

Stereoelectronic Effects and General Trends in Hyperconjugative Acceptor Ability of σ Bonds

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Received November 30, 2001

Abstract: A systematic study of general trends in σ acceptor properties of C–X bonds where X is a main group element from groups IVa–IIa is presented. The acceptor ability of the C–X σ bonds in monosubstituted ethanes increases when going to the end of a period and down a group. Enhancement of acceptor ability of C–X σ bonds as one moves from left to right in periods parallels the increase in electronegativity of X, whereas augmentation of acceptor ability in groups is opposite to the changes in electronegativity of X and in the C–X bond polarization, following instead the decrease in the energy of $\sigma^*_{\text{C-X}}$ orbitals when one moves from the top to the bottom within a group. This simple picture of acceptor ability of σ bonds being controlled by electronegativity in periods and by σ^* orbital energy in groups is changed in monosubstituted ethenes where the role of electronegativity of the substituent X becomes more important due to increased overlap between σ orbitals. The combination of several effects of similar magnitude influences acceptor ability of σ bonds in monosubstituted ethenes in a complex way. As a result, the acceptor ability of σ bonds can be significantly modified by substitution and is conformer dependent. Stereoelectronic effects displayed by C–X bonds with X from second and third periods are highly anisotropic. For example, C-chalcogen bonds are excellent σ acceptors at the carbon end but poor σ acceptors at the chalcogen end. This effect can be relied upon in the design of molecular diodes with σ bridges with unidirectional electron conductivity. While the general trends revealed in this work should be useful for the qualitative understanding of stereoelectronic effects, one should bear in mind that the magnitude of hyperconjugative effects is extremely sensitive to small variations in structure and in substitution. This advocates for the increased role of theoretical methods in analysis of stereoelectronic effects.

Introduction

Chemical reactions involve interactions between electronic orbitals accounting for the increasingly important role of the concept of stereoelectronic effects in modern organic chemistry.¹ Stereoelectronic interactions involving π -bonds (conjugation) are generally regarded as being among the most important chemical phenomena. Interactions between σ orbitals (hyperconjugation) have received less attention, although as early as 1941 Robert Mulliken pointed out its importance and, indeed, hyperconjugative stereoelectronic effects were later found to be ubiquitous in chemistry. Depending on the nature of interacting orbitals, hyperconjugative stereoelectronic interactions can provide electron density to electron-deficient centers² or withdraw it from electron-rich centers, and may stabilize incipient bonds and radical centers.³ These effects influence conformational equilibria (anomeric effect,^{4,5} conformational behavior of the phosphodiester backbone in nucleic acids,⁶ conformational stability of collagens,⁷ and torsional barrier in

ethane⁸ and other molecules⁹). Hyperconjugation has been shown to modify reactivity,¹⁰ control selectivity,¹¹ and play an

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important role in intermolecular interactions, both in ground¹² and in transition states.^{13,14} Even weak hyperconjugative interactions are enhanced dramatically in radical and ionic species and in electronically excited molecules.¹⁵

Carbo- and heterocyclic molecules lend themselves to the study of stereoelectronic effects⁵ because their rigid cyclic geometry keeps interacting orbitals in a well-defined geometry. However, the same rigid arrangement may prevent the orbitals from attaining the optimum geometry for displaying their donor/acceptor properties or it may artificially enhance the interaction by forcing the orbitals to overlap more strongly.

An illustration of such a complex influence was given in our recent computational study,¹⁶ in which stereoelectronic effects involving C–H bonds in cyclohexane, 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane were examined using natural bond orbital (NBO) analysis, a powerful, state-of-the-art technique that allows one to estimate the energy of hyperconjugative effects quantitatively and to unravel their relative importance. We have confirmed that results of NBO analysis correlate well with observable properties such as bond lengths and NMR one-bond coupling constants.

An interesting observation was that the acceptor ability of C–X fragments varies widely depending on the nature of X and on the direction of the bond dipole. For example, C–S bonds in 1,3-dithiane are excellent acceptors in one direction but poor acceptors in another.¹⁷ We have found that the largest part of this phenomenon stems from a stereoelectronic effect imposed by the cyclic structure—a different overlap of C5–H and C1–H bonds with the opposite ends of the σ^*_{C4S3} orbitals. The finding that the σ^*_{C4-S3} orbital in 1,3-dithiane is a better

acceptor than the σ^*_{C4-O3} orbital in 1,3-dioxane is intriguing because σ_{C-X} bonds are often considered to be poor σ acceptors when X is an element from second or higher rows.¹⁸

In general, stereoelectronic effects depend on the orbital overlap and on the intrinsic properties of the interacting orbitals such as their polarization and energy. While the orbital overlap can be estimated from the molecular geometry, the influence of the intrinsic properties of C–X bonds is less amenable to intuitive analysis. In this paper, we rely on theory to provide data on the donor and acceptor ability of σ bonds in acyclic systems where the inherent properties of the corresponding orbitals are not masked by effects imposed by the cyclic structure. An understanding of the general trends of acceptor ability of σ bonds in such systems is necessary for the successful use of stereoelectronic hyperconjugative interactions as a general mechanistic guide. Much to our surprise, we were unable to find a study that compares acceptor ability of σ bonds for a large number of σ substituents in a unified and comprehensive way.^{19,20} Such a comparison is crucial for placing experimental studies of hyperconjugative stereoelectronic effects on a sound basis. A critical reevaluation of stereoelectronic effects becomes increasingly important because, as shown in a recent series of papers by Perrin and co-workers, the concept is often misused and stereoelectronic effects that were proposed to be important in nucleophilic addition to amidinium ions,²¹ hydrolysis of cyclic guanidinium ions,²² and some other reactions²³ are, in fact, very weak.

In this paper, we provide a set of benchmark values for the relative acceptor ability of C–X bonds. We will apply NBO analysis to show how the influence of substituent X on the internal properties of the C–X bond such as bond polarization and bond energy affects the acceptor ability of that bond. Our analysis addresses several important issues. First, we analyze how the donor and acceptor abilities of σ bonds change when moving from left to right in the periodic table, and, in particular, how these changes relate to the change in electronegativity of X. Second, we discuss how donor/acceptor abilities of σ_{C-X}

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bonds change within a group when going down the periodic table. Although it is sometimes assumed that elements below the second row are rather poor σ acceptors,²⁴ our analysis of 1,3-dithiane¹⁶ has shown that this is not always true for C–X bonds. In this paper, we extend the analysis to other elements to determine if this finding is general. Third, we establish how the intrinsic donor/acceptor abilities of σ_{C-X} bonds are attenuated by the nature of substituents on X, the properties of the bridge connecting donor and acceptor orbitals, and by the direction of the bond dipole.

To have a definitive answer about relative acceptor ability of different σ acceptors, it is important to use the same set of reference donor orbitals for such a comparison. To this end, we have selected four such donors—the aliphatic C–H bond in substituted ethanes, the olefinic C–H bond in substituted ethenes, the nitrogen lone pair in primary amines, and the lone pair of anionic carbon. This set of donor orbitals has widely varying donor ability and allows one to probe dependence of hyperconjugative effects on the distance between the interacting orbitals.

Details of the Computations and Method. All structures were fully optimized at the B3LYP²⁵/6-31G** level using the GAUSSIAN 98 package.²⁶ Since the 6-31G**²⁷ basis set which is commonly used in computational studies of the anomeric effect^{28,29} applies only to elements from H to Kr, we have limited this study to the first four periods.

