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HYPERCONJUGATION AND ITS ROLE IN GROUP IV CHEMISTRY

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SUMMARY

The perturbational molecular orbital treatment of hyperconjugation (σ–π conjugation), in conjunction with CNDO/2 calculations, is applied to rationalize trends in a number of experimental properties of compounds of C, Si, Ge, and Sn. The molecular features, *i.e.* geometries, overlap and resonance integrals, orbital energies, and electron densities, which determine the magnitude of hyperconjugation are defined, and estimated from either experimental properties or from CNDO/2 calculations on model compounds. The relative roles of hyperconjugation, $(p\text{–}d)\pi$ bonding, and inductive effects, in determining trends in properties such as ionization and reduction potentials, electrophilic reactivity, electronic spectra, and charge distribution are analyzed. In addition, speculations on the importance of σ–n and σ–σ conjugation in organometallic compounds are presented, and supported by CNDO/2 calculations and experimental data.

A common approximation in the electronic theory of organic chemistry is that the σ and π electrons of a molecule may be treated as separate if not entirely independent systems[1]. For example, in descriptive models the effect of a σ-substituent on π-electron properties is frequently rationalized solely by inductive and field-effects. In quantum mechanical terms this is equivalent to the construction of a π-electron Hamiltonian wherein the σ electrons enter only via the effective potential created by their distribution. While this description is only strictly correct for planar molecules, where true σ and π symmetry is maintained, it is still a reasonable assumption for non-planar molecules if a relatively large difference in energy of the σ and π electron systems minimizes σ–π conjugation. However, in organometallic compounds, where the energies of the σ and π electrons are often comparable, the assumption is no longer valid. This has been clearly shown in a number of recent publications which have experimentally[2–6] and theoretically[7–9] confirmed the long postulated* importance of σ–π conjugation in determining trends in the ionization potentials, electronic spectra, reaction rates, and charge distribution of organometallic compounds. The general subject has been discussed by Traylor[10], and termed metallohyperconjugation.

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* For reviews, see ref. 10.

To date most attention has been directed toward σ–π conjugation in organometallic molecules where the metal and π-system are connected via a saturated carbon atom, for example $ArCH_2MR_n$, where M is Si, Ge, Sn, Pb, Hg, Mn, Mo, W, Fe, and Co[10]. It is of some interest to consider to what extent σ–π conjugation contributes to the properties of other structural types. Perturbation MO theory[11] represents a potential means of answering this question semiquantitatively, and in this paper we have evaluated the ability of PMO theory to explain and to predict the role of σ–π, and also σ–n and σ–σ, conjugation in determining the properties of Group IV derivatives.

PERTURBATIONAL MO TREATMENT OF σ–π CONJUGATION

σ–π conjugation, a concept which has long been postulated to explain the weak mesomeric interaction of alkyl groups with π-hydrocarbons, was first described in MO terms by Mulliken[12], and subsequently in perturbational MO terms by Dewar[11,13]. To summarize, consider a phenyl-substituted compound Ph–MR_3 (with the conformation shown in Fig. 1) prior to any interaction of the phenyl and MR_3 groups. Linear combinations of the three orthogonal σ(MR) bonding (or antibonding) orbitals which belong to the A_1 and E symmetry species of the three fold rotational (C_{3v}) group may be constructed, *i.e.**:

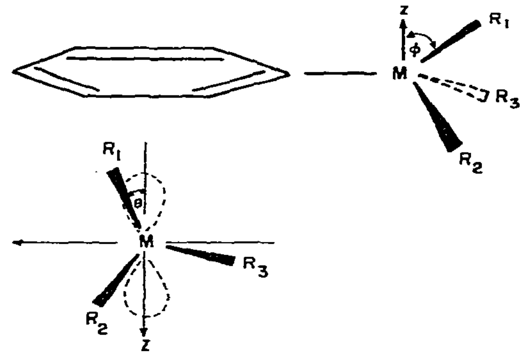

Fig. 1. Conformation of MR_3 group relative to benzenoid π- and σ-systems.

$$\psi_x(A_1) = \sqrt{\tfrac{1}{3}}\cdot[\sigma(MR_1)+\sigma(MR_2)+\sigma(MR_3)]$$

$$\psi_y(E) = \sqrt{\tfrac{2}{3}}\cdot[\sin\theta\cdot\sigma(MR_1)+\sin(\theta+2\pi/3)\cdot\sigma(MR_2)+\sin(\theta+4\pi/3)\cdot\sigma(MR_3)]$$

$$\psi_z(E) = \sqrt{\tfrac{2}{3}}\cdot[\cos\theta\cdot\sigma(MR_1)+\cos(\theta+2\pi/3)\cdot\sigma(MR_2)+\cos(\theta+4\pi/3)\cdot\sigma(MR_3)]$$

Since the wave function $\psi_z(E)$ has the correct symmetry to interact with any of the $p_z-\pi$ wave functions of the benzene ring, linear combinations may be derived, *e.g.*, $C_1\cdot\psi_\pi+C_2\cdot\psi_\sigma$ and $C_2\cdot\psi_\pi-C_1\cdot\psi_\sigma$, which now have both σ and π character. Similarly, the $\psi_x(A_1)$ and $\psi_y(E)$ wave functions of the MR_3 group have the requisite symmetry to mix with the x and y components of the benzenoid σ system, leading to what may

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* For Pictorial representations, see ref. 14.

be termed σ–σ conjugation. As each σ(MR) bond has components of both σ and π symmetry, the σ–π and σ–σ interactions in $C_6H_5MR_3$ are not independent, and the MR_3 group serves to interconnect the originally orthogonal benzenoid σ and π MO's. Strictly speaking, an all valence electron SCF–MO calculation is therefore necessary to determine the importance of σ–π or σ–σ mixing in any given molecule. However, for the purpose of understanding how the magnitude of σ–π interaction may vary with molecules structure it is more instructive[15] to use perturbational MO theory.

When a σ-bonded group MR_3 is connected to a π-electron system, the perturbed wave functions ψ', energies, and charge distributions, which result from mixing a σ and π MO may be derived from the secular determinant (1)[16]:

$$\begin{vmatrix} E(\pi_i)-S_{ii}E & P(\pi_i\sigma_j)-S_{ij}E \\ P(\pi_i\sigma_j)-S_{ij}E & E(\sigma_j)-E \end{vmatrix} = 0 \tag{1}$$

where $P(\sigma_i\pi_j)$ is the perturbation operator $\psi(\pi_i)\,P\,\psi(\sigma_j)\,d\tau$, and $E(\pi_i)$ and $E(\pi_j)$ are the energies of the unperturbed ith and jth MO's of the π and σ systems, respectively. Following the common practice of neglecting differential overlap, the perturbation of the energy δE resulting from σ–π mixing is then given by

$$\delta E(\sigma_j) = -\delta E(\pi_i) = \pm \sum_{i\text{ or }j} [(4P^2(\pi_i\sigma_j)+\Delta E_{ij}^2)^{\frac{1}{2}} - \Delta E_{ij}]/2 \tag{2}$$

where ΔE_{ij} is the energy separation $E(\pi_i)-E(\sigma_j)$. When the orbitals are degenerate δE is equal to P; at the other extreme, when ΔE is large relative to P, the relationship is approximated by

$$\delta E = \pm P^2/\Delta E_{ij} \tag{3}$$

From (1) and (2), the perturbed wave functions ψ' which result from σ–π mixing are

$$\psi'_{\pi i} = (1+\gamma^2)^{-\frac{1}{2}}\cdot(\psi_{\pi i} - \gamma\cdot\psi_{\sigma i}) \tag{4}$$
$$\psi'_{\sigma j} = (1+\gamma^2)^{-\frac{1}{2}}\cdot(\psi_{\sigma j} + \gamma\cdot\psi_{\pi i})$$

where γ is $\Sigma_{i\text{ or }j}\{[(4P^2(\pi_i\sigma_j)+\Delta E_{ij}^2)^{\frac{1}{2}} - \Delta E_{ij}]/2P(\pi_i\sigma_j)\}$. In the case where the orbitals are degenerate γ becomes unity, while when ΔE is large γ may be approximated by $P(\pi_i\sigma_j)/\Delta E_{ij}$.

If the wave functions of the σ and π-MO's are expressed as linear combinations of atomic orbitals, *i.e.* $\psi_i = \Sigma_i(a_{ix}\cdot\phi_x)$, where a_{ix} is the coefficient of the xth atomic orbital in the ith MO, then the perturbation operator becomes

$$P(\pi_i\sigma_j) = a_{\pi i}\cdot a_{\sigma j}\cdot P \tag{5}$$

Since only the p_z orbital of the atom M has the correct symmetry to mix with the p_z–π orbital framework, $a(\sigma_j)$ is the p_z orbital coefficient of M in the $\sigma(MR_3)$ MO, $a(\pi_i)$ is the p_z orbital coefficient of the adjacent π-carbon atom, and P is the perturbation integral of the $C(p_z)$–$M(p_z)$ bond. Combining eqns. (3) and (5) leads to

$$\delta E = \pm(a^2(\pi_i)\cdot a^2(\sigma_j)\cdot P^2)/\Delta E_{ij} \tag{6}$$

Since the value a^2 corresponds to electron density, the perturbation is proportional to the electron density in the connecting p_z atomic orbitals, and inversely proportional to the energy separation of the σ and π-MO's.

