ples, and only two values are reported: *D*, one half the absolute value of the largest fine-structure splitting; and *E*, one sixth the range of splittings in the perpendicular plane.
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Lone Pair–Polar Bond Hyperconjugation in Carbon–Halogen Chemistry

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Abstract: Molecular orbital theory suggests that the importance of vicinal lone pair–polar bond hyperconjugation (e.g., $XCH_2\text{-}CH_2^- \leftrightarrow X^-CH_2{=}CH_2$) should increase, when X represents halogen, in the order F < Cl < Br < I. This pattern, which is determined by the carbon–halogen bond strengths, contrasts with that predicted by the valence bond description of this phenomenon. A variety of available experimental data, including the conformational equilibria of 2-halotetrahydropyrans (the anomeric effect), 2-halocyclohexanones and allyl halides, the rotational barriers of *N,N*-dimethylcarbamyl halides, and the acidities of haloacetic acids, support the molecular orbital interpretation. These results serve to demonstrate that anionic hyperconjugation is, indeed, a very real, general, and important concept.

The possible importance of lone pair–polar bond hyperconjugation in organic fluorine chemistry was first suggested in 1950.[1] The subject remains controversial to this date, primarily because the effects typically attributed to such hyperconjugation are generally small and therefore difficult to interpret unambiguously for the isolated fluorine case.[2]

Lone pair–polar bond hyperconjugation is described in valence bond terminology by the resonance hybrids **1** and **2**.

$$X\text{—}CH_2\text{—}CH_2^- \qquad\qquad X^-\ CH_2{=}CH_2$$

1 2

In this view, hybrid **2** should be stabilized by electronegative X. The importance of hyperconjugation should increase correspondingly. Fluorine, by virtue of its high electronegativity, is therefore expected to be more disposed to hyperconjugate with vicinal lone pairs than other substituents.[3] More sophisticated analyses of this subject based on simple perturbation theory advocate the same conclusion.[4] We submit, on the contrary, that the following discussion strongly indicates that, in the halogen series, the importance of lone pair–polar bond hyperconjugation actually increases in the order C–F < C–Cl < C–Br < C–I. Recognition of this trend provides a new basis upon which to judge the general significance of hyperconjugation of this type.

Lone pair–polar bond hyperconjugation is best described as a stabilizing, internal charge transfer between the doubly occupied lone pair orbital (n) and the unoccupied σ^* orbital of the vicinal polar bond (Figure 1a).[4] The magnitude of this interaction, and hence the degree of stabilization derived therefrom, increases as the energy separation (ΔE) between the orbitals decreases.[4,5]

In the molecular orbital theory of bonding, the energy separation between the σ and σ^* (or π and π^*) orbitals of a chemical bond increases with increasing bond strength. Carbon–halogen bond strengths decrease in the order C–F > C–Cl > C–Br > C–I (see Table I).[6] The σ–σ^* splitting of these bonds should decrease proportionally. Assuming a symmetrical displacement of σ and σ^* orbitals below and above, respectively, an arbitrary nonbonding level, the energy of the σ^* orbitals of carbon–halogen bonds should increase in the order I < Br < Cl < F as illustrated in Figure 1b.

Both the σ and σ^* orbitals of a C–X bond are expected to be lowered in energy as the electronegativity of X increases.[4] While this shift should be largest for fluorine, it is not unreasonable to expect that the overall trend in orbital energies will remain as predicted by the relative bond strengths. Two sets of experimental data provide support

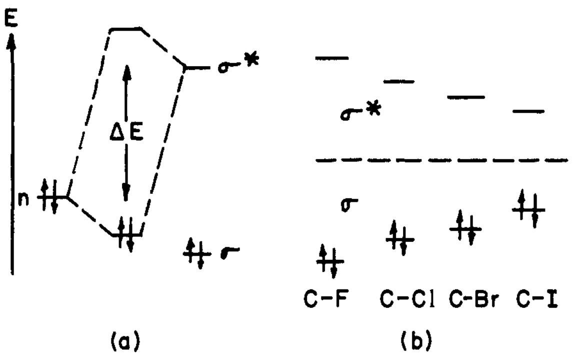


Figure 1. (a) Interaction between a doubly occupied lone pair orbital (n) and the unoccupied σ^* orbital of a vicinal σ bond. (b) Relative σ and σ^* energies of carbon-halogen bonds.