The NBO 4.0³⁰ program was used as implemented in the GAUSSIAN 98 package. The NBO analysis transforms the canonical delocalized Hartree–Fock (HF) MOs into localized orbitals that “are closely tied to chemical bonding concepts”. This process involves sequential transformation of nonorthogonal atomic orbitals (AOs) to the sets of “natural” atomic orbitals (NAOs), hybrid orbitals (NHOs) and bond orbital (NBOs). Each of these localized basis sets is complete and orthonormal. Importantly, these sets also describe the wave function in the most “economic” way since electron density and other properties are described by the minimal amount of filled orbitals in the most rapidly convergent fashion. Filled NBOs describe the hypothetical, strictly localized Lewis structure. The interactions

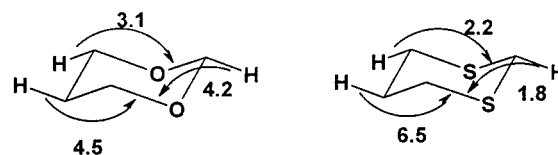


Figure 1. Selected “equatorial” hyperconjugative interactions in dioxane and dithiane. (Numbers correspond to interaction energies in kcal/mol at the B3LYP/6-31+G** level).¹⁶

between filled and antibonding (or Rydberg) orbitals represent the deviation of the molecule from the Lewis structure and can be used as a measure of delocalizations. Since the occupancies of filled NBOs are highly condensed, the delocalizing interactions can be treated by a standard second-order perturbation approach [we will refer to these values as $E(2)$ energies] or by deletion of the corresponding off-diagonal elements of the Fock matrix in the NBO basis (referred to as E_{del} energies). Detailed descriptions of the NBO calculations are available.^{30,31,32}

Results and Discussion

Substituted Ethanes, CH_3CH_2X . Substituted ethanes exhibit the most general and ubiquitous stereoelectronic effect, interaction between the vicinal σ bonds (Figure 2). Two vicinal orbitals (σ and σ^*) overlap strongly, and the resulting hyperconjugative interaction has important consequences for structure and reactivity. For example, the textbook treatment of the conformational equilibrium in ethane as controlled by steric effects is not accurate, and the well-known preference for the staggered conformation of ethane is, in fact, a consequence of hyperconjugative $\sigma_{C-H} \rightarrow \sigma^*_{C-H}$ interactions between the vicinal orbitals.⁸

The NBO C–X bond polarization correlates remarkably well with the Pauling electronegativity of X as reflected in the excellent correlation of the square of the polarization coefficient of the C–X bond³³ with electronegativity for all compounds in this study (Figure 5). Even very subtle differences in electronegativity (Si vs Ge or C vs P) are accurately reflected by the NBO analysis. Also, as expected, in each period there is a good correlation between the energies of σ_{C-X} and σ^*_{C-X} NBOs and electronegativity of X (Figures 3 and 4). As we will show below, these changes account for rather complicated trends in the acceptor abilities of C–X bonds—the main problem we address in this paper.

The summary of the NBO analysis of $\sigma_{C-H} \rightarrow \sigma^*_{C-X}$ interactions for monosubstituted ethanes, CH_3CH_2X , where X is a main group element of groups IVa–VIIa, is given in Table 1 and Figure 6. Within each period, the acceptor ability of the σ^*_{C-X} orbitals smoothly increases from left to right in parallel to the increase in electronegativity of X as predicted by chemical intuition. The same trend is observed for second and third row elements—in each case, the carbon–halogen bond is the best acceptor of all C–X bonds in the corresponding period (Figure 6). The differences in acceptor ability within periods are significant; for example, the energy of the $\sigma_{C-H} \rightarrow \sigma^*_{C-X}$ interaction increases from 3.1 to 4.7 kcal/mol (more than 50%)

(24) It is known that the $p_X \rightarrow \sigma^*_{C-X}$ hyperconjugation is less effective for second and third row substituents. For the most recent discussion, see: Roux, M. V.; Jiménez, P.; Dávalos, J. Z.; Notario, R.; Juaristi E. *J. Org. Chem.* **2001**, *66*, 5343. This difference was explained by poorer acceptor ability of C–X bonds and lower donor abilities of nonbonding electron pair on X. Salzner, U.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1993**, *115*, 10231. However, it is not clear which of these two factors is controlling. We believe that the reason of the lower energy of $p_X \rightarrow \sigma^*_{C-X}$ interaction is the lower donor ability of the lone pairs.

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(33) A typical σ bond C–X can be described as: $\sigma_{C-X} = \alpha(sp^n)_C + \beta(sp^m)_X$ where α and β are polarization coefficients for the C- and X-centered hybrids $(sp^n)_C$ and $(sp^m)_X$. α^2 and β^2 are proportional to electron density at the C- and X-hybrids with $\alpha^2 + \beta^2 = 1$. When X is more electronegative than C, $\alpha^2 > 0.5 > \beta^2$ (ref 31).

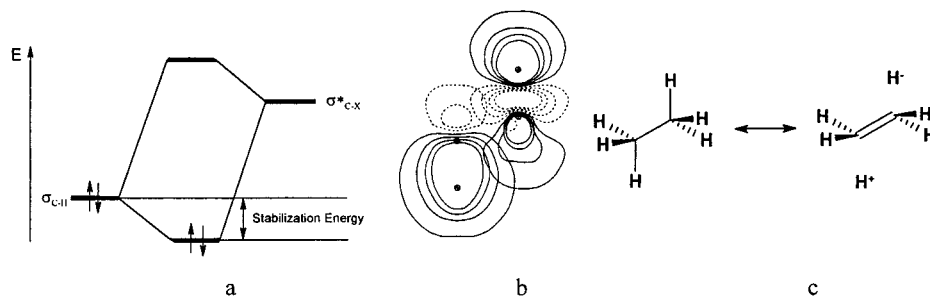


Figure 2. (a) Energy lowering due to hyperconjugative interaction between σ_{C-H} and σ^*_{C-X} orbitals. (b) NBO plots illustrating overlap of vicinal σ_{C-H} and σ^*_{C-H} orbitals in ethane. (c) Description of the vicinal $\sigma_{C-H} \rightarrow \sigma^*_{C-H}$ interaction in ethane in terms of resonance theory (“double bond/no bond resonance”).

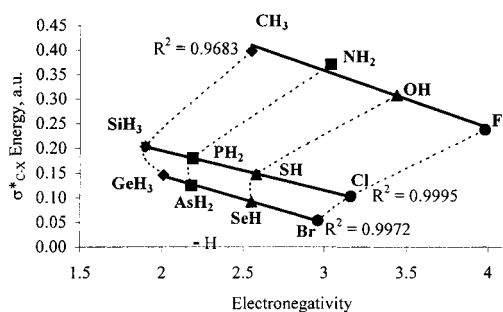


Figure 3. Correlation of energy of σ^*_{C-X} orbitals with electronegativity of element X in substituted ethanes, CH_3CH_2X .

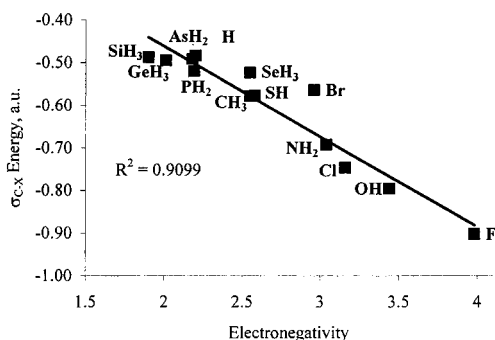


Figure 4. Correlation of energy of σ_{C-X} orbitals with electronegativity of element X in substituted ethanes, CH_3CH_2X .