$(p\text{–}d)\pi$ conjugation

Although generally treated as an independent electronic effect, $(p\text{–}d)\pi$ conjugation cannot *a priori* be separated from $\sigma\text{–}\pi$ conjugation. This is because the availability of d orbitals in the valence set of M will result in their mixing into the $\sigma(MR_3)$ orbitals, to an extent which is determined by their energy match. This mixing of $\sigma(sp)$ and d orbitals, *i.e.* $\psi'(\sigma_j) = a(\sigma_j)\cdot\psi(\sigma_j) + a_d\cdot\phi_d$, will modify the charge distribution and energy of the σ orbitals, and hence the magnitude of $\sigma\text{–}\pi$ interaction, and eqn. (6) becomes

$$\Delta E = a^2(\pi_i)\cdot(a^2(\sigma_j)\cdot P^2 + a_{dj}^2\cdot P_d^2)/\Delta E_{ij} \tag{7}$$

where P_d is the perturbation integral of the $C(p_z)\text{–}M(d_{xz})$ bond. The question of whether one is dealing with $\sigma\text{–}\pi$ or $d\text{–}\pi$ conjugation then depends on the relative importance of the respective $a^2\cdot P^2$ terms. CNDO/2 calculations (*vide infra*) indicate that when M is silicon the atomic orbital in the highest occupied σ-MO is primarily p, while the lowest unoccupied MO is a mixture of p and d atomic orbitals.

Inductive and field effects

To a first approximation the change in energy (δE) of the ith MO which results from a modification in the coulomb integral ($d\alpha$) of any atomic orbital r is given by

$$\delta E_i = 2\Sigma_r(a_{ir}^2\cdot d\alpha_r) \tag{8}$$

Since it is the total electron distribution in the molecule which determines the effective potential of an atomic orbital, $d\alpha$ will be influenced by both the π and σ electron distributions, and eqn. (8) may be partitioned into σ-inductive and π-inductive terms:

$$\delta E_i = 2\Sigma_r a_{ir}^2[\delta\alpha_r(\sigma) + \delta\alpha_r(\pi)] \tag{8a}$$

In the CNDO/2 method[17], $\delta\alpha_r(\pi) = 0.5\ \delta q_r\gamma_{rr} + \Sigma_s\delta q_s\gamma_{rs}$, where γ_{rr} and γ_{rs} are the one and two center repulsion integrals of the p_π atomic orbitals r and s, and δq is the electron density change.

VARIATION OF CONJUGATION WITH MOLECULAR STRUCTURE

The above equations provide a means of estimating how changes in molecular structure will affect the magnitude of $\sigma\text{–}\pi$ and $d\text{–}\pi$ conjugation and, in turn, the various electronic properties which are influenced by these electronic interactions. Strictly speaking these equations should be summed over all occupied and unoccupied MO's. However, the magnitude of perturbation is inversely proportional to the energy separation of the orbitals, and so it is generally sufficient to limit consideration to the highest occupied and lowest unoccupied MO's of the σ and π systems (hereafter abbreviated to σ,π and σ_{-1},π_{-1}, respectively).

Estimation of ΔE

On the basis of Koopmans' theorem[18], the values of $E(\pi)$ and $E(\sigma)$ may be estimated from the ionization potentials (IP's) of suitable model compounds. For example, the π-IP of benzene together with the appropriate* σ-IP's of $H\text{–}SiH_3$ and $H\text{–}CH_2SiH_3$ may be used to estimate the relative $\sigma\text{–}\pi$ energy separations in the

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* The IP of the σ orbital involved in the conjugation.

TABLE 1

VERTICAL IONIZATION POTENTIALS (eV) OF σ(MR) ORBITALS IN VARIOUS GROUP IV SERIES

	M–H[a]	M–C[b]	M–M[c]	M–P[d]	M–S[e]
C	14.1	11.2	11.2	12.4	15.1
Si	12.6	10.6	8.7	11.6	12.5
Ge	12.2	10.2	7.8	11.4	12.5
Sn		9.7	7.4		

[a] Average of Jahn–Teller split maxima of MH_4, ref. 85. [b] Values for $M(CH_3)_4$, ref. 86; corresponding values[63] for CH_3CH_3 and CH_3SiH_3 are 11.7 and 10.7 eV, respectively. [c] Values for $M_2(CH_3)_6$, refs. 87 and 88. [d] Values for MH_3PH_2, ref. 89. [e] Values for MH_3SH, ref. 90.

molecules C_6H_5–SiH_3 and C_6H_5–CH_2SiH_3, respectively, prior to mixing the σ and π orbitals. Table 1 lists the σ-IP's of a number of Group IV compounds. The values range from 15 eV to 7 eV and show the expected decrease as the Group is descended, although few reliable data on tin compounds are yet available. When these values are compared with the IP's of typical π-hydrocarbons, *e.g.*, acetylene (11.4 eV), ethylene (10.5 eV), benzene (9.25 eV), and naphthalene (8.12 eV), it is apparent that σ–π conjugation with Si, Ge, and Sn groups is not restricted by any large σ–π separation. In contrast to organic molecules, where $E(\sigma) \gg E(\pi)$, the separation *and* the ordering of the σ and π levels in Si, Ge and Sn compounds will vary considerably. Pentamethyldisilanylbenzene is one example where the highest occupied MO has been shown experimentally to have both σ and π character, with the former dominant[5].

The estimation of $E(\pi_{-1})$ and $E(\sigma_{-1})$ is less easily accomplished, although on the basis of the relative energies of electronic transitions, $E(\sigma\rightarrow\sigma^*) > E(\sigma\rightarrow\pi^*) > E(\pi\rightarrow\pi^*)$, in most Main Group organometallics[19], and the lower reduction potentials of π-electron systems, it appears that σ_{-1} levels generally lie above π_{-1} levels. Most theoretical and experimental estimates place the π_{-1} MO's of organic molecules above -3 eV, although exceptional stabilization is observed in some cases, *e.g.*, tetracyanoethylene, where $E(\pi_{-1}) \approx -6$ eV[20].

There is similarly little direct experimental information on the energy of *d*-orbitals. Estimates based on SCF calculations and *atomic* promotional energies place the energies of Si, P, S, and Cl at ca. -2 eV[21–24]. The Si (3*d*) atomic orbitals have been estimated to lie 0.8 eV[25] and 3.3 eV[23] above the π_{-1} orbitals of ethylene and acetone, respectively. Keeping in mind the fact that the energy and size of *d* orbitals are believed to be critically dependent on the charge of the atom (see *e.g.* refs. 21–24, 26), reduction potentials and ESR spectra indicate that the 3*d* orbitals of Si, Ge, and Sn lie above the π_{-1} levels of naphthalene[27], benzene[27–29] and butadiene[30,31].

Estimation of the perturbation integral $P(\sigma\pi)$

In semi-empirical MO theory[32] the one electron Hamiltonian $H_{\mu\nu}$ is taken as the sum of the kinetic energy and the potential energy terms associated with the atomic orbitals μ and ν alone, *i.e.*, $H_{\mu\nu} = \int \phi_\mu \cdot (\frac{1}{2}\nabla^2 + V_\mu + V_\nu) \cdot \phi_\nu$, and both $1/2\ \nabla^2$ and $V_\mu + V_\nu$ are estimated from their proportionality[33,34] to the average of the valence state ionization potentials[35–37], $(I_\mu + I_\nu)/2$, and to the overlap integrals of the two atomic orbitals.

TABLE 2

RELATIVE VSIP's, OVERLAP (S)[a], PERTURBATION (P), AND REPULSION (γ)[b] INTEGRALS FOR VARIOUS C–M [$p(\pi)$] BONDS[c]

	Be	*Mg*	*B*	*Al*	*C*	*Si*	*Ge*	*Sn*	*N*	*P*	*As*	*Sb*	*O*	*S*	*Se*	*Te*
$\frac{I(\mathrm{C})+I(\mathrm{M})}{2}$	0.76	0.70	0.87	0.79	1.0	0.91	0.92	0.87	1.12	0.98	0.91	0.89	1.27	1.05	1.02	0.99
S	1.29	0.96	1.18	1.02	1.0	0.99	0.92	0.82	0.81	0.92	0.86	0.77	0.67	0.83	0.80	0.71
P	0.98	0.68	1.03	0.81	1.0	0.90	0.85	0.71	0.91	0.89	0.79	0.68	0.85	0.87	0.81	0.70
γ	0.87	0.72	0.94	0.77	1.0	0.81	(0.85)	(0.71)	1.05	0.84	(0.79)	(0.68)	1.10	0.87	(0.81)	(0.70)

[a] Calcd. assuming interatomic distance (Å) of 1.63 (Be), 1.55 (B), 1.50 (C), 1.47 (N), 1.43 (O), 2.03 (Mg), 1.91 (Al), 1.84 (Si), 1.79 (P), 1.75 (S), 1.95 (Ge), 1.92 (As), 1.89 (Se), 2.14 (Sn), 2.11 (Sb), 2.08 (Te). [b] Calcd. from one center p orbital repulsion integrals[24] using the Ohno relationship[91]; values in parentheses calcd. from weighted average of s,p repulsion integrals[35–37]. [c] Non-normalized values of C–C bond are: I(C), 11.27 eV; S, 0.21; γ, 7.03 eV.