Table I. Bond Dissociation Energies and Ionization Potentials of the Carbon-Halogen Bonds of the Methyl Halides (CH_3X)

X	Bond energy, kcal/mol[a]	Ionization potential, eV[b]
F	108	16.2
Cl	84	14.4
Br	70	13.5
I	56	12.5

[a] Reference 6. [b] Reference 7.

for this proposal. As indicated in Table I, the ionization potentials of carbon-halogen bonds decrease with decreasing bond strength,[7] as expected if Figure 1b correctly represents the trend in the occupied σ-orbital energies. Similarly, the expected pattern in σ^* orbital energies is supported by indirect evidence derived from the ultraviolet spectra of α-halocyclohexanones. These compounds are known to exhibit pronounced red shifts in their n-π^* transitions when the halogen is axial.[8] Calculations[8a] indicate that an interaction between the carbonyl π^* level and the higher energy vicinal C-X σ^* orbital, which moves the former to lower energy,[9] is responsible for the observed red shift. Experimentally, the magnitude of this shift increases in the order F < Cl < Br.[8] Since the magnitude of the interaction between the π^* and σ^* orbitals is inversely proportional to their energy separation,[4,5] the experimental results indicate that the energies of the σ^* orbitals of carbon-halogen bonds must decrease in the order F > Cl > Br. Figure 1b does, therefore, accurately represent the trend in both the σ and σ^* orbital energies of carbon-halogen bonds. Consequently, the importance of lone pair—carbon-halogen bond hyperconjugation must increase in the order C-F < C-Cl < C-Br < C-I, inversely proportional to the n-σ^* energy separations (ΔE) associated with each bond (cf. Figure 1).[10]

This conclusion is supported by a variety of experimental data. Lone pair-polar bond hyperconjugation, for example, provides an elegant interpretation of the anomeric effect.[11] While only limited data are available, the magnitude of this effect in 2-halotetrahydropyrans increases in the order Cl < Br,[12] as expected if the σ^* orbital energies of carbon-halogen bonds increase inversely. Molecular orbital calculations[13] on model compounds serve to extend these observations, indicating that the anomeric effect diminishes, and thus that the σ^* orbital energy increases, even further for fluorine.

The conformational equilibria of 2-halocyclohexanones[8b,14] and allyl halides[15] exhibit an analogous "anomeric effect". Again, the tendency of halogens to adopt conformations which maximize hyperconjugation, in this case with vicinal double bonds, increases in the order F < Cl < Br < I.[8b,14-16]

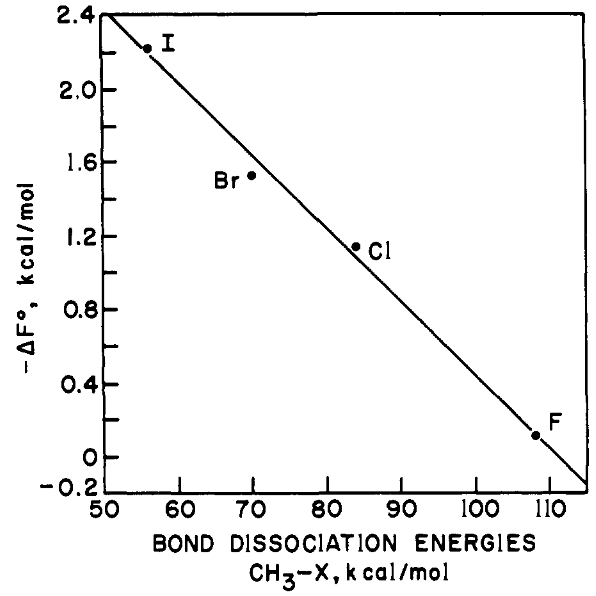


Figure 2. Correlation of the "ketone anomeric effect" ($-\Delta F°$) of α-halocyclohexanones with the carbon-halogen bond dissociation energies of the corresponding methyl halides.