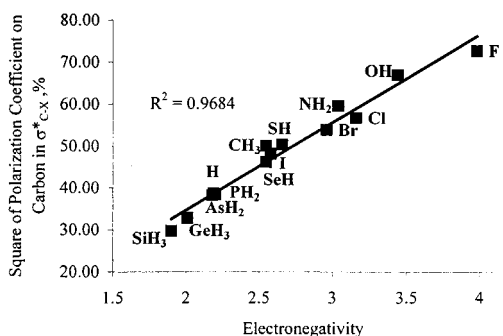


Figure 5. Correlation of polarization of σ^*_{C-X} orbitals with electronegativity of element X in substituted ethanes, CH_3CH_2X .

when X is changed from carbon to fluorine.³⁴ Below we will show that this difference increases even further in the case of a stronger donor orbital (vide infra).

(34) We do not know at this point how accurately the absolute values of the NBO energies correspond to the physically measurable properties. This is a topic for another study. But we believe that the trends that are based on the NBO relative energies are indeed in a good agreement with the experimental data and comparisons between different molecules are meaningful as long as the same level of theory is used. Alabugin, I. V. *J. Org. Chem.* **2000**, *65*, 3910.

Table 1. NBO Analysis of Hyperconjugative Interactions in Substituted Ethanes, C_2H_5X

| donor orbital | acceptor orbital | energy of deletion (E_{del}), kcal/mol | $E(2)$, kcal/mol | ΔE (au) | F_{ij} (au) | % of electron density at X in σ_{C-X} |
|----------------|-----------------------|--|-------------------|-------------------|--------------------|--|
| σ_{C-H} | σ^*_{C-H} | 3.17 | 2.67 | 0.95 | 0.045 | 38.43 |
| σ_{C-H} | σ^*_{C-F} | 5.09 | 4.72 | 0.74 | 0.053 | 72.55 |
| σ_{C-H} | σ^*_{C-Cl} | 6.20 | 5.66 | 0.61 | 0.052 | 56.64 |
| σ_{C-H} | σ^*_{C-Br} | 6.29 | 5.82 | 0.56 | 0.051 | 53.77 |
| σ_{C-H} | σ^*_{C-I} | 7.81 ^a | 6.92 ^a | 0.52 ^a | 0.053 ^a | 50.26 ^a |
| σ_{C-H} | $\sigma^*_{C-OH(1)}$ | 4.22 | 3.90 | 0.79 | 0.050 | 66.90 |
| σ_{C-H} | $\sigma^*_{C-OH(2)}$ | 4.74 | 4.37 | 0.80 | 0.053 | 66.90 |
| σ_{C-H} | $\sigma^*_{C-SH(1)}$ | 4.70 | 4.31 | 0.64 | 0.047 | 48.11 |
| σ_{C-H} | $\sigma^*_{C-SH(2)}$ | 5.36 | 4.88 | 0.65 | 0.050 | 47.96 |
| σ_{C-H} | σ^*_{C-SeH} | 4.68 | 4.33 | 0.59 | 0.045 | 46.08 |
| σ_{C-H} | $\sigma^*_{C-NH2(1)}$ | 3.82 | 3.52 | 0.85 | 0.049 | 59.49 |
| σ_{C-H} | $\sigma^*_{C-NH2(2)}$ | 4.46 | 4.11 | 0.86 | 0.053 | 59.46 |
| σ_{C-H} | $\sigma^*_{C-PH2(1)}$ | 4.01 | 3.65 | 0.67 | 0.044 | 38.68 |
| σ_{C-H} | $\sigma^*_{C-PH2(2)}$ | 4.61 | 4.17 | 0.67 | 0.047 | 38.47 |
| σ_{C-H} | σ^*_{C-AsH2} | 4.55 | 4.19 | 0.62 | 0.045 | 38.19 |
| σ_{C-H} | σ^*_{C-CH3} | 3.38 | 3.12 | 0.88 | 0.047 | 49.94 |
| σ_{C-H} | σ^*_{C-SiH3} | 3.63 | 3.29 | 0.70 | 0.043 | 29.69 |
| σ_{C-H} | σ^*_{C-GeH3} | 3.80 | 3.58 | 0.64 | 0.043 | 32.78 |
| σ_{C-H} | σ^*_{C-N2+} | 7.61 | 6.77 | 0.70 | 0.061 | 69.12 |

^a Since a different basis set (SDD) was used, the data for the C–I bond were not used in the general correlations.

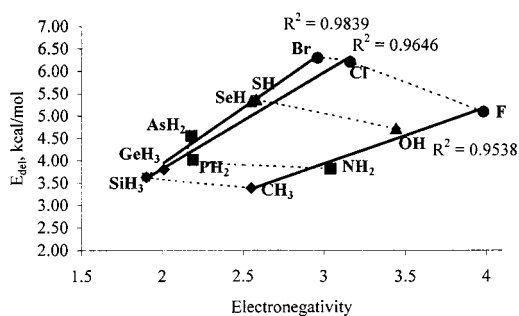


Figure 6. Correlation of energy of $\sigma_{C-H} \rightarrow \sigma^*_{C-X}$ interaction, E_{del} , with electronegativity of element X in substituted ethanes, CH_3CH_2X .

However, the trend of σ acceptor ability being directly proportional to electronegativity is reversed when moving down a group. This reversal is most paradoxical for halogens, where the acceptor ability of C–Hal bonds shows a good linear correlation with the electronegativity of X (Figure 7) but this correlation is *inverse*. In other words, despite the fact that electronegativity *decreases* in the order $F > Cl > Br$, the acceptor ability of σ^*_{C-X} orbitals *increases* in the order $\sigma^*_{C-F} < \sigma^*_{C-Cl} < \sigma^*_{C-Br}$.³⁵ These results are especially intriguing

(35) The “ σ acceptor” ability of a C–X bond should not be confused with another variable referred to as “ σ acceptor” ability of an atom X which can be characterized via polarization of σ_{C-X} bonds. Sigma acceptor ability of an atom X correlates well with its electronegativity (Figure 5).

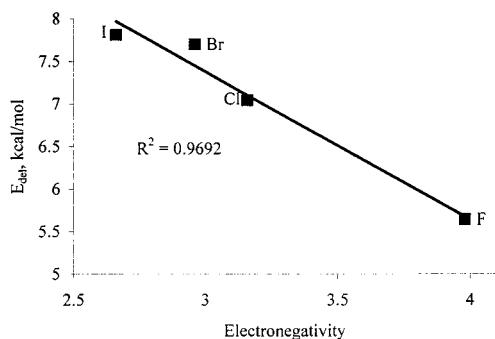


Figure 7. Correlation of energy of $\sigma_{\text{C-H}} \rightarrow \sigma^*_{\text{C-X}}$ interaction, E_{del} , with electronegativity of element X in monohalogenated ethanes, $\text{CH}_3\text{CH}_2\text{Hal}$ at the B3LYP/SDD level of theory.

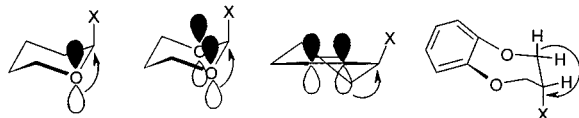


Figure 8. Systems with larger axial preference for heavier halogens. The dominant stereoelectronic interaction is indicated with an arrow.

since the high acceptor ability of $\sigma^*_{\text{C-F}}$ bonds has a large number of chemical consequences as thoroughly analyzed by Borden in a recent paper.^{9f} The consequences of higher acceptor ability of other C–Hal bonds should also be significant.