Trends in $P(\sigma\pi)$ may be approximated by assuming the same relationship, *i.e.*

$$P(\sigma\pi) = -K \cdot S(\sigma\pi) \cdot [I(\sigma)+I(\pi)]/2 \qquad (9)$$

where $I(\sigma)$ and $I(\pi)$ now refer to the atomic p_z orbitals which connect the σ and π systems and K is a proportionality constant. The values of $P(\sigma\pi)$ for a series of C(p_z)–M(p_z) bonds, determined from (9) and normalized with respect to the C–C bond, are shown in Table 2. Although the values are somewhat dependent on the choice of bond length, the trend in Table 2 indicates that σ–π mixing is favored when M is a first row element, and decreases as any given Periodic Group is descended (*e.g.*, C > Si > Ge > Sn). However, at most a factor of two is involved, and it does not appear that the variation in P alone should lead to large differences in σ–π mixing.

Expansion of (9) to include electron repulsion terms does not change this generalization. For example, if P takes the form of an off-diagonal element of a Fock matrix with zero differential overlap[17,32], then

$$P(\sigma\pi) = -K \cdot S \cdot [I(\sigma)+I(\pi)]/2 - a(\sigma) \cdot a(\pi) \cdot \gamma(\sigma\pi) \qquad (9)$$

where $\gamma(\sigma\pi)$ is the two centre electron repulsion integral of the C(p_z)–M(p_z) orbitals. Values of $\gamma(\sigma\pi)$ for a series of C–M bonds are shown in Table 2, and here again the values are largest for first row elements and decrease as a given Periodic group is descended. The values of the coefficients $a(\sigma)$ and $a(\pi)$, which tend to reinforce this trend, are discussed below.

The estimation of P for (p–d)π interaction is hampered by uncertainty about values of the valence state IP's of d orbitals and the degree of contraction which d orbitals undergo in molecules[21–24,26]. Assuming the extreme case where the d-orbital exponent is the same as that of the s and p orbitals, the (p–d)π overlap integrals C–Si, C–P and C–S bonds are 0.303, 0.279, and 0.242, respectively. These values, together with the estimated valence state energies (−2 eV), lead to $P(p$–$d)$ values of 0.87, 0.80, and 0.69, respectively, relative to the C(p_z)–C(p_z) value of 1.0. The fact that these values compare favorably with $P(\sigma\pi)$ values is largely due to the overlap term.

Estimation of $a(\pi)$ and $a(\sigma)$

The values $a^2(\pi)$ and $a^2(\sigma)$ correspond to the electron densities in the p orbitals of the connecting atoms in the highest occupied MO's of the σ and π systems *prior* to σ–π interaction. Values of $a(\pi)$ are available from simple Huckel calculations and, for alternate π-hydrocarbons, $a(\pi)=a(\pi_{-1})$. The variation of $a^2(\pi)$ with molecular structure is usually consistent with the intuitive feeling that the magnitude of perturbation of a π system should be inversely proportional to its size, *e.g.*, ethynyl (0.500), vinyl (0.500) > phenyl (0.333) > 1-naphthyl (0.181) > 2-naphthyl (0.069)[38].

Trends in $a^2(\sigma)$ may be estimated intuitively on the basis of the polarity of the σ(M–R) bond and for a given MR_3 group the order M = C > Si > Ge > Sn is predicted. CNDO/2 calculations provide a quantitative assessment, and the calculated values of $a^2(\sigma)$ and $a^2(\sigma_{-1})$ for several alkyl and silyl groups are compared in Table 3. Using an *sp* basis set, the values of $a(\sigma)$ for the $-SiH_2R$ group are of the order of 10–20 % lower than the corresponding $-CH_2R$ group. Importantly, this is reversed when the values of $a(\sigma_{-1})$ are compared, corresponding to the generally observed reversal of ground state charge distribution. This means that, other things being equal, the silyl group will be less effective with respect to σ–π conjugation but more effective in σ_{-1}–π conjugation. Including *d* orbitals in the silicon basis set tends to reinforce this charge distribution pattern, although the charge density becomes partitioned between *p* and *d* orbitals in both the vacant and occupied σ orbitals. Comparison of the values of the coefficients of the *d* and *p* orbitals in both the σ and σ_{-1} orbitals suggests that, contrary to popular opinion, the *p* orbitals rather than the *d* orbitals of silicon are primarily involved in electronic interactions. The *d* orbitals do, however, play a significant role by stabilizing the energy levels of the σ and σ_{-1} orbitals of silyl groups. Because of the energy difference term (ΔE) in eqn. (7) this will, in many cases, lead to decreased σ–π and σ–π_{-1} mixing but increased σ_{-1}–π and σ_{-1}–π_{-1} mixing.

Another predictable feature of these calculations is the apparent decrease in the value of $a(\sigma)$ as the size of the σ group increases (*cf.* CH_3 *vs* C_2H_5 ; SiH_3 *vs* SiH_2CH_3). This will tend to offset any increase in σ–π conjugation which would result from the decrease in the IP of the σ group as its size increases.

TABLE 3

CALCULATED σ ORBITAL ENERGIES AND COEFFICIENTS (a^2, a^2_{-1}) OF METHYL, ETHYL[a], SILYL, METHYLSILYL[a], AND SILYLMETHYL[a] GROUPS

MR_3	*σ orbital*			*σ_{-1} orbital*[b]		
	p_z	*d_{xz}*	*Energy (eV)*[c]	*p_z*	*d_{xz}*	*Energy (eV)*[c]
CH_3	0.50		−15.72	0.50		12.96
SiH_3 (*sp*)	0.40		−11.25	0.60		7.88
SiH_3 (*spd*)	0.28	0.03	−12.24	0.54	0.12	5.97
CH_2CH_3	0.37		−13.56	0.05		10.69
CH_2SiH_3 (*sp*)	0.41		−10.40	0.04, 0.24		5.70, 9.15
CH_2SiH_3 (*spd*)	0.45		−11.14	0.02, 0.05		6.13, 6.65
SiH_2CH_3 (*sp*)	0.31		−10.40	0.02, 0.56		5.70, 9.15
SiH_2CH_3 (*spd*)	0.21	0.02	−11.14	0.05, 0.39	0.01, 0.12	6.13, 6.65

[a] For unsymmetrical groups, MH_2R, the MR bond lies in the *xz* plane (Fig. 1). [b] Values of the second lowest unoccupied MO (σ_{-2}) are included if a^2_{-1} is very small or if $E(\sigma_{-1}) \approx E(\sigma_{-2})$. [c] Energies are corrected by +4 eV.

Conformational requirements

When the σ-MR_n group has an n fold rotational symmetry about the x axis the two $\psi(E)$ MO's are degenerate, and the magnitude of σ–π conjugation is invariant with respect to rotation and the value of the dihedral angle θ (Fig. 1). However, if the MR_n group is not rotationally symmetrical, because of local geometry (*e.g.*, AsH_2) or because of differing R groups (*e.g.*, CH_2SiH_3), then the degeneracy of the $\psi(E)$ MO's is lifted, and conformation dependency will be observed. In the case of the CH_2SiH_3 group, mixing of the p_z–π and $\psi_z(E)$–σ orbitals will be optimum when the contribution of the σ(Si–C) orbital to the $\psi_z(E)$ MO is greatest, because of the more favorable $a(\sigma)$ and $E(\sigma)$ terms associated with this σ bond. This will occur when the $p(\pi)$ and σ(CSi) orbitals are coplanar. When these orbitals are orthogonal only π–$\sigma(CH_2)$ conjugation will occur. Such conformation dependence has already been demonstrated experimentally[2–4,6] for a number of organometallic systems and is most convincing of metallohyperconjugation.

The angle ϕ, defined in Fig. 1, is determined by the local geometry of the atom M. Consequently, although invariant to rotation, it will vary with the particular atom M. For example, σ–π conjugation is impossible when M is a *divalent* Group II element ($\phi = 90°$), but should become increasingly important for Group III elements ($\phi \approx 30°$), Group IV elements ($\phi \approx 20°$), and Group V and VI elements ($\phi = 0$–$10°$), as the M–R bonds assume greater p_z character.

