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Preliminary communication

Hyperconjugation: an alternative to the concept of the p_π–d_π bond in Group IV chemistry

COLIN G. PITT

Chemistry and Life Sciences Laboratory, Research Triangle Institute, Research Triangle Park, N.C. 27709 (U.S.A.)

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It has long been known that, in contrast to electrostatic expectations, the R_3MCH_2 group (M = Si, Ge, Sn) exhibits a greater electron releasing ability than the R_3M-group[1]. This is commonly cited as evidence of p_π–d_π bonding. Recently, however, good evidence has been found[2] for believing that σ–π hyperconjugation may be at least partially responsible for this order of electron release★. With the intention of quantitatively evaluating the separate contributions of electrostatic, p_π–d_π, and hyperconjugative effects, we have measured the ionization potentials (IP's) of the π system of a series of silyl and germyl substituted indanes (Fig.1), making use of the dependence of the magnitude of σ–π interaction on the cosine of the dihedral angle ϕ between the two orbitals[4].

The IP's were determined from the electronic spectra of the charge transfer complexes with tetracyanoethylene utilizing the well documented[5] linear relationship (for a family of compounds), first derived in the form (1) for substituted benzenes by Voigt[6]. As expected[7], the original degeneracy of the e_{1g} molecular orbitals of benzene is

$$h\nu_{CT} = 0.83\ \text{IP} - 4.42 \qquad (1)$$

lifted by 1,2-annelation, and the resulting charge transfer spectra consist of two partially resolved absorption bands. These bands were deconvoluted by assuming a log-normal

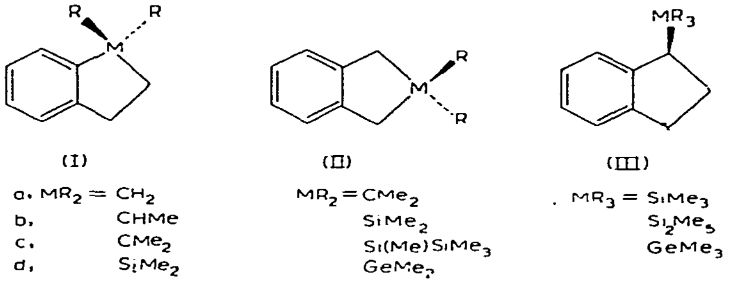

Fig.1.

★Two important papers (Ref. 3a,b) concerned with the electronic properties of the R_3M and R_3MCH_2 groups have been published subsequent to the submission of this manuscript. Both papers describe the use of charge transfer spectra and in one paper (Ref. 3a) somewhat different evidence of hyperconjugation is presented.

TABLE I

FREQUENCIES AND IONIZATION POTENTIALS DERIVED FROM CHARGE TRANSFER COMPLEXES WITH TETRACYANOETHYLENE

Compound	$\overline{\nu_1}$, $\times 10^{-4}$ cm^{-1}	$\overline{\nu_2}$, $\times 10^{-4}$ cm^{-1}	IP, (eV)
o-xylene	2.20	2.49	8.61
o-diethylbenzene	2.13	2.43	8.51
indane (Ia)	2.14	2.48	8.52
tetralin	2.10	2.38	8.47
Ib	2.10	2.46	8.47
Ic	2.10	2.48	8.47
Id	2.15	2.44	8.54
IIa	2.10	2.46	8.47
IIb	2.07	2.37	8.41
IIc	2.04	2.39	8.37
IId	2.05	2.37	8.39
IIIa	1.88	2.38	8.13
IIIb	1.84	2.38	8.07
IIIc	1.80	2.33	8.02
toluene	2.26	2.56	8.71
$PhCH_2SiMe_3$	2.04	2.51	8.37
$PhCH_2Si_2Me_5$	1.97	2.51	8.27
$PhCH_2GeMe_3$	1.96	2.52	8.26

distribution[8], and determining the best least squares fit by an iterative procedure[9]. The absorption maxima, and the corresponding IP's of the highest occupied MO's derived from (1) are listed in Table 1.