Several experimental observations support this trend in acceptor ability of C–Hal bonds. The anomeric effect³⁶ is larger for Br than for Cl,^{5a,37,38} and there is a stronger preference for Br than for Cl to be in a pseudoaxial position in α -halocyclohexenes (Figure 8).³⁹ Similarly, Cuevas et al. found recently that hyperconjugative contributions to the anomeric effect at the C2 position in 1,3-dioxanes are more important for Cl than for F.⁴⁰ In addition, Dionne and St-Jacques attributed the experimental trends in conformational equilibrium of 3-halo-1,5-benzodioxepins⁴¹ to the increase in the energy of the $\sigma_{\text{C-H}} \rightarrow \sigma^*_{\text{C-X}}$ interactions when X is a heavier halogen (I, Br, Cl).

Also, the observed trend in acceptor ability of $\sigma_{\text{C-Hal}}$ bonds is in excellent agreement with delocalization patterns in haloethanes⁴² and with the observed differences in leaving group ability of halogen anions in $\text{S}_{\text{N}}1$ and E2 elimination reactions.^{43,44} The striking similarity between the structural changes in an E2 process and the classic description of hyperconjugative

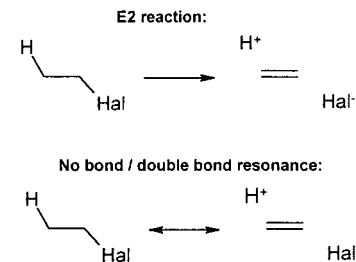


Figure 9. The similarity between the electronic structure of an E2 transition state and the “no bond/double bond” resonance structure in substituted haloethanes. Note that the only difference between the two schemes is the type of arrow!

interactions, the “no bond/double bond” resonance structure, is illustrated in Figure 9. In fact, the hyperconjugative donation from a $\sigma_{\text{C-H}}$ orbital to a vicinal $\sigma^*_{\text{C-Hal}}$ orbital is associated with weakening of the C–H and C–Hal bonds, increase of the double bond character between the carbon atoms, and effective charge transfer from the hydrogen to the halogen atom. The same changes occur as the beginning of the E2 reaction.

The increased σ acceptor ability of C–X bonds when X is a second row element was found not only for halogens but also for elements in groups IVa–VIa and thus represents a general phenomenon (see Table 1).⁴⁵ The relative order of acceptor ability of $\sigma^*_{\text{C-X}}$ bonds is as follows (the energies of $\sigma_{\text{C-H}} \rightarrow \sigma^*_{\text{C-X}}$ interactions are given in parentheses): X = Br (6.3) > Cl (6.2) > SH(1) (5.4) > F (5.1) > OH(1) (4.7) \approx SH(2) (4.7) \approx SeH (4.7) \approx PH₂(1) (4.6) \approx AsH₂ (4.5) \approx NH₂(1) (4.5) > OH(2) (4.2) > PH₂ (2) (4.0) > NH₂(2) (3.8) \approx GeH₃ (3.8) > SiH₃ (3.6) > CH₃ (3.4) > H (3.2), where \approx means that the difference in the energy of $\sigma_{\text{C-H}} \rightarrow \sigma^*_{\text{C-X}}$ interactions is smaller than 0.1 kcal/mol.⁴⁶ X(1) and X(2) correspond to two different conformations of the group X (vide infra). The energies of the $\sigma_{\text{C-H}} \rightarrow \sigma^*_{\text{C-X}}$ interactions are given in Table 1. We proceeded further to determine what factors are behind this highly intriguing behavior with the use of the NBO method. This method gives hyperconjugative energies both by deletion of the off-diagonal Fock matrix elements between the interacting orbitals and from the second-order perturbation approach

$$E(2) = -n_{\sigma} \frac{\langle \sigma / F / \sigma^* \rangle^2}{\epsilon_{\sigma^*} - \epsilon_{\sigma}} = -n_{\sigma} \frac{F_{ij}^2}{\Delta E} \quad (1)$$

where $\langle \sigma / F / \sigma^* \rangle$, or F_{ij} is the Fock matrix element between the orbitals (NBOs) i and j , ϵ_{σ} and ϵ_{σ^*} are the energies of σ and σ^* NBOs, and n_{σ} is the population of the donor σ orbital.⁴⁷ There is an excellent linear correlation (Figure 10) between the deletion (E_{del}) and perturbation analysis ($E(2)$) hyperconjugative energies. We, therefore, relied on the second-order perturbation equation to dissect the interaction energies into components and analyze the general trends quantitatively.⁴⁸

(36) Note, however, that the anomeric effect is a combination of several factors: stereoelectronic, electrostatic, and steric. The hyperconjugative contribution that we discuss is only one of these components.

(37) Eliel, E. L.; Wilen, S. H.; Doyle, M. P. *Basic Organic Stereochemistry*; Wiley-Interscience: New York, 2001.

(38) Tvaroska I.; Carver, J. P. *J. Phys. Chem.* **1996**, *100*, 11305.

(39) Sakashita, K. *Nippon Kagaku Zasshi* **1960**, *81*, 49; *Chem. Abstr.* **1960**, *54*, 12015b.

(40) Cortes, F.; Tenorio, J.; Collera, O.; Cuevas, G. *J. Org. Chem.* **2001**, *66*, 2918.

(41) Dionne, P.; St-Jacques, M. *J. Am. Chem. Soc.* **1987**, *109*, 2616.

(42) For example, Cioslowski had found on the set of 55 distinct fluorochloroethanes (92 distinct rotamers) of the general formula $\text{C}_2\text{H}_2\text{F}_m\text{Cl}_l$ ($n + m + l = 6$) that anticonvic contributions to total energy, zero point correction energy, and C–C bond length are larger for CHCCl moiety as compared the CHCF moiety (–0.57 vs –0.43 for E_{tot}). Cioslowski, J.; Vamali T. *J. Phys. Chem.* **1996**, *100*, 18725.

(43) Thibblin, A.; Ahlberg, P. *J. Am. Chem. Soc.* **1977**, *99*, 7926. For more information on the dichotomy between E2 and E1cB mechanisms, see: Meng, Q.; Thibblin, A. *J. Am. Chem. Soc.* **1995**, *117*, 1839. Meng, Q.; Thibblin, A. *J. Am. Chem. Soc.* **1995**, *117*, 9399. Meng, Q.; Thibblin, A. *J. Chem. Soc., Chem. Commun.* **1996**, 345. More O’Ferrall, R. A. *J. Chem. Soc. B* **1970**, 274–277. Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948. Gandler, J. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 1937.

(44) For more recent papers on the mechanism of elimination reactions, see: Meng, Q. S.; Du, D. A.; Thibblin, A. *J. Phys. Org. Chem.* **1999**, *2*, 116. Meng, Q. S.; Thibblin, A. *J. Chem. Soc. Perkin Trans. 2* **1998**, *3*, 583. Meng, Q. S.; Thibblin, A. *J. Am. Chem. Soc.* **1997**, *119*, 4834. Meng, Q. S.; Thibblin, A. *Chem. Commun.* **1996**, *3*, 345. Meng, Q. S.; Gogoll, A.; Thibblin, A. *J. Am. Chem. Soc.* **1997**, *119*, 1223. Thibblin, A. *Chem. Soc. Rev.* **1993**, *22*, 427.

(45) The same trend was found at the HF/6-31G** level.

(46) The absolute values as well as the ordering in the case of the very close neighbors are expected to be sensitive to the level of theory, and, therefore, at this point, the very small energy differences [e.g., OH(1) vs NH₂(1)] should not be considered as important.