Summarizing, the optimum requirements for hyperconjugation are*:

1. The energies of the σ and π orbitals involved should be similar. This is most likely for σ-MR_n groups when M and/or R are electropositive elements.
2. The perturbation integral, which incorporates overlap, should be large. It is therefore better that the connecting atom M of the σ group be in the first row of a given Periodic Group, although no more than a factor of two appears to be associated with this term if repulsion integrals are ignored.
3. There should be high electron density in the p orbitals of the atoms connecting the π and σ systems. This factor is generally inversely proportional to the size of the σ and π systems. The σ-electron density can be conformationally dependent, and is favored by polar bonds, *i.e.* M^-–R^+ which also have high p character. Interaction involving the σ_{-1} orbitals of the MR_n group is favored by the reverse polarity.

GEMINAL σ–σ AND σ–n CONJUGATION

The preceding perturbational MO model may readily be extended to the analyses of geminal σ–σ and σ–n orbital conjugation. Consider, for example, the purely σ-bonded molecule $R_3MM'R_3$. Starting with the $\psi(A)$ and $\psi(E)$ bonding (or antibonding) MO's of each MR_3 group, linear combinations may be constructed which have σ and π symmetry with respect to the M–M bond, *i.e.*:

$$\begin{aligned}\psi(A)(R_3MM'R_3) &= \psi(A)(R_3M) \pm \psi(A)(R_3M')\\ \psi(E)(R_3MM'R_3) &= \psi(E)(R_3M) \pm \psi(E)(R_3M')\end{aligned} \qquad (11)$$

The $\psi(A)$ MO's have the correct symmetry to mix with the σ(MM) orbitals, while the $\psi(E)$ MO's do not. The electronic properties of the latter will therefore be

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* These requirements correspond closely to the qualitative rules presented by Traylor *et al.*[10].

determined by the pseudo-π conjugation of the formally localized geminal σ(MR) orbitals. σ–n Conjugation will similarly arise when one of the σ(MR) orbitals is replaced by a lone pair (n) orbital. As described for σ–π systems, strong geminal σ–σ or σ–n conjugation will be favored by (*a*) comparable MO energies, (*b*) a large perturbation integral, and (*c*) polar bonds which result in high electron density in the p orbitals of the connecting atoms.

Linear combinations of the localized σ and σ_{-1} orbitals, or σ_{-1} and σ_{-1} orbitals, of the MR_3 group may similarly be constructed and correspond to σ–σ_{-1} and σ_{-1}–σ_{-1} conjugation, respectively. The latter will be favored by the reverse bond polarity, $M^{\delta+}$–$R^{\delta-}$, which will tend to increase the orbital coefficients in σ_{-1} orbitals, while σ_{-1}–σ conjugation will be favored by alternating polarity, *i.e.* $R^{\delta+}$–$M^{\delta-}$–$M^{\delta+}$–$R^{\delta-}$.

σ–π CONJUGATION AND EXPERIMENTAL PROPERTIES

A. π-Hydrocarbon derivatives

Much of the recent effort to understand the origin of the differences and trends in the electronic properties of Group IV compounds has centered on the measurement of ionization and reduction potentials, electronic spectra, charge distribution, and Hammett type reactivity constants (for reviews, see refs. 39 and 40). Table 4 summarizes these experimental properties for a series of aryl ($ArMR_3$) and arylmethyl ($ArCH_2MR_3$) derivatives, where the aryl group is phenyl and 1-naphthyl. Though the conformational dependence of these electronic properties has already established[2–4,6] the role of hyperconjugation in the $ArCH_2MR_3$ series, it is of interest to analyze the observed trends in terms of the preceding perturbation treatment. The analysis will then be extended to the properties of the $ArMR_3$ series, where the role of σ–π conjugation is less well defined.

TABLE 4

IONIZATION AND REDUCTION POTENTIALS, ELECTRONIC SPECTRA, HAMMETT σ^+ CONSTANTS AND ^{19}F SUBSTITUENT CHEMICAL SHIFTS OF 1-NAPHTHYL- AND PHENYL-SUBSTITUTED GROUP IV COMPOUNDS

R	*Ionization potential (eV)*		*^1L_a Transition (nm)*		*$E_{\frac{1}{2}}$(eV)* *1-$C_{10}H_7R$*[c]	*σ^+ constant*[e]	*^{19}F-SCF (ppm)*[g]
	C_6H_5R[a]	*1-$C_{10}H_7R$*[c]	*C_6H_5R*[d]	*1-$C_{10}H_7R$*[c]			
H	9.25	8.12	195	274.9	−2.946	0	0
CH_3	8.73	7.98	200	281.3	−2.964	−0.31	+5.48
CMe_3	8.64		208	280	−3.002	−0.26	+5.60
SiH_3	9.25[b]	8.12		283.0	unstable		−2.60
$SiMe_3$	8.79	8.03	211	281.6	−2.845	+0.02	−0.50
$GeMe_3$	≈8.75	8.00	208	281.2	−2.882		+0.55
$SnMe_3$	≈8.75	7.99	209	281.5	−2.881		+0.20
CH_2SiMe_3	8.27	7.83	221	290.5	−3.006	−0.54[f]	+7.05
CH_2GeMe_3	8.19	7.78	225	294.7	−3.013		+7.05
CH_2SnMe_3	7.91	≈7.6	236	300.0	unstable		+7.75

[a] Calculated from TCNE transfer spectra[3,4,47] using the relationship $h\nu = 0.82\ IP - 4.28$ (ref. 92). [b] Photoelectron value. [c] Refs. 27 and 93. [d] Ref. 19. [e] Ref. 94. [f] Ref. 95. [g] Ref. 96.

π-Ionization potentials and reduction potentials. Based on Koopmans' theorem[18] the IP's of the phenyl and naphthyl derivatives may be equated with the negative of the energy of the highest occupied (π) MO. Polarographic reduction on the other hand involves addition of an electron to the lowest unoccupied (π_{-1}) MO and, for a series of similar compounds where diffusion and solvation energy differences may be neglected, the half-wave reduction potential ($E_{\frac{1}{2}}$) is a measure of the relative energy of the π_{-1} level[41-44]. Eqn. (7) may, therefore, be used directly to relate the structural features of the σ group to the magnitude of hyperconjugative perturbation of the IP and $E_{\frac{1}{2}}$ of the π system, depicted qualitatively in the familiar MO diagram (Fig. 2).

Considering first the $ArCH_2MR_3$ series, the P, $a(\pi)$ and $E(\pi)$ terms are properties of the $ArCH_2$ part of the molecule and will remain constant for a given aryl group. Both the increase in $a(\sigma)$ associated with the increasing polarity of the $C^{\delta-}-M^{\delta+}$ bond and the decrease in the ΔE term as M changes from carbon to tin, predict a perturbation of the π-IP in the order $Sn > Ge > Si > C$, which is in agreement with the experimental facts. The decreases in $a(\pi)$ (0.42 *vs.* 0.58) and $E(\pi)$ (8.12 eV *vs.* 9.25 eV) for naphthalene, compared to benzene, also account for the smaller perturbations observed in the 1-napthyl series relative to the phenyl series. The role of σ_{-1}–π conjugation, which operates to increase the π-IP could also be considered but, because of the relatively large $E(\pi)-E(\sigma_{-1})$ term and the probably small $a(\sigma_{-1})$ term (*cf.* Table 3), it is likely to be minor in this series. This conclusion is supported by the trend in $E_{\frac{1}{2}}$. Here σ_{-1}–π_{-1} conjugation (stabilizing) might be expected to dominate σ–π_{-1} conjugation (destabilizing) because of the more favorable ΔE term. The experimental result is *slight* destabilization of $E(\pi_{-1})$, in the order $Me_3GeCH_2 > Me_3SiCH_2 > CH_3$, meaning that σ_{-1}–π_{-1} mixing is unable to offset the destabilizing influence of the σ–π_{-1} effect.

Although the trend in the IP and $E_{\frac{1}{2}}$ is correctly predicted by the inductive sequence in the CH_2MR_3 series, conformation experiments[3,4] have shown that hyperconjugation is much more important. Estimation of the inductive effect using eqn. (8), where the $d\alpha$ terms are derived from the diagonal elements of the CNDO/2 Hartree–Fock matrix, also indicates only a small inductive effect, even when the silicon is alfa to the π system. For example, in the case of methyl, silyl, and silylmethyl ethylene, the change in the π-IP which results from the σ-inductive effect is calculated to be*: CH_3 (+0.44 eV), SiH_3 (−0.33 eV) and CH_2SiH_3 (+0.87 eV); that resulting from the π-inductive effect is CH_3 (−0.27 eV), SiH_3 (+0.19 eV), and CH_2SiH_3 (−0.72 eV).

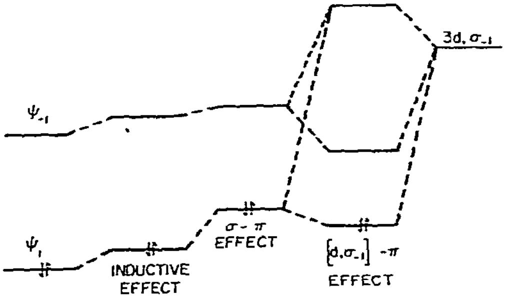

Fig. 2. Perturbation of ψ_1 and ψ_{-1} orbitals of a π-hydrocarbon by a Group IV substituent.