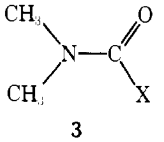
Table II. Conformational Energies of α-Halocyclohexanones and Cyclohexanes

X	$-\Delta G_X$-(cyclohexanone)[a,b]	$-\Delta G_X$-(cyclohexane)[a]	Ketone "anomeric effect"[e]
F	−0.12	0.25[c]	0.13
Cl	0.71	0.43[d]	1.14
Br	1.16	0.38[d]	1.54
I	1.8	0.43[d]	2.23

[a] In kcal/mol. [b] Reference 8b. [c] L. H. Scharpen, *J. Am. Chem. Soc.*, 94, 3737 (1972). [d] Reference 18. [e] $-[\Delta G_X(\text{cyclohexanone}) + \Delta G_X(\text{cyclohexane})]$. Cf. reference 8b.

The axial-equitorial equilibria of α-halocyclohexanones are particularly well characterized. The data[8b] are summarized in Table II together with the conformational energies (*A* values)[18] of the halogens in cyclohexane itself. The sum of the free energy provides a true measure of the "ketone anomeric effect".[8b] As illustrated in Figure 2, the magnitude of this effect correlates linearly with the bond dissociation energies of the corresponding methyl halides. This result clearly substantiates quantitatively the proposal that the importance of hyperconjugation between carbon-halogen bonds and adjacent donor orbitals should increase as the carbon-halogen bond strength decreases.

Similar quantitative relationships are exhibited by a number of related phenomena. Thus, hyperconjugation should contribute to the observed C-N rotational barriers of *N,N*-dimethylcarbamyl halides. While nitrogen lone pair and vicinal carbon-halogen bond are orthogonal in the planar ground state (**3**), they should be aligned for maximum interaction in the rotational transition state (**4**). Lower rotational barriers due to transition state stabilization should therefore result. As indicated in Table III, the barriers decrease in the anticipated order, F > Cl > Br.[19] As demonstrated by Figure 3, the experimental rotational barriers



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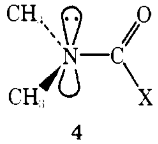

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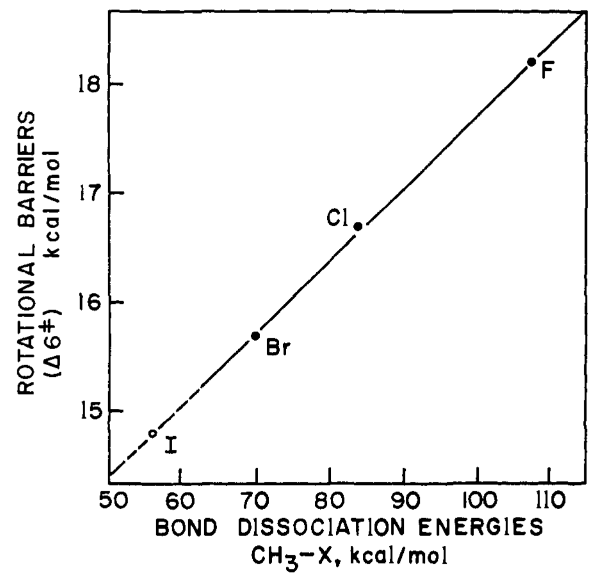

Figure 3. Correlation of the rotational barriers of *N,N*-dimethylcarbamyl halides (**3**) with the carbon-halogen bond dissociation energies of the corresponding methyl halides.

