exactly as expected for changes due to neutral hyperconjugation. The coupling varies by no more than 0.1 Hz from MeO to NO_2 for C ($^1J(^{13}CH_2-^{13}C)$). For Si, however, $^1J(^{13}CH_2-^{29}Si)$ varies from 46.9 Hz for MeO to 43.8 Hz for CN. The smallest coupling is for CN, the most electron-withdrawing group. This group best stabilizes structure **5** through inductive and resonance withdrawal of negative charge and results in the lowest CH_2-Si bond order. The effect is even more impressive in the Sn series, because Sn couplings are larger and more sensitive and because Sn better stabilizes the positive charge. Thus, $^1J(^{13}CH_2-^{119}Sn)$ varies from 294 Hz for the least effective group, MeO, to 239 Hz for the most effective group, CN. The X group is six bonds away from the CH_2-M bond, so these are not direct effects of X. These results suggest that neutral hyperconjugation of C (and presumably of H) is not important but that the phenomenon is real and of increasing magnitude for Si, Ge, and Sn.

When positive charge is moved to M through hyperconjugation, there can then be a second-order effect if this charge is further delocalized onto the methyl protons. Such an effect could be represented by nine resonance structures $^+M-CH_3 \leftrightarrow M=CH_2 H^+$. We²⁴ and others²⁵ have provided evidence for such double-hyperconjugation when positive charge is delocalized. The present effect is the first evidence for charged (isovalent) hyperconjugation on top of neutral hyperconjugation. It is best seen in the CH_3-M coupling for Sn (Table II), which varies from 310 Hz for MeO to 321 Hz for CN. The increase in the coupling indeed supports a higher CH_3-M bond order when the X group is better able to enhance neutral hyperconjugation, as is the case for CN. The effect is much smaller for Si, a variation of only 0.5 Hz (51.3 Hz for MeO to 51.8 Hz for CN), and it is essentially absent for C. As expected, the effect on the CH_3-M coupling is in the opposite direction from that on the CH_2-M coupling, since double-hyperconjugation increases the CH_3-M bond order, whereas simple hyperconjugation (**5**) decreases the CH_2-M bond order.

Bond order effects generally are harder to discern from chemical shifts, and less reliable, because of the variety of phenomena to which shielding is sensitive. Previous studies, however, have been able to provide some evidence for neutral hyperconjugation,^{15–18} and our data substantiate these observations. The X series of Table I shows strong trends at both the benzylic and aromatic carbons. The benzylic carbon moves from δ 31.7 to 20.1 between C and Sn (X = H), a shielding trend that is expected when neutral

hyperconjugation places negative charge on the CH_2 group. This negative charge is delocalized onto the ortho and para aromatic positions (although bond orders are not modulated by neutral hyperconjugation, electron densities are), so that $\delta(p)$ shows a shielding trend of 125.8 to 123.0 and $\delta(o)$ of 130.5 to 126.8 (X = H). The meta carbons, as expected, experience the opposite effect, a deshielding trend of δ 127.6 to 128.2 (X = H). Analogous trends are seen for X = Me and MeO.

The benzylic chemical shifts of Table I substantiate that neutral hyperconjugation increases from C to Sn. For C, the shift changes by only 0.3 Hz from MeO to NO_2 , but for Si and Sn the changes from MeO to CN are, respectively, 2.4 and 2.7 Hz. The trends within the aromatic ring are governed by direct substituent effects of X and are not relevant to the problem of neutral hyperconjugation.

Summary

One-bond carbon–carbon coupling constants provide the first structural evidence for hyperconjugation in a neutral ground state. When X is held constant and M becomes more able to receive positive charge (C < Si < Ge < Sn), there is an increase in the CH_2-C_1 coupling constant (Table II), as expected for the higher bond order in structure **5**. Similarly, the decreased CH_2-M bond order causes the coupling constant to decrease. The pattern indicates negligible neutral hyperconjugation for C and steadily increasing values for Si, Ge, and Sn. Double-hyperconjugation between M and the methyl groups results in a small increase in the $M-CH_3$ bond order and in the coupling constant for M = Sn. The C–C coupling constants within the aromatic ring are not perturbed by neutral hyperconjugation, as electrons at the benzylic positions donate into a nonbonding aromatic orbital. These trends are supported by higher shielding at the benzylic, ortho, and para carbons as M moves from C to Sn.

Experimental Section

Benzyltrimethylsilane (4, M = Si, X = H, abbreviated Si/H) and neopentylbenzene (C/H) were commercially available. The remaining compounds were known and were prepared by standard procedures. The Grignard reagent²⁶ of the benzyl chloride was coupled with chlorotrimethylsilane (or germane or stannane) for 4, M/X = Si/Me, Si/MeO, Ge/H, Ge/Me, Ge/MeO, Sn/H, and Sn/Me. *tert*-Butyllithium or trimethylstannyl lithium²⁷ was coupled with the benzyl chloride²⁸ for C/Me, C/MeO, and Sn/MeO. Hexamethyldisilane or -distannane was allowed to react with α -bromo-*p*-tolunitrile in the presence of tetrakis(triphenylphosphine)palladium(0) for Si/CN and Sn/CN.²⁹ Neopentylbenzene was nitrated to give C/ NO_2 .³⁰

The one-dimensional INADEQUATE experiments were carried out on 10 M solutions of $CDCl_3$ containing 10^{-2} M chromium acetylacetonate. The standard Freeman $90^\circ(x)-\tau-180^\circ(y)-\tau-90^\circ(x)$ INADEQUATE pulse sequence followed by phase cycling was used. The 90° pulse was optimized by locating the best 360° pulse and reducing the pulse time by a factor of 4. The delay time τ between pulses of $1/(4J(C-C))$ was selected with $J = 45$ Hz, so that all carbon–carbon coupling constants could be measured in a single experimental. The ^{29}Si and ^{119}Sn couplings were read directly from the spectra. An acquisition time of about 5 s was necessary for a precision of at least 0.15 Hz. Usually, 1024 transients were sufficient to obtain good spectra. The delay time between sequences of 2 s after acquisition was sufficient because of the presence of the relaxation reagent, chromium acetylacetonate.

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