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* +eV *indicates an increase in the IP.*

TABLE 5

CALCULATED AND EXPERIMENTAL[a] IONIZATION POTENTIALS (eV) OF METHYL, SILYL, AND SILYLMETHYL ETHYLENE, BENZENE, AND 1-NAPHTHALENE

	H	SiH_3	CH_3	CH_2SiMe_3
CH_2CH-	(10.5)	10.1 (10.4)	10.0 (10.0)	9.2 (9.1)
C_6H_5-	(9.25)	9.06 (9.25)	9.0 (8.99)	8.6 (8.35)
$C_{10}H_8-$	(8.12)	8.05 (8.12)	7.98 (8.00)	7.87 (7.83)

[a] Experimental values in parentheses.

The σ and π systems apparently act in concert to produce electroneutrality and the sum inductive effect is small, *i.e.* SiH_3 (−0.14 eV)[*] > H > CH_2SiH_3 (+0.15 eV) > CH_3 (+0.17 eV). The inductive effects are calculated to be even smaller in larger π-hydrocarbons.

The experimental trend shown by the Ar–MR_3 series provides a dramatic contrast to the $ArCH_2MR_3$ series, the change in the π-IP being much smaller and in the order $CMe_3 > CH_3 > SnMe_3 > GeMe_3 > SiMe_3 > SiH_3 \approx H$. The fact that even the electropositive $SnMe_3$ group is less effective than the methyl group is particularly striking. As with the $GeMe_3$ and $SiMe_3$ groups, this result might be attributed to partial negation of the inductive effect by a combination of σ_{-1}–π and d–π conjugation. Yet PMO considerations suggest that (lack of) σ–π conjugation is also important. Thus, although the $E(\pi)-E(\sigma)$ term for this series still decreases in the order C > Si > Ge > Sn, the $a(\sigma)$ and P terms will now also decrease in this order. Consequently the magnitude of σ–π splitting is the resultant of two opposing trends and, if the inductive effects are minimal, there is no good reason to expect much variation in this series. Simple calculations serve to demonstrate this point. Consider, for example, the change in the π-IP of ethylene brought about by methylation and silylation. If the decrease of 0.5 eV resulting from methylation is assumed to be solely the result of σ–π interaction, the P(C–C) integral is calculated from eqn. (2) to be 2.84 eV. Using the values of $a(\pi)$, $a(\sigma)$, $E(\sigma)$, and P(Si–C) from Tables 1–3, the calculated change in the IP resulting from silyl hyperconjugation is 0.4 eV, *i.e.* less than for methyl hyperconjugation. As expected, the calculated ΔIP for the CH_2SiMe_3 group is much larger (1.4 eV) and in good agreement with the experimental value[9]. The calculated values for the 1-napthyl and phenyl analogs, also calculated assuming P(C–C) = 2.84 eV, show the same reasonable agreement with experiment (Table 5).

These conclusions about the magnitude of σ–π interaction do not negate the role of $[d, \sigma_{-1}]$–π interaction in determining the trend in IP's, rather they suggest complementary roles.

The destabilization of $E(\pi_{-1})$ *i.e.*, $E_{\frac{1}{2}}$, by alkyl groups but stabilization by silyl, germyl and stannyl groups must be interpreted similarly, but here the better energy match of the π_{-1} and $[\sigma_{-1}, d]$ orbitals produces an even more favorable interaction. Although stabilization of $E_{\frac{1}{2}}$ by silyl groups has long been cited as evidence of d-orbital participation[28–31,45,46], it would appear that the availability of low lying σ_{-1} orbitals is also important.

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[*] Using a *spd* basis set the values for the SiH_3 group are $I(\sigma)$ (−2.65 eV), $I(\pi)$ (+2.69 eV), $I(\pi+\sigma)$ (+0.04 eV). This illustrates the second mechanism by which d orbitals may increase IP's, namely by a $p(\pi) \rightarrow d$ inductive mechanism.

Electronic spectra. The ^1L_a band of benzene and naphthalene is derived from an electronic transition from the highest occupied to lowest occupied π MO, *i.e.* $\pi^2 \rightarrow \pi \cdot \pi_{-1}$. If singlet–triplet splitting is comparable, and if there is no configurational interaction with substituent transitions, then the ability of a series of σ substituents to perturb the ^1L_a band may be assumed[19,41–44] to be related to their ability to perturb the $E(\pi)$ and $E(\pi_{-1})$ levels are discussed above. Comparison of the trends in $E(\pi)$ and $E(\pi_{-1})$ with the trend in the ^1L_a transition for the MR_3 and CH_2MR_3 groups (Table 4) qualitatively justified these assumptions; the larger shifts of the ^1L_a band in the CH_2MR_3 series may be attributed to destabilization of $E(\pi)$ by σ–π splitting, while the smaller shifts in the MR_3 series are derived from less effective σ–π perturbation of $E(\pi)$ coupled with d, σ_{-1} stabilization of $E(\pi_{-1})$.

Some caution must be exercised in interpreting large shifts in electronic transitions as evidence of strong hyperconjugative interaction because σ, σ_{-1}, and d levels in certain organometallics may lie between the π and π_{-1} levels, resulting in *new* $\sigma \rightarrow \pi_{-1}$ or $\pi \rightarrow \sigma_{-1}$ transitions at unusually long wavelengths[19]. This has been shown[27] to be the case for the anomalously long wavelength absorption of phenyl polysilanes and other Group IV catenates, which is related more to the ordering of the σ and π levels than the magnitude of σ–π splitting.

Charge distribution. The effect of a σ substituent on the π-electron distribution of a π hydrocarbon may be partitioned into (*a*) the redistribution of electron density *within* the π system and (*b*) the transfer of electronic charge *between* the σ substituent and the π systems. The former arises as a result of the σ-inductive and field effects, which lead to a modification of the core potentials experienced by the $p(\pi)$ atomic orbitals, coupled with a minimization of electron-electron repulsions.

The second factor, the transfer of charge between the σ substituent and the π system, depends critically on the occupancy of the molecular orbitals involved[13]. If both MO's are doubly occupied, then mixing will lead to a redistribution of charge within each of two linear combinations, *i.e.* $\psi_\sigma + \psi_\pi$ and $\psi_\sigma - \psi_\pi$, but the net charge transfer will be zero. This follows from summation of the σ and π coefficients of eqn. (4). Only when one of the MO's is empty or singly occupied will there be any transfer of charge. The magnitude and direction of charge in a σ-substituted π-hydrocarbon will therefore depend on the relative importance of σ–π_{-1} *vs.* $[\sigma_{-1}, d]$–π interaction (see, however, ref. 13, pp. 31–40, for some limitations to this statement). From eqn. (4), with $\gamma = P/\Delta E$, the charge transfer is given by

$$\delta q = -P^2(\pi\sigma_{-1})/[P^2(\pi\sigma_{-1}) + \Delta E^2(\pi\sigma_{-1})] - P^2(\pi d)/[P^2(\pi d) + \Delta E^2(\pi d)] + \\ + P^2(\sigma\pi_{-1})/[P^2(\sigma\pi_{-1}) + \Delta E^2(\sigma\pi_{-1})] \qquad (12)$$

On the basis of the trends in P and ΔE, electron transfer is expected to be toward the π system in the case of CH_2MR_3 σ groups (3rd term dominant), but away from the π system for MR_3 groups (1st, 2nd terms dominant).

Unfortunately experimental measurements of charge distribution do not differentiate between charge redistribution *vs.* charge transfer. For example, the ^{19}F chemical shift data listed in Table 4 relate only to the electron density in the carbon $p(\pi)$ atomic orbital bonded to the fluorine atom; measurement of the density at all positions is necessary to determine whether the redistribution or the transfer mechanism predominates. CNDO/2 calculations (Table 6) of the π-charge distribution of a series of acetylenes suggest there is considerable variation depending on the substi-

TABLE 6

π-ELECTRON CHARGE DISTRIBUTION (q) AND CHARGE TRANSFER (δq_{CT}) OF VARIOUS SUBSTITUTED ACETYLENES, $R{-}C_\alpha{\equiv}C_\beta{-}H$

R	BH_3^-	CH_2SiH_3 (sp)	CH_3	SiH_3 (sp)	SiH_3 (spd)	CF_3	SiF_3 (sp)	SiF_3 (spd)	NH_3^+
q_α	0.911	0.965	0.985	1.001	0.984	1.026	1.034	1.000	1.070
q_β	1.104	1.076	1.033	0.993	0.898	0.967	0.950	0.911	0.942
δq_{CT}[a]	0.015	0.041	0.018	−0.006	−0.118	−0.007	−0.016	−0.089	0.012

[a] $\delta q_{CT} = (q_\alpha + q_\beta) - 2.000$; values of other substituents are $R = Me_2N$ (0.071); HO (0.064); F (0.048); NO_2 (−0.014); CHO (−0.031); BF_2 (−0.098)[54].

tuent. Groups which bear a formal charge ($-NH_3^+$, $-BH_3^-$) or strongly electronegative substituents (CF_3) interact by a redistribution mechanism, while both charge redistribution and (σ–π_{-1}) transfer operate in the case of the CH_3 and CH_2SiH_3 substituents. The calculations indicate that the SiH_3 group is weakly electron withdrawing by π–σ_{-1} charge transfer even if *d* orbitals are omitted from the basis set; inclusion of *d* orbitals in the basis set results in a much greater electron transfer, primarily from the β carbon atom. The calculated charge distribution for the SiF_3 group is less dependent on the basis set employed, apparently because the *d* orbitals accept more charge from the fluorine *n* orbitals than from the π-orbitals.