Since replacement of an annular carbon atom by silicon or germanium changes the dimensions of the non-benzenoid ring, it is necessary to assess any effect that this may have on the IP's. This was accomplished by comparing the IP's of *o*-xylene, *o*-diethylbenzene, tetralin, and indane (Ia). It can be seen (Table 1) that ring strain effects are minimal, and the small differences in the IP's of these compounds are best interpreted in terms of the increasing electron supply of the larger alkyl substituents. Methyl substitution at the α or β position of indane (Ib,c; IIa) also produces relatively small changes in the IP of the π system, consistent with the idea that C–C and C–H hyperconjugation are of comparable magnitude.

The effects of silyl and germyl substitution depend markedly on the position of substitution. When the methylene group β to the benzene ring is replaced by a Me_2Si, $Me_3Si(Me)Si$ or Me_2Ge group (IIb,c,d), the IP decreases by $\sim$ 0.1 eV relative to the carbon analog. Since the benzylic M–C bonds are in the nodal plane of the π-system, no σ–π interaction is possible, and this increment must be associated primarily with the electrostatic effect of the electropositive silicon and germanium atoms.

In contrast, extra-annular substitution by the Me_3Si, Me_5Si_2, or Me_3Ge groups (series IIIa–c) results in a decrease in the IP of 0.4–0.5 eV. In these three compounds the dihedral angle between the π-system and the β M–C σ bond is now 30°, and since the electrostatic contribution must be $\leqslant$ 0.1 eV (based on the increments in series II), the additional reduction of the IP's must logically be associated with the $\sigma_{M-C}-\pi$ interaction. That is to say, Si–C and Ge–C hyperconjugation is ca. 0.3 eV greater than C–H hyperconjugation in these systems, The IP's of benzyl derivatives (Table 1 and Ref. 3) support this conclusion, although for these compounds the dihedral angle is not known.

Unfortunately, the charge transfer complexes of the tin analogs of series II and III are unstable.

Introduction of a dimethylsilyl group α to the π-system (Id) causes a small increase in the IP. One might justifiably ask why σ—π interaction in this molecule, involving the two extra-annular Si—C bonds of the $SiMe_2$ group, together with the greater inductive effect of the α-silicon atom does not result in an even larger reduction in the IP than that observed for 1-trimethylsilylindane (IIIa), instead of the small increase actually observed. One explanation might involve synergic p_π—d_π delocalization of π electron density. However, in view of the estimated[10] energy (≈ - 2 eV) of the silicon 3*d* orbitals, an alternative explanation deserves consideration. We propose that the crucial factor is the length of the (annular) Si—C bond relative to the C—C bond, and that this is responsible for a substantial diminution in σ—π interaction. A crude estimate of the dependence of σ—π interaction on bond length can be obtained from the Slater overlap integrals[11], which indicate that π—σ overlap decreases by approximately 50% on increasing the bond length from 1.54 Å in Ia—Ic to 1.87 Å in Id. It is therefore reasonable to believe that the increased inductive electron supply of the electropositive silicon atom will be negated by a reduction in σ—π hyperconjugation, with the result that the Me_2Si group and the methylene group have comparable electronic properties[1,2,3].

σ—π hyperconjugation also explains some puzzling features of the electronic spectra of Group IV derivatives★. For example, the spectra of the α-metalloketones and esters, R_3M—CO—R, cannot satisfactorily be explained by a p_π—d_π model, but are quite consistent with σ—π interaction, which is maximum between the σ_{M-C} and oxygen lone pair electrons ($\phi = 0°$) and minimum between the σ_{M-C} and $\pi_{C=O}$ electrons ($\phi = 90°$). This is not to say that p_π—d_π bonding in Group IV chemistry must be rejected entirely, for there is ample evidence to indicate its importance in the excited state[1]. However, we suggest that σ—π interaction, and not p_π—d_π bonding, may be the major factor in determining ground state electronic properties.

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★For an excellent discussion including hyperconjugative effects, see Ref. 12.