(47) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

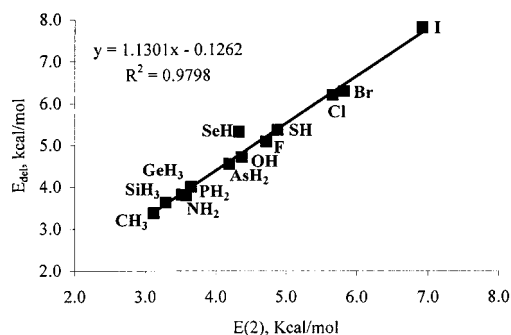


Figure 10. Correlation of E_{del} , energy of $\sigma_{C-H} \rightarrow \sigma^*_{C-X}$ interaction, calculated by deletion of the Fock matrix elements with $E(2)$, energy of $\sigma_{C-H} \rightarrow \sigma^*_{C-X}$ interaction estimated by eq 1.

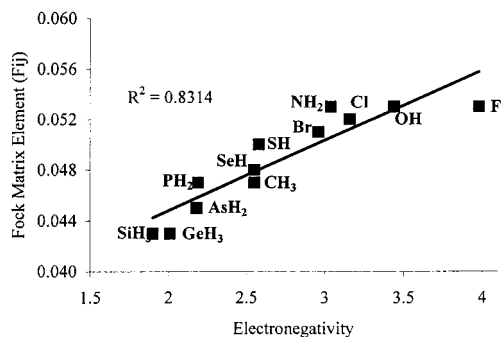


Figure 11. Correlation of Fock matrix element, F_{ij} , corresponding to $\sigma_{C-H} \rightarrow \sigma^*_{C-X}$ interaction with electronegativity of element X in substituted ethanes, CH_3CH_2X .

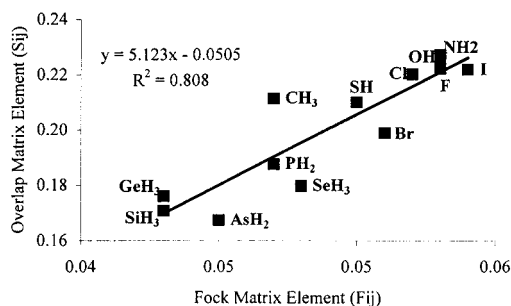


Figure 12. Correlation of overlap matrix element, S_{ij} , with the Fock matrix element, F_{ij} , corresponding to $\sigma_{C-H} \rightarrow \sigma^*_{C-X}$ interaction in substituted ethanes, CH_3CH_2X .

The results of this analysis are given in Figures 3 and 11. The two main terms controlling the magnitude of a $\sigma_i \rightarrow \sigma^*_j$ interaction are the difference in energy between the interacting orbitals (the $\Delta E = \epsilon_{\sigma^*} - \epsilon_{\sigma}$ term) and the magnitude of the Fock matrix element, F_{ij} (Figures 11 and 12), which varies in parallel to the overlap matrix element, S_{ij} , as expected from the Mulliken or Wolfsberg-Helmholtz approximations⁴⁹ (Figure 12). The F_{ij} term is roughly proportional to the electronegativity of X for all X throughout the periodic table (Figure 11). This can be explained by the favorable polarization of σ^* bonds when X is more electronegative (Figure 5).^{50,51,52} At the same time, the ΔE term changes in a more complicated way, and these

(48) Note that this assumption is not *always* valid. The E_{del} is estimated through a variational procedure and, if combined effects of several interactions are desired, E_{del} may differ from $E(2)$. These deviations are the most interesting when studying cooperativity between several interactions (I. V. Alabugin, manuscript in preparation).

(49) Mulliken, R. S. *Phys. Rev.* **1932**, *41*, 49. Wolfsberg, M.; Helmholtz, L. J. *Chem. Phys.* **1952**, *20*, 837. Hoffmann, R. J. *Chem. Phys.* **1963**, *39*, 1397. Carpenter, J. E.; Weinhold, F. A. *Theochem.-J. Mol. Struct.* **1988**, *169*, 41.

Table 2. NBO Analysis of Hyperconjugative Interactions in Disubstituted Ethanes, YCH_2CH_2X

| XCH_2CH_2Y | donor NBO | acceptor NBO | $E(2)$ kcal/mol | ΔE (au) | F_{ij} (au) |
|---------------|-----------------|-------------------|-----------------|-----------------|---------------|
| X = F Y = Cl | σ_{C-F} | σ^*_{C-Cl} | 2.27 | 1.02 | 0.043 |
| | σ_{C-Cl} | σ^*_{C-F} | 3.10 | 0.88 | 0.047 |
| X = Br Y = F | σ_{C-Br} | σ^*_{C-F} | 4.09 | 0.81 | 0.051 |
| | σ_{C-F} | σ^*_{C-Br} | 2.29 | 0.97 | 0.042 |
| X = Cl Y = Br | σ_{C-Cl} | σ^*_{C-Br} | 3.77 | 0.69 | 0.046 |
| | σ_{C-Br} | σ^*_{C-Cl} | 4.68 | 0.67 | 0.050 |

changes can explain the relative order of acceptor ability of C–Hal bonds.

Since the energy of the donor σ_{C-H} orbital changes only to a small extent in the above series of monosubstituted ethanes (Figure 2 in the Supporting Information), the energy gap, ΔE , is controlled mainly by the energy of the σ^*_{C-X} orbitals. The energies of σ^*_{C-X} orbitals decrease significantly when moving down the periodic table.⁵³ For example, the energy of the σ^*_{C-Br} orbital in bromoethane (0.0538 au at the B3LYP/6-31G** level) is significantly lower than the energy of the σ^*_{C-F} orbital in fluoroethane (0.2378 au) despite the higher electronegativity of fluorine. The σ^*_{C-X} energy lowering results in a decrease of the ΔE term, and since the interaction energy is inversely proportional to the ΔE term, the σ^*_{C-Br} orbital becomes a better σ acceptor than the σ^*_{C-F} orbital. A similar analysis can be performed for the other C–X bonds.

Competition between C–Hal Bonds as σ -Donors and σ -Acceptors in Dihaloethanes. Thus far, we have compared acceptor ability of two σ bonds C–X and C–Y using the energies of $\sigma_{C-H} \rightarrow \sigma^*_{C-X}$ and $\sigma_{C-H} \rightarrow \sigma^*_{C-Y}$ interactions in two different molecules, C_2H_5X and C_2H_5Y , using a third orbital (C–H) as a reference. This is an indirect way to do such a comparison. It might seem that direct *intramolecular* comparison of energies $\sigma_{C-Y} \rightarrow \sigma^*_{C-X}$ and $\sigma_{C-X} \rightarrow \sigma^*_{C-Y}$ interactions in disubstituted ethanes, XCH_2CH_2Y , is a better way to compare acceptor ability of two C–Hal bonds. An advantage is that the C–X and C–Y orbitals are in the same molecule, and they interact with each other directly. However, when $\sigma_{C-Y} \rightarrow \sigma^*_{C-X}$ energies in disubstituted ethanes are compared, the apparent order of acceptor ability is changed and data from Table 2 give an impression that the C–F bond is a better acceptor than the C–Cl and C–Br bonds. What is the reason?

In the second approach, the acceptor abilities of σ^* orbitals (σ^*_{C-Y} and σ^*_{C-X}) are compared relative to different donor orbitals (σ_{C-X} and σ_{C-Y}), and it is the difference in the *donor* properties of these orbitals that is the controlling factor. For example, the larger energy of the $\sigma_{C-Cl(Br)} \rightarrow \sigma^*_{C-F}$ interaction compared to that of $\sigma_{C-F} \rightarrow \sigma^*_{C-Cl(Br)}$ interaction stems from

(50) Sigma is polarized towards more electronegative substituent, but σ^* is polarized towards in the mirror way towards the less electronegative of the atoms that form the bond in question. Hence, when X is more electronegative, the coefficient on carbon in σ^* is increasing. This increases the overlap with the donor σ CH orbital and thus the magnitude of the interaction. These trends are illustrated by the plots of F_{ij} vs $E(-)$ and F_{ij} vs S_{ij} .