Electrophilic substitution and cation stabilization. The electronic stabilization derived from σ–π conjugation is critically dependent on the occupancy of the orbitals involved. Using either eqn. (2) or (3), it would follow that when both orbitals are doubly occupied the net stabilization is zero, while if one of the orbitals is singly occupied or empty the stabilization is δE and 2 δE, respectively. However, these equations were derived neglecting differential overlap, and if overlap terms are included, the energy perturbation takes the form[16]:

$$\delta E_j = (P - S_{ij} \cdot E_j)^2 / \Delta E_{ij} \tag{13}$$

The orbitals, therefore, do not split equally about their center of gravity, the higher orbital being destabilized to an extra extent. This difference is not particularly serious in correlating trends in experimental properties which depend on a single energy level, *e.g.* IP's, $E_{\frac{1}{2}}$'s, but cannot be neglected otherwise. Thus mixing of doubly occupied σ and π is predicted to lead to a small net destabilization of the molecule when eqn. (13) is employed. When one of the orbitals is singly occupied, the extent of stabilization is ambiguous, depending on the values of the *P*, *S*, and *E* terms. Only when the sum orbital occupancy is 2 or 1 can net stabilization be confidently predicted.

Since a cation is an example of a vacant MO (π_0), mixing with an occupied σ MO will result in net electronic stabilization. The variation of the magnitude of this stabilization with the structure of the σ group and the cation can be expected to follow the same pattern discussed for σ–π interaction, the only difference being the terms associated with the π_0 MO. Stabilization by a Me_3MCH_2 ($M = Sn > Ge > Si > C$) group will, therefore, be greater than that associated with a Me_3M ($M = C \approx Sn \approx Ge \approx Si \approx H$). Transfer of σ electron density to the cationic MO will follow the same order.

As others have recently pointed out[2,4,47–50] this stabilization sequence explains a number of experimental observations, including the rate and the orientation of electrophilic attack at Group IV substituted π-hydrocarbons and the ease of electrophilic cleavage of aryl–metal bonds and the slow S_N1 solvolysis of Me_3SiCMe_2Br relative to a carbon analog. CNDO/2 calculations are consistent with these conclusions, the extent of electron transfer to the formally vacant $p(\pi)$ orbital of the carbenium ion RCH_2^+ being in the order $R=CH_2SiH_3$ (*spd*), 0.423 $>CH_2SiH_3$ (*sp*), 0.415 $> CH_3CH_2$, 0.220 $> CH_3$, 0.201 $> SiH_3$ (*sp*), 0.121 $> SiH_3$ (*spd*), 0.073 $>$ H, 0.0.

Traylor and coworkers[4,10] have found that the ability of a σ (or lone pair) group to stabilize carbonium ions and facilitate electrophilic aromatic substitution is linearly related to the ability of the group to perturb the π IP. This is surprising because the IP reflects the perturbation of only the highest occupied π MO and is not obviously related to electrophilic reactivity, which is a measure of the energy perturbation of all occupied σ and π MO's. The origin of this correlation is explored in an appendix.

σ–π_0 conjugation should similarly influence the properties of Group II and III Lewis acids, and transition metals derivatives with vacant *d* orbitals, although this has yet to be demonstrated experimentally. While the *trans* effect in the d^8 complexes, *cis*-$[(Ph_3P)_2Pt\,R_2]$ and *trans*-$[(Ph_3P)_2Pt\,ClR]$, has been shown[51] to differ little when $R=Me$, CH_2Ph, or CH_2SiMe_3 and to be much larger when $R=H$ or $SiMePh_2$, this would appear to be a reflection of σ–σ rather than $(\sigma \rightarrow d)\pi$ effects. Comparison of carbonyl force constants (*k*) in compounds such as $R_3MCH_2Co(CO_4)$, $M=C$ to Pb, may provide an estimate of synergic interaction of the σ(CM) and π(C≡O) orbitals, although previous studies[52] on $R_3MCo(CO_4)_4$, $M=C$, Si, shown the value k_a–k_e is relatively insensitive to the nature of R. The greatest effect of $(\sigma$–$d)\pi$ charge transfer and stabilization should be observed to the left of the transition series, where *d*-orbital occupancy is incomplete.

Of the main groups elements, boron is most likely to participate in σ–π_0 conjugation (favorable *P* and E_π terms). The exceptional air stability of $B(CH_2SiMe_3)$ may in part be a reflection of this. CNDO/2 calculations on the model compounds $Me_3SiCH_2BX_2$ indicate the electron population of the boron p_π orbital varies with its dihedral angle θ to the Si–C bond as follows: $X=H$, 0.2516 ($\theta=0°$), 0.1465 ($\theta=90°$); $X=F$, 0.4420 ($\theta=0°$), 0.4070 ($\theta=90°$). The difference between the two conformations reflects the relative contributions of π_0–σ(C–Si) *vs.* π_0–σ(C–H) conjugation, and is smaller when $X=F$ because of competing $p(F) \rightarrow p(B)$ conjugation.

The calculated B–C rotational barriers in these model compounds are 22 kcal ($X=H$) and 13 kcal ($X=F$). The values must be too large because no effort was made to optimize geometries*. A single experimental attempt to observe restricted B–C rotation in $MeB(CH_2SiMe_3)_3$, based on the NMR non-equivalence of the methylene protons, was unsuccessful; no line broadening was observed at $-100°$. Assuming that the resolution of the two protons is $\geqslant 5$ Hz in the preferred conformation, the estimated[56] rotational energy barrier is < 9 kcal. The B–O rotational barrier in

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* It is also well known[32,53] that the CNDO/2 method leads to heats of atomization and IP's which are too large, partly because of its use of theoretical repulsion integrals[36,37]. Its greatest success appears to be in the calculation of charge distribution (see, for example refs. 54 and 55). Because of the uncertainty in some of the parameters for second row elements[21], the calculations reported here for silicon compounds might better be regarded as reflecting the electronic properties of "a Group IV element of a higher row than that of carbon."

$(Me_2B)_2O$, resulting from $n \rightarrow \pi(B)$ conjugation, is 8.6 kcal[57].

σ–π conjugation may influence rotational barriers in other subtle ways. For example, the B–N rotational barrier in R_2B–$NHMH_3$ (M = Si, Ge, Sn) can be expected to be smaller than when M = C because of both destabilization of the planar conformation by reduction of $n(N) \rightarrow \pi(B)$ conjugation (due to competing $n(N) \rightarrow \sigma_{-1}$, $d(M)$ conjugation), and stabilization of the non-planar conformation by more effective $\sigma(N\text{–}M) \rightarrow \pi(B)$ conjugation.

C. Radicals

Evaluating the role which hyperconjugation plays in determining the stability of radicals is problematical. For example, although it is known[58–60] that radicals $R_nMCH_2CH_2^{\bullet}$ (M = Si, Ge, Sn, P, S, As) adopt a preferred conformation where the σ(MC) bond is coplanar with the radical p orbital ($\pi^{\bullet}$), this cannot *a priori* be ascribed to mixing with the filled σ(MR) MO because the neglect of overlap is a questionable approximation when applied to three electron interaction (*vide supra*). Only $[\sigma_{-1}, d]$–$\pi^{\bullet}$ orbital mixing can be confidently predicted to result in stabilization. Significantly, hydrogen abstraction from $R_3MCH_2CH_3$ (M = Si, Ge, Sn) produces the secondary radical $R_3MC^{\bullet}HCH_3$ with only minor amounts of the primary radical $R_3MCH_2CH_2^{\bullet}$. This suggest that, *in contrast to the cation case*, σ–π stabilization of the primary radical by the R_3MCH_2 group differs little from that achieved by the combined effects of the CH_3 and R_3M groups in the secondary radical. With regard to the electron distribution, a distinction between charge and spin density must be made. Although $[\sigma_{-1}, d]$–$\pi^{\bullet}$ mixing will decrease both spin and charge, σ–$\pi^{\bullet}$ mixing will increase charge but decrease spin. Consequently spin density will be the sum of these terms and always decrease, while the charge density is their difference. This behavior is reproduced in CNDO/2 calculations for substituted methyl radicals $RCH_2^{\bullet}$, the charge and spin density, respectively, being R = CH_2SiH_3 (*sp*), 1.081, 0.860; CH_2SiH_3 (*spd*), 1.074, 0.837; CH_2CH_3, 1.046, 0.925; CH_3, 1.037, 0.917, SiH_3 (*sp*), 1.000, 0.941; SiH_3 (*spd*), 0.840, 0.813. These numbers may be used to derive the magnitude of electron transfer via σ–$\pi^{\bullet}$ and via $[\sigma_{-1}, d]$–$\pi^{\bullet}$ conjugation, respectively, for each R group: R = CH_2SiH_3 (*spd*), 0.118, 0.044; CH_2SiH_3 (*sp*), 0.110, 0.029; CH_2CH_3, 0.061, 0.014; CH_3, 0.060, 0.023; SiH_3 (*sp*), 0.030, 0.030; SiH_3 (*spd*), 0.013, 0.174. The relative importance of the two mechanisms follows the sequence expected, *i.e.* the ratio of σ–$\pi^{\bullet}/[\sigma_{-1}, d]$–$\pi^{\bullet}$ electron transfer decreases in the order $H_3SiCH_2 > CH_3CH_2 > CH_3 > SiH_3$ (*sp*) $\gg SiH_3$ (*spd*).