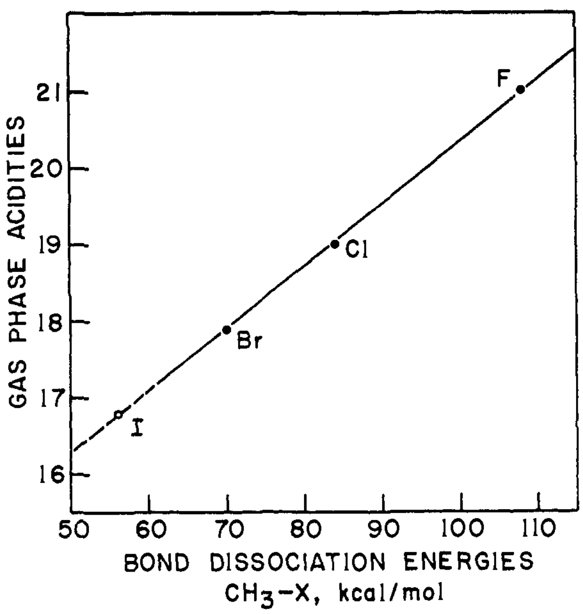

Figure 4. Correlation of the gas-phase acidities of haloacetic acids (XCH_2COOH) with the carbon-halogen bond dissociation energies of the corresponding methyl halides.

Table III. Rotational Barriers of *N,N*-Dimethylcarbamyl Halides and Gas-Phase Acidities of Haloacetic Acids

X	Rotational barriers in $(CH_3)_2NCOX$, $\Delta G^{\ddagger}$, kcal/mol[a]	Gas phase acidities of XCH_2COOH[b]
F	18.2	21.0
Cl	16.7	19.0
Br	15.7	17.9
I	(14.8)[c]	(16.8)[d]

[a] Reference 19. [b] Reference 21. [c] Value predicted from Figure 3. [d] Value predicted from Figure 4.

again correlate linearly with the bond dissociation energies of the corresponding methyl halides.[20]

The acidities of haloacetic acids (XCH_2COOH) may be interpreted similarly. Both hyperconjugative and inductive effects should influence the acidities of these compounds. Experimentally, the gas phase acidities increase in the anticipated hyperconjugative order, F < Cl < Br (Table III),[21] exhibiting the excellent correlation with the methyl halide bond dissociation energies illustrated in Figure 4.[20] In aqueous solution, on the other hand, the acidity order is reversed (Br < Cl < F).[21] In this case, strong solvation stabilizes the carboxyl anion, increasing the energy separation (ΔE) between it and the adjacent σ^* orbital of the carbon-halogen bond. The hyperconjugative interaction is thus reduced, and the normal inductive effect comes to the fore.[22]

Clearly, a consistent pattern of hyperconjugative effects involving carbon-halogen bonds exists. Previous discussions of lone pair-polar bond hyperconjugation have focused primarily on fluorine chemistry[2,4] where simple theoretical arguments indicate that the effect should be small and thus understandably controversial.[2] From the broader perspective of carbon-halogen chemistry as a whole, however, the significance of such hyperconjugation is readily apparent. Both theory and experiment[23] support the conclusion that the importance of anionic hyperconjugation involving carbon-halogen bonds should increase in the order F < Cl < Br < I. Obviously, the importance of such hyperconjugation cannot be evaluated on the basis of the oversimplified valence bond pictures **1** and **2**. Simple perturbation theory, on the other hand, does provide a reliable, qualitative interpretation of this very real, important phenomenon.

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Cycloaddition of Disilacyclobutenes in the Presence of Nickel Tetracarbonyl

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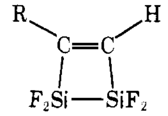
Abstract: 3-*tert*-Butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobut-3-ene (**1**), one of the products from the reaction between $(CH_3)_3CC{\equiv}CH$ and SiF_2, is shown to undergo further cycloaddition to $(CH_3)_3CC{\equiv}CH$ in the presence of $Ni(CO)_4$. The apparent function of $Ni(CO)_4$ is to assist the cleavage of Si–Si bonds through d → d back π bonding to form chelate intermediates which react readily to form new cycloaddition products. These intermediates were isolated by reacting **1** directly with $Ni(CO)_4$. An oxidative addition of the Si–Si bond to nickel resulted in the first well-characterized metal chelate with two silicon atoms bound to a metal atom. A reaction mechanism is proposed and is compared with those of other related catalytic systems.