(51) The C–F σ bonds are more polarized towards the halogen than C–Cl and C–Br bonds. As a consequence, since polarization of the σ^* bonds mirrors polarization of the σ bond, a σ^*_{C-F} bond has larger coefficient on carbon as compared to the corresponding σ^*_{C-Cl} and σ^*_{C-Br} bonds.

(52) The fact that the overlap is not decreasing dramatically when X is a second or third row element might seem surprising. However, the overlap is controlled by the hybrid orbital on carbon. The role of X is mediated by this orbital and is limited to changing polarization and energy of the C–X bond.

(53) This order is consistent with that suggested in Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R. I.; Bernardi, F. *Top. Curr. Chem.* **1977**, *70*.

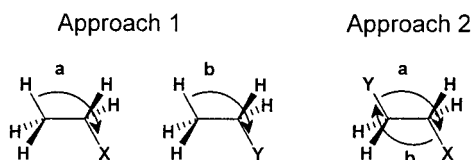


Figure 13. Two alternative approaches for comparing acceptor ability of C-X and C-Y bonds.

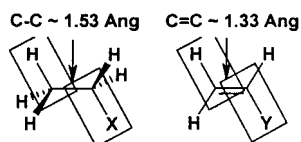


Figure 14. Vicinal $\sigma_{C-H} \rightarrow \sigma^*_{C-X}$ interactions in ethenes. The boxes around C-H and C-X bonds illustrate the difference in the overlap (the difference is exaggerated for illustrative purposes).

the higher donor ability of $\sigma_{C-Cl(Br)}$ bonds and not from the higher acceptor ability of σ^*_{C-F} bond.

When the acceptor abilities of the C-F and the C-Cl orbitals are compared toward the same donor, C-Br orbital, then the order of acceptor ability is C-Cl > C-F as in monosubstituted ethanes. Analogously, the order of acceptor ability toward a C-F orbital is C-Br > C-Cl, and the order of acceptor abilities toward the C-Cl orbital is C-Br > C-F. Hence, all of the trends in the relative acceptor ability of C-Hal bonds in monohaloethanes are maintained when the donor orbital is a C-Hal bond as long as the *same* C-Hal bond is used for such a comparison. The only significant difference is that the energies of hyperconjugative interactions are weaker since C-Hal bonds are weaker donors than C-H bonds.

σ Acceptor Ability of C-X Bonds in Ethenes. So far, we have derived a simple and clear picture of acceptor ability of σ bonds as being controlled by electronegativity in periods and energy of σ^* orbitals in groups. Unfortunately, this simple picture, which works well for substituted ethanes, is not directly transferable to substituted ethenes. This observation is not surprising because stereoelectronic effects depend on a number of factors, and the net changes in hyperconjugative energies can follow a complex pattern. This complexity is illustrated by the results below. In our opinion, these results stress the need for a *quantitative* estimation of hyperconjugative interactions in every specific case. Without such an estimation, it is dangerous to transfer stereoelectronic effects from one molecule to another.

As we have discussed above, the acceptor ability of a C-X bond mainly depends on two factors, F_{ij} and ΔE , both of which decrease when going down a group. Since the F_{ij} term is in the numerator of eq 1 and the ΔE term is in the denominator, these changes influence the energy of $\sigma_{C-H} \rightarrow \sigma^*_{C-X}$ interactions in opposite directions. In *ethanes*, the ΔE term is more important and its variations control the relative order of acceptor ability of C-X bonds in groups. In *ethenes*, the role of the F_{ij} term significantly increases. Figure 14 illustrates a very simple reason for this increase. Double bonds are shorter than single bonds, and when the interacting orbitals are connected by a C=C bridge, the overlap between the σ and σ^* orbitals increases. The F_{ij} term which carries exponential dependence on the distance increases in parallel.

The increased importance of the F_{ij} term leads to two significant changes in the relative magnitude of $\sigma_{C-H} \rightarrow \sigma^*_{C-X}$ interactions. First, the energy of the interactions is dramatically

Table 3. NBO Analysis of Hyperconjugative Interactions in Substituted Ethenes, C_2H_3X

| donor orbital | acceptor orbital | $E_{del},^a$ kcal/mol | $E(2),^b$ kcal/mol | ΔE (au) | F_{ij} (au) | σ^*_{C-X} polarization, ^c % |
|----------------|--------------------------|--------------------------|-----------------------|--------------------|------------------|--|
| σ_{C-H} | σ^*_{C-H} | 5.18 | 4.35 | 1.00 | 0.059 | 39.04 |
| σ_{C-H} | σ^*_{C-F} | 8.66 | 8.05 | 0.80 | 0.072 | 73.06 |
| σ_{C-H} | σ^*_{C-Cl} | 9.67 | 8.80 | 0.68 | 0.069 | 55.59 |
| σ_{C-H} | σ^*_{C-Br} | 9.58 | 8.80 | 0.62 | 0.066 | 52.18 |
| σ_{C-H} | $\sigma^*_{C-OH(1)}$ | 8.78 | 8.10 | 0.88 | 0.075 | 67.75 |
| σ_{C-H} | $\sigma^*_{C-OH(2)}$ | 8.16 | 7.54 | 0.87 | 0.072 | 67.70 |
| σ_{C-H} | $\sigma^*_{C-O^-}$ | 6.18 | 5.64 | 1.08 | 0.070 | 64.63 |
| σ_{C-H} | $\sigma^*_{C-OSiH_3(1)}$ | 9.42 | 8.67 | 0.90 | 0.079 | 68.62 |
| σ_{C-H} | $\sigma^*_{C-OSiH_3(2)}$ | 8.69 | 8.00 | 0.89 | 0.075 | 68.44 |
| σ_{C-H} | $\sigma^*_{C-OCH_3(1)}$ | 9.33 | 8.61 | 0.89 | 0.078 | 68.14 |
| σ_{C-H} | $\sigma^*_{C-OCH_3(2)}$ | 8.40 | 7.76 | 0.89 | 0.074 | 68.01 |
| σ_{C-H} | $\sigma^*_{C-OCF_3(1)}$ | 10.70 | 9.90 | 0.84 | 0.081 | 69.46 |
| σ_{C-H} | $\sigma^*_{C-OCF_3(2)}$ | 8.89 | 8.26 | 0.83 | 0.074 | 69.32 |
| σ_{C-H} | $\sigma^*_{C-OCOCH_3}$ | 10.98 | 10.15 | 0.84 | 0.083 | 69.45 |
| σ_{C-H} | $\sigma^*_{C-OCOCF_3}$ | 11.19 | 10.33 | 0.83 | 0.083 | 70.12 |
| σ_{C-H} | $\sigma^*_{C-OSO_2CF_3}$ | 9.35 | 8.67 | 0.81 | 0.075 | 70.32 |
| σ_{C-H} | $\sigma^*_{C-OH_2^+}$ | 12.19 | 11.24 | 0.66 | 0.077 | 75.35 |
| σ_{C-H} | $\sigma^*_{C-SH(1)}$ | 8.93 | 8.04 | 0.71 | 0.068 | 47.43 |
| σ_{C-H} | $\sigma^*_{C-SH(2)}$ | 8.18 | 7.40 | 0.71 | 0.065 | 47.52 |
| σ_{C-H} | $\sigma^*_{C-SCH_3(1)}$ | 8.70 | 7.88 | 0.73 | 0.068 | 46.43 |
| σ_{C-H} | $\sigma^*_{C-SCH_3(2)}$ | 7.80 | 7.10 | 0.73 | 0.064 | 46.34 |
| σ_{C-H} | $\sigma^*_{C-SCF_3(1)}$ | 9.58 | 8.68 | 0.71 | 0.070 | 47.60 |
| σ_{C-H} | $\sigma^*_{C-SCF_3(2)}$ | 8.05 | 7.33 | 0.72 | 0.065 | 47.43 |
| σ_{C-H} | $\sigma^*_{C-S^-}$ | 5.075 | 4.59 | 0.84 | 0.056 | 42.65 |
| σ_{C-H} | $\sigma^*_{C-SH_2^+}$ | 10.29 | 9.25 | 0.64 | 0.069 | 53.55 |