Krusic and Kochi[58] have derived experimental spin densities for the series of radicals $RC^{\bullet}HCH_3$, R = H (0.917), CH_3 (0.842), and Et_3Si (0.859), from ESR coupling constants. These compare very well with CNDO/2 calculated spin densities, R = H (0.917), CH_3 (0.842), SiH_3, *sp*, (0.862), SiH_3, *spd*, (0.717). If the SiH_3 and $SiEt_3$ groups are not too dissimilar, the CNDO/2 parameters for silicon *d* orbitals overemphasize the role of $\pi^{\bullet}$–d conjugation.

D. Lewis bases (anions and unshared electron pairs)

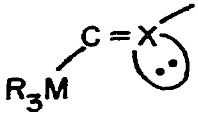
Ionization potentials. Anions and lone pair electrons (n) are examples of doubly occupied orbitals which are formally localized on one atomic center. If the orbital(s) has purely π symmetry, *e.g.* the $n(p)$ orbitals of halides, then the perturbation model is analogous to that of σ–π conjugation. Mixing of the n orbital with the σ, σ_{-1} and d

orbitals of a substituent group can therefore generally be expected to result in a perturbation of the IP in the order $R_3MCH_2 > R_3M > H$. Even if the n electrons do not have pure π symmetry, *e.g.* the $n(sp^3)$ and $n(sp^2)$ orbitals of amines and imines, this order will hold for the IP of the $\psi(E)$ MO.

This generalization is supported both by CNDO/2 calculations and by experimental data. For example, the calculated n_p-IP's of the series of alkyl and silyl chlorides, RCl, decrease in the order $R = H$ (12.49 eV) $> SiH_3$, *spd*, (12.42 eV) $> CH_3$ (11.25 eV) $> CH_2CH_3$ (11.00 eV) $> CH_2SiH_3$, *spd*, (10.60 eV) (absolute values reduced by 3.0 eV).

The experimental IP's of CH_2SiMe_3 substituted amines and ethers show a similar large decrease[61]. For the ethers, ROMe, the n IP decreases in the order $R = H$ (10.80 eV) $> CH_3$ (10.00 eV) $> CH_2CH_3$ (9.81 eV) $> SiMe_3$ (9.37 eV) $> CH_2SiMe_3$ (8.49 eV), while for the amines RNH_2 the order is H (10.15 eV) $> CH_3$ (8.97 eV) $>$ CH_2CH_3 (8.86 eV) $> CH_2SiMe_3$ (8.08 eV)*.

σ–n conjugation should be particularly strong in structures of the type:



where the $\sigma(MR_3)$–n orbital overlap is maximized by the coplanarity and the short C–X bond length. This is evidenced by the unusually low n IP's and strongly bathochromically shifted $n \rightarrow \pi^*$ transitions of α-silyl ketones[64,65]**, pyridines[66], imines[67], and diimines[68,69].

Charge distribution. If the n orbital is an sp^2 or sp^3 hybrid, both the $\psi(A)$ and $\psi(E)$ MO's will contribute to the electron density in this orbital, and a simple analysis is no longer possible. Consequently, the perturbation model is restricted to molecules where the n orbital has purely π symmetry, *e.g.* ketones, planar carbanions and amines, halides. Here σ–n conjugation, a 4 electron interaction, has no net effect on the electron distribution. The electron density in the n orbital is, therefore, determined solely by the magnitude of $n \rightarrow [\sigma_{-1}, d]$ interaction, for which an order $H < CH_2MR_3 < MR_3$ is predicted.

CNDO/2 calculations are not in total agreement with this prediction, the charge density in the carbon p_π orbital of the series of planar carbanions, RCH_2^-, decreasing in the order $R = H$ (2.00), CH_2CH_3 (1.93), CH_3 (1.90), SiH_3, *sp*, (1.87), CH_2SiH_3, *sp*, (1.77), CH_2SiH_3, *spd*, (1.72), SiH_3, *spd*, (1.46). A similar trend is found for the oxyanions, RO^-: H (2.00), CH_2CH_3 (1.95), CH_3 (1.94), SiH_3, *sp*, (1.94), CH_2SiH_3, *sp*, (1.89), SiH_3, *spd*, (1.62), and for the corresponding hydroxides and chlorides. (For previous MO calculations of charge distribution in alcohols and alkoxides, see refs. 70–74.) As expected, the extent of electron transfer to a given group R increases with the basicity of the n electrons, *e.g.* $RCH_2^- > RO^- > RCl \approx ROH$. In the perturbational model this results from the decreasing value of the ΔE term. How-

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* IP's of silicon compounds determined by electron impact using Honig critical slope procedure[62]; IP's for carbon compounds are PE spectroscopic[63] adiabatic values.

** Interestingly, β-silyl ketones show no spectral shifts[64]; whereas σ–π mixing might be expected to produce a strongly red shifted $\pi \rightarrow \pi^*$ and a weakly blue shifted $n \rightarrow \pi^*$ transition. We tentatively suggest the conformation requirement of σ–π overlap is not met.

ever, the perturbational model does not account for the exceptional acceptor ability of the CH_2SiH_3 group, which is greater rather than less than that of the CH_3 and CH_2CH_3 groups. This appears to be the result of an antibonding $1,3n \rightarrow Si$ interaction and is not greatly affected by the inclusion of *d* orbitals in the basis set. The charge acceptability (measured as the increase in electron density in the conversion $RCH_3 \rightarrow RCH_2^-$) of the ethyl and silylmethyl (*sp*) groups is compared in Fig. 3.

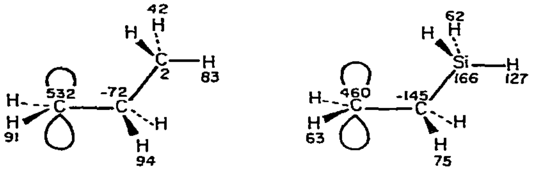
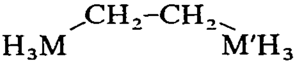


Fig. 3. Electron acceptability ($\delta_q \times 10^3$) of ethyl and silylmethyl groups.

The silylmethyl group thus appears to act as a readily polarizable group, donating to electron deficient centers (cations) and accepting from electron rich centers (anions). This duality of behavior has yet to be verified experimentally, although it may contribute to the stability of transition metal derivatives[51,75,76] and to the exception acidity of Me_3MCH_2OH, $M=Si$, Ge[77].

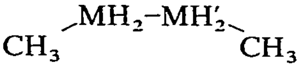
E. *σ–σ conjugation*

This form of orbital interaction is of most interest in molecules where the highest occupied or lowest unoccupied MO's have pseudo π or E symmetry. The series of substituted ethanes (I), where M and M′ are Si, Ge, Sn, or any electropositive element, is a case in point, and the σ-IP, electronic spectrum and oxidizability, can be



$H_3M{-}CH_2{-}CH_2{-}M'H_3$

(I)



$CH_3{-}MH_2{-}MH'_2{-}CH_3$

(II)

expected to be strongly influenced by the geminal interaction of the σ(CM) bonds. The splitting of the formally degenerate σ(CM) MO's will be favored when $M=M'$ ($\Delta E=0$), and is predicted to increase in the order $M=Sn>Ge>Si>C$ [$a(\sigma)$ increases, $P(CC)$ constant]. On the other hand, in the isomeric series (II) the geminal σ(CM) interaction will increase in the reverse order because of the decreasing values of both the $a(\sigma)$ and $P(MM)$ terms, and the $\psi(A)$ MO, *i.e.* σ(MM), will dominate the electronic properties of the molecule.