The study of the addition reactions of the carbene-like difluorosilylene to unsaturated organic compounds has led to the synthesis of a series of unusual new organosilicon compounds.[2-5] Our experiments on the addition reactions of a number of alkyne systems have established a plausible reaction mechanism which involved a reactive species $SiF_2(SiF_2)_nSiF_2$ (n = 0, 1, 2 . . .) on condensation of monomeric SiF_2 which is thermally generated according to the method of Timms et al.[6] The assumption in our proposed mechanism is that the most reactive silicon–fluorine species toward these unsaturated molecules is a dimeric SiF_2 unit, which the ESR[7] indicates is probably a diradical species. The dimeric species $\cdot SiF_2SiF_2\cdot$ reacts with alkynes ($RC{\equiv}CH$) in the ratios of 1:1 and 1:2 to form, in addition to other products resulted from H migration, cyclic products **1** and **2**, respectively.



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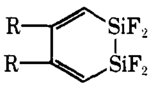

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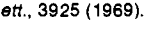
While this reaction mechanism accounts for all existing reaction data, there remains one alternative—that an intermediate formed between monomeric SiF_2 and the reagent molecule reacts so rapidly with other such intermediates to form silicon-silicon bonds that the products from the initial "monomeric intermediate" are not observed.

Our previous evidence was not really sufficient to distinguish between these two possibilities. However, if the latter mechanism was important in this type of reaction, one might expect, for example, in the reaction of $(CH_3)_3CC{\equiv}CH$ to find compounds such as **3** formed from linking two $(CH_3)_3C{-}\dot{C}{=}CH{-}\dot{S}iF_2$ intermediates. Our previous results did not indicate that this type of product was formed in any significant yield. When a six-membered ring was formed, the spectral data[4] seem to favor **2** (R = t-Bu) rather than **3**.



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Based on the argument described above, it seemed to us that, if a compound with structure **3** could be synthesized and the spectral data compared with those of **2**, a more conclusive confirmation of the structures would greatly strengthen the reaction mechanism proposed previously.

We approached this problem by thinking of the possibility of a further cycloaddition of the four-membered ring compound **1** (R = t-Bu) to an alkyl-substituted alkyne $RC{\equiv}CH$. The silicon-silicon bond is known to be relatively weak (Si–Si bond energy 51 kcal/mol compared with 83 kcal/mol for C–C bond[8]) and is expected to be even weaker in a small ring compound involving a double bond such as **1**. If the Si–Si bond in compound **1** can be cleaved and the two Si atoms add to the alkyne molecule, compounds with structure **3** should be formed.

Experimental Section

Materials. 3,3-Dimethyl-1-butyne was prepared by the pinacol rearrangement reaction from acetone followed by chlorination and dehydrohalogenation.[9] Nickel tetracarbonyl (99% purity) and metal silicon (98% purity) were commercially available products used without further purification.

Reactions. All reactions were carried out in a greaseless vacuum system. Silicon difluoride was generated and reacted with $(CH_3)_3CC{\equiv}CH$ as previously described.[4] The volatile products were manipulated in the vacuum system and separated by trap-to-trap fractionation. 3-*tert*-Butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobut-3-ene (compound **1**, R = t-Bu), volatile at 0 °C, was collected at −22 °C. All the reactions between **1** and other reactants were carried out at room temperature in a tube sealed under the vapor pressure of the reactants at −196 °C.

Synthesis of 1,1,4,4-Tetrafluoro-1,4-disilacyclohexa-2,5-dienes. Approximately equimolar amounts of compound **1**, $(CH_3)_3CC{\equiv}CH$, and $Ni(CO)_4$ were reacted in a sealed tube. A vigorous exothermic reaction occurred immediately as the frozen reactant mixture began to melt. The color changed from colorless