^a Energy of $\sigma_{C-H} \rightarrow \sigma^*_{C-X}$ interaction calculated by deletion Fock matrix element between these two orbitals. ^b Energy of $\sigma_{C-H} \rightarrow \sigma^*_{C-X}$ interaction estimated from eq 1. ^c Square of orbital coefficient on carbon in the σ^*_{C-X} NBO.

increased (up to 80% of its value in corresponding ethanes). Second, the order of acceptor ability in groups becomes different. For example, for halogens the general order of acceptor ability is F < Cl > Br.⁵⁴ A similar trend is observed for chalcogens.

Since the magnitude of stereoelectronic effects and the role of the F_{ij} term are increased in ethenes, we examined the possibility that substituted ethenes might show greater sensitivity to rather subtle changes in the F_{ij} term. Such changes, achieved by changing the polarization of the C-X bond using different substituents at X are well suited for NBO analysis. The next section discusses the sensitivity of acceptor ability of a C-O bond to changes in substitution on oxygen.

Modification of the Acceptor Ability of C-X Bonds in Ethenes by Substitution. Since stereoelectronic effects that involve oxygen-containing functional groups are of primary interest for understanding and control of numerous organic reactions,^{1,5a,55,56} we decided to investigate effect of substitution on the acceptor ability of C-O bonds.

The effects of substituents are dramatic; the acceptor ability of C-O bonds can be more than doubled by appropriate substitution (Table 3). The weakest acceptor is, as expected, the C-O bond in an enolate anion (XR = O⁻), followed by XR = OH, OMe, and OSiH₃.⁵⁷ When XR = OCF₃ and OSO₂-CF₃, the acceptor ability of C-X bonds reaches that of C-Hal

(54) Note, however, that the difference in the acceptor ability of the σ^*_{C-Cl} and σ^*_{C-Br} bonds is not large and it might be sensitive to the nature of substitution and the level of theory applied.

(55) A fascinating example of hyperconjugative interaction with σ^*_{C-O} orbital that controls conformational equilibrium in organolithium compounds: Cohen, T.; Lin, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 1130. See also *Tetrahedron Lett.* **1989**, *30*, 3011 and *J. Chem. Soc., Chem. Commun.* **1985**, 894.

(56) Romero, J. A. C.; Tabacco, S. A.; Woerpel, K. A. *J. Am. Chem. Soc.* **2000**, *122*, 168. Larsen, C. H.; Ridgway, B. H.; Shaw, J. T.; Woerpel, K. A. *J. Am. Chem. Soc.* **1999**, *121*, 12208.

Table 4. NBO Analysis of $n_N \rightarrow \sigma^*_{C-X}$ Hyperconjugative Interactions in α -Halogen Amines

| H ₂ NCH ₂ X | donor NBO | acceptor NBO | $E(2)$, kcal/mol | ΔE (au) | F_{ij} (au) |
|-----------------------------------|--------------|------------------|----------------------|--------------------|------------------|
| X = H | n_N | σ^*_{C-X} | 8.07 | 0.74 | 0.069 |
| X = F | n_N | σ^*_{C-X} | 20.49 | 0.52 | 0.092 |
| X = Cl | n_N | σ^*_{C-X} | 27.55 ⁵⁸ | 0.37 | 0.090 |
| X = Br | n_N | σ^*_{C-X} | 29.87 | 0.33 | 0.088 |

bonds, and when XR = OCOCH₃ or OCOCF₃, the XR group becomes a stronger σ acceptor. The maximum acceptor ability is displayed by C–O bonds in a protonated enol (XR = OH₂⁺) which is a very strong σ acceptor—much stronger than the corresponding C–Hal bonds. The reason for such a strong influence of substitution on oxygen on the acceptor ability of C–O bond is a favorable combination of changes in F_{ij} and ΔE terms. Both of these changes are favorable when OR becomes a stronger acceptor because the energy of the σ^*_{C-X} orbitals decreases and the polarization of C–X bonds increases. The relative importance of these two factors can be estimated from eq 1. For example, the energy of a $\sigma_{C-H} \rightarrow \sigma^*_{C-O(CF_3)}$ interaction is 1.3 kcal higher than that of a $\sigma_{C-H} \rightarrow \sigma^*_{C-O(CH_3)}$ interaction. Forty percent of this increase in the hyperconjugative energy comes from the change in the ΔE term, whereas the changes in the F_{ij} term (favorable polarization of C–X bond) account for the other 60%. Interestingly, protonation at oxygen increases the acceptor ability of the OH group mainly through the decrease in the energy of σ^*_{C-O} orbital (a field effect?). In a similar fashion, the decrease of acceptor ability of σ^*_{C-O} orbital upon deprotonation mainly stems from the increase in the σ^*_{C-O} energy. Note that similar trends are also observed for C–S bonds, but the changes in the σ^*_{C-S} energies are much smaller.

Another interesting observation is that there are several conformations differing in the relative position of oxygen lone pairs toward the C=C bond. The acceptor abilities of C–O bonds in these conformations are noticeably different, and these differences become higher when the electronegativity of the substituent at oxygen increases. We will discuss the origin and importance of these effects below in the section dealing with C-chalcogen bonds.

Nitrogen Lone Pair as a Donor. The C–H bond is a mediocre σ donor. It is interesting to compare the acceptor ability of C–Hal bonds toward a considerably better donor, a lone pair at nitrogen. The NBO data show a noticeable increase in the energy of the hyperconjugative interactions (Table 4). Both the high energy of the nonbonding orbital (decreasing the ΔE term) and its higher polarizability (increasing the F_{ij} term) account for enhanced energy of the interaction. Interestingly, relatively subtle differences in the hyperconjugative energies become more pronounced and chemically significant. The increased energy of stereoelectronic interactions when a stronger donor is present is in excellent agreement with the increased reactivity of the C–Hal bonds in α -halogen amines.

Carbanion as a Donor. A carbanionic center is even a better donor than a lone pair on nitrogen. Therefore, the hyperconjugative donor–acceptor interactions in β -halogen anions are expected to be very strong. Indeed, when we attempted to estimate these effects, we found that in the course of geometry optimization, the anions were undergoing barrierless elimination

(57) Aped, P.; Apeloig, Y.; Ellencweig, A.; Fuchs, B.; Goldberg, I.; Karni, M.; Tartakovsky, E. *J. Am. Chem. Soc.* **1987**, *109*, 1486.