CNDO/2 calculations indicate the magnitude of geminal σ–σ interactions in molecules such as (I) can be considerable. For example, the IP of 1,2-disilylethane is decreased by 1.7 eV in the *trans* configuration, and 1.9 eV in the *cis* configuration, relative to silylethane. (These numbers refer to *sp* basis set calculations.) No decrease is observed in the orthogonal conformation. The corresponding decrease in the $\psi(E)$ IP of *trans*-butane, relative to propane, is only 0.3 eV.

Some indirect experimental support for the importance of σ–σ interaction is provided by the bathochromic shifts of the absorption band which has been assigned to a $\sigma \rightarrow \pi^*$ transition in a series of trimethylsilyl-substituted ethylenes[19,78]. Here the geminal σ(Si–C) bonds are constrained to a single plane. The energy of the transition is decreased by at least 0.5 eV in the *cis*- and *trans*-1,2-bis(trimethylsilyl)ethylenes, and by at least 1.5 eV in the trisubstituted ethylene. Unfortunately changes in the π^* energy level may contribute[78], and IP measurements will be necessary to confirm the magnitude of σ–σ interaction.

F. Cation and anion conjugation

Carbenium ions are capable of conjugation with alkyl substituents ($\sigma \rightarrow \pi_0$), alkenyl and aryl substituents ($\pi \rightarrow \pi_0$), and groups bearing lone pair electrons ($n \rightarrow \pi_0$). (For reviews, see ref. 79.) It follows from the trends in the a, P and $E(\pi_0)$ terms* of the Group IV elements that these mechanism of stabilization and charge delocalization will be of lesser significance for cations of silicon, germanium and tin. The same conclusion is derived from CNDO/2 calculations which show, for example, that monomethylation of the SiH_3^+ cation results in less stabilization (0.93 eV) and charge delocalization (0.085) compared to methylation of the CH_3^+ cation (2.57 eV, 0.216)**. Similar differences (Table 7) are calculated for the ethynyl substituted cations, and also for the corresponding anions. (This stabilization energy contains both inductive and hyperconjugative contributions[80].)

TABLE 7

CHARGE DELOCALIZATION (δq)[a] AND STABILIZATION (δE)[b] RESULTING FROM ETHYNYLATION OF SILYL AND METHYL ANIONS[c] AND CATIONS[d]

R	CH_2^+	SiH_2^+ (*sp*)	SiH_2^+ (*spd*)	CH_3^-	SiH_2^- (*sp*)	SiH_2^- (*spd*)
q_α	1.093	1.074	1.036	0.876	0.914	0.909
q_β	0.617	0.835	0.807	1.260	1.103	1.034
δq	0.290	0.091	0.157	−0.136	−0.017	0.057
δE	2.60	0.71	0.95	1.78	0.75	0.10

[a] $\delta q = 2.000 - (q_\alpha + q_\beta)$, where q_α and q_β are occupancies of ethynyl $p(\pi)$ orbitals in the plane of the anionic/cationic orbital. [b] $\delta E(\text{eV}) = E(MH_4 \rightarrow M^{\pm}H_3) - E(HC_2MH_3 \rightarrow HC_2M^{\pm}H_2)$. [c] Values for tetrahedral anions, planar geometry being less stable. [d] Planar geometry.

Since no attempt was made to optimize geometries and because the CNDO/2 method is known to reproduce molecular energies rather poorly, these calculations should only be regarded as suggestive. Nevertheless, they are consistent with experimental facts such as the relatively minor effect which phenyl substituents have on the stability of silicenium ions[81,82] and the charge delocalization of silyl and germyl anions[83].

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* Assuming that all cations R_3M^+ are planar, the $a(M^+)$ term will be unity and independent of M. The trend in the energy of the vacant p orbital expected on electronegativity grounds is confirmed by CNDO/2 calculations: CH_3^+ (−0.411 a.u.); SiH_3, *sp* (−0.332 a.u.); SiH_3, *spd* (−0.335 a.u.).

** The CNDO/2 calculated energies $E(M^-)$ of the highest occupied MO of the tetrahedral anions MH_3^- are the reverse of that expected on electronegativity grounds: CH_3^- (−0.011 a.u.); SiH_3^-, *sp*, (−0.041 a.u.); SiH_3^-, *spd*, (−0.046 a.u.). Similarly, for planar anions: CH_3^- (+0.032 a.u.); SiH_3^-, *sp*, (+0.008 a.u.); SiH_3^-, *spd*, (+0.007 a.u.). This is primarily a result of the polarity of the $Si^{\delta+}$–$H^{\delta-}$ σ bonds, which effectively increases the silicon nuclear-electron potential.

APPENDIX

The relationship between the IP and electrophilic reactivity

Considering the case of electrophilic attack on a substituted benzene, and using the Wheland cation localization model[84] for the transition state (Fig. 4), the change in the free energy of activation ($\Delta\Delta G$) effected by a substituent X is

$$\Delta\Delta G = [E(\pi^+) - E(\pi)]_X - [E(\pi^+) - E(\pi)]_H \tag{14}$$

Here $E(\pi)$ and $E(\pi+)$ refer to the energies of the substituted benzene and pentadienyl cation, summed over all occupied MO's which are non-nodal at the C–X bond. If the substituent effect is purely inductive then, from eqns. (8) and (14):

$$\Delta\Delta G \approx 2 \sum_{\text{occ}} \sum_{r} [a^2(r\pi^+)\cdot\delta\alpha_r - a^2(r\pi)\cdot\delta\alpha_r] \tag{15}$$

where $a^2(r\pi^+)$ and $a^2(r\pi)$ are the electron densities in the $p(\pi)$ atomic orbitals of atom r whose coulomb potential is inductively modified by $\delta\alpha$. Since the inductive perturbation of the π-IP takes the same form, *i.e.*

$$\Delta IP = \sum_{r} (a^2(r\pi)\cdot d\alpha_r)_{\text{HOMO}} \tag{16}$$

a linear correlation between ΔIP and $\Delta\Delta G$ is anticipated.

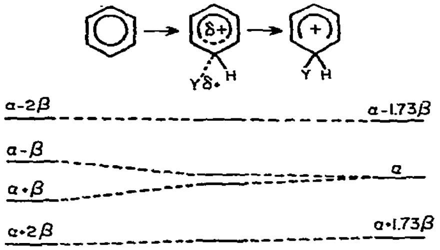

Fig. 4. Wheland cation localization model and changes in energy of non-nodal MO's.

If there is also conjugative mixing of the σ MO's of the substituent with the π MO's, it is necessary to include $E(\sigma)$ terms in eqn. (14), and a simple relationship between $\Delta\Delta G$ and ΔIP can only be derived after a number of approximations. First the small destabilization which results from interaction of doubly occupied σ and π MO's (*vide supra*) is neglected. $\Delta\Delta G$ is, therefore, determined by energy terms involving doubly occupied and empty MO's, *i.e.* σ–π_{-1} and π–$[\sigma_{-1},d]$ terms. The σ–π_{-2} and π_2–$[\sigma_{-1}, d]$ terms may be neglected both because of the unfavorable energy separation, and because the π_2 and π_{-2} MO's undergo a relatively small change in energy on conversion to the cation (*cf.* Fig. 4). $\Delta\Delta G$ can then be expressed as:

$$\Delta\Delta G = 2\delta E(\sigma\pi_{-1}) + 2\delta E(\sigma_{-1}\pi) - 2\delta E(\sigma\pi_0) \tag{17}$$

The corresponding expression for the change in the IP is

$$\Delta IP = \delta E(\pi\sigma) - \delta E(\pi\sigma_{-1}) \tag{18}$$

and only a coincidental correlation between ΔIP and $\Delta\Delta G$ is predicted. However, the cases where a linear correlation has been experimentally observed involve substituents where σ–π (or n–π) interaction is dominant, and the first two terms of eqn. (17) and the last term of eqn. (18) are minor. For such substituents,

$$\begin{aligned}\Delta IP/\Delta\Delta G &= \delta E(\sigma\pi)/2\delta E(\sigma\pi_0) = [a^2(\pi)/\Delta E(\sigma\pi)]/2[a^2(\pi_0)/\Delta(E\sigma\pi_0)] \\ &= [a^2(\pi)/a^2(\pi_0)]/2[1+\Delta E(\pi\pi_0)/\Delta E(\sigma\pi)]\end{aligned} \tag{19}$$

This expression will still only be linear in ΔIP and $\Delta\Delta G$ if $\Delta E(\sigma\pi) \gg \Delta E(\pi\pi_0)$, a condition which will be met if $\Delta E(\sigma\pi)$ is large, *i.e.* hyperconjugation is relatively weak, or if $\Delta E(\pi\pi_0)$ is small, *i.e.* the transition state is less than that of a fully formed pentadienyl cation. Alternatively, the extent to which the transition state resembles the pentadienyl cation (Fig. 4) may vary with the hyperconjugative capability of the σ group; the ratio $\Delta E(\pi\pi_0)/\Delta E(\sigma\pi)$ will then tend to be constant and a linear correlation will be observed.

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