Table 5. NBO Analysis of Hyperconjugative Interactions in Substituted Hydrocarbons, C₂H₅X^a

| donor orbital | acceptor orbital | $E_{del.}$ kcal/mol | $E(2)$, kcal/mol | ΔE (au) | F_{ij} (au) | % of electron density at X in σ_{C-X} |
|------------------|--------------------------|------------------------|----------------------|--------------------|------------------|---|
| σ_{C-H} | $\sigma^*_{C-CH_3}$ | 3.38 | 3.12 | 0.88 | 0.047 | 49.94 |
| σ_{C-H} | $\sigma^*_{C-CH_2Me}$ | 3.31 | 3.08 | 0.88 | 0.047 | 50.00 |
| σ_{C-H} | $\sigma^*_{C-CHMe_2}$ | 4.23 | 3.94 | 0.86 | 0.052 | 49.96 |
| σ_{C-H} | $\sigma^*_{C-CMe_3}$ | 3.93 | 3.69 | 0.86 | 0.051 | 50.54 |
| σ_{C-H} | $\sigma^*_{C-vinyl(1)}$ | 3.76 | 3.48 | 0.93 | 0.051 | 49.32 |
| σ_{C-H} | $\sigma^*_{C-vinyl(2)}$ | 3.21 | 2.98 | 0.93 | 0.047 | 49.48 |
| σ_{C-H} | $\sigma^*_{C-acetylene}$ | 3.51 | 3.19 | 0.97 | 0.050 | 49.99 |
| σ_{C-H} | $\sigma^*_{C-CF_3}$ | 3.59 | 3.45 | 0.85 | 0.049 | 48.92 |

^a The data are for C_s conformers.

of halogen anions with formation of an alkene molecule—a reaction that is analogous to the second step of a E1cB elimination.⁵⁹ These results illustrate the increased importance of hyperconjugative interactions in anionic species and show how an extremely strong hyperconjugative interaction (a resonance arrow) is “transformed” into a chemical reaction (a reaction arrow).

Bond cleavage during geometry optimizations of β -halogen anions was observed earlier.^{60,61} The observation that all of the C–Hal bonds were essentially broken in β -halogen carbanions is in good agreement with a suggestion of Saunders that the E2 and E1cB(irrev) mechanisms might be distinguished by observation of a leaving-group isotope effect or element effect only in the former but not in the latter case.⁶²

On the basis of the elegant work of Lambert et al.,⁶³ we anticipated that the acceptor ability of C–Hal bonds could be estimated by comparing the stability of the two isomers of a γ -halogen cyclohexyl anion with either pseudoaxial or pseudoequatorial orientation of the anionic p-orbital at carbon. In this case, interaction between the anionic p-orbital and the C–X bond can be classified as double hyperconjugation. Remarkably, even when the donor and acceptor are separated by an extra σ bridge, the acceptor ability of the C–Cl bond is so large that a Grob fragmentation (Figure 15) is observed directly in the process of geometry optimization when the anionic p-orbital occupies the equatorial position optimal for the double hyperconjugation. The fragmentation is not observed when the acceptor is a C–F bond or when the anionic orbital is axial. Again, this observation illustrates how a rather small difference in acceptor ability of σ bonds is accentuated in highly active reactive intermediates.

(58) It is interesting to compare this value with the energy of $n_N \rightarrow \sigma^*_{Si-Cl}$ interaction (21 kcal/mol). Fleischer, H.; Brain, P. T.; Ranklin, D. W. H.; Robertson, H. E.; Bühl, M.; Thiel, W. *J. Chem. Soc., Dalton Trans.* **1998**, 593.

(59) For Br and Cl, as the result of the optimization, the halogenide anions migrated to the ethylene plane forming C–H...Hal hydrogen bonds with the vinyl hydrogen atoms. Interestingly, the fluoride anion behaved differently and remained weakly coordinated to the p-system. (See Supporting Information).

(60) Schleyer, P. v. R.; Kos, A. *Tetrahedron* **1983**, *39*, 1141–1150.

(61) (a) Bach, R. D.; Badger, R. C.; Lang, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2845–2848. (b) Roy, M.; McMahon, T. B. *Can. J. Chem.* **1985**, *63*, 708–715. (c) Merrill, G. N.; Gronert, S.; Kass, S. R. *J. Phys. Chem. A* **1997**, *101*, 208–218. (d) Apeloig, Y. *J. Chem. Soc. Chem. Comm.* **1981**, 396–398. (e) Holtz, D.; Streitwieser, A.; Jesaitis, R. G. *Tetrahedron Lett.* **1969**, 4529–4532. (f) Hoffmann, R.; Radom, L.; Pople, J. A.; Schleyer, P. v. R.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 6221–6223.

(62) Saunders, W. H., Jr. *J. Org. Chem.* **1999**, *64*, 861. Saunders, W. H., Jr. *J. Org. Chem.* **1997**, *62*, 244–245. Saunders, W. H., Jr. *Acc. Chem. Res.* **1976**, *8*, 19–26.

(63) Lambert, J. B.; Ciro, S. M. *J. Org. Chem.* **1996**, *61*, 1940. See also Lambert, J. B.; Salvador, L. A.; So, J. H. *Organometallics* **1993**, *12*, 697. Adcock, W.; Kristic, A. R.; Duggan, P. J.; Shiner, V. J.; Coope, J.; Ensinger, M. *W. J. Am. Chem. Soc.* **1990**, *112*, 3140.

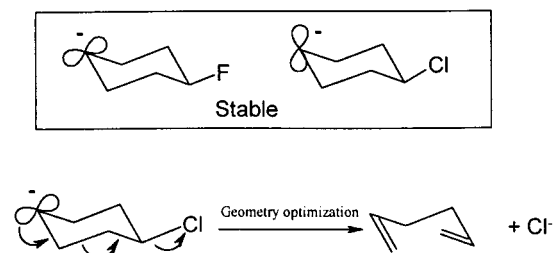


Figure 15. Difference in stability of γ -halogenocyclohexyl anions (B3LYP/6-31G** geometry optimization).

Acceptor Ability of C–X Bonds in Groups IVa–VIa. So far, we have concentrated our discussion on the general trends in acceptor ability using mainly C–Hal σ bonds as an illustration. In addition to being among the strongest σ acceptors, the C–Hal bonds have several features that simplify general discussion. First, there are no complications arising from the presence of different conformers. Second, all of the C–Hal bonds are polarized toward halogen, and there are no changes in the direction of bond polarization when moving down the group. In general, the situation is more complex in the other groups (except for group IVa), and there are interesting features related to this complexity. We will comment briefly about acceptor ability in different groups of the periodic table below.

Group IVa. For this group, the conformational equilibrium is of little importance due to the symmetry of XH_3 moieties. We have used the all-staggered conformations of propane, ethylsilane, and ethylgermane (Figure 3 in the Supporting Information section).

Structural changes in EtX molecules within this group are relatively minor. When going down the group, the central C–C bond becomes longer and the C–H bonds antiperiplanar to the C–X are also slightly elongated but to a smaller extent.

Where X is a group IV element, the C–X bonds are weaker σ acceptors as compared with the C–X bonds when X is from groups V–VII. Note also that the difference between acceptor properties of C–X bonds in this group is the smallest. When moving down the group from C to Ge, the acceptor ability of the $\sigma^*_{\text{C-X}}$ orbitals increases only by 0.4 kcal (compare with the increase of 1.2 kcal for C–halogen bonds). The C–Si and C–Ge bonds are only marginally better acceptors than the C–C bond since the favorable decrease in the energy of σ^* orbitals is mostly compensated by the unfavorable polarization of these orbitals. On the other hand, changes in the donor ability of the C–X bonds are more pronounced, and donor properties of $\sigma_{\text{C-X}}$ bond increase significantly when moving down the group.⁶⁴

Comparison of energies of the $\sigma_{\text{C-H}} \rightarrow \sigma^*_{\text{C-H}}$ interaction in ethane with the energy of the $\sigma_{\text{C-H}} \rightarrow \sigma^*_{\text{C-C}}$ interaction in propane shows that the C–C bond is a slightly better acceptor than the C–H bond. At the same time, the relative energies of the $\sigma_{\text{C-H}} \rightarrow \sigma^*_{\text{C-H}}$ interaction in ethane and the $\sigma_{\text{C-C}} \rightarrow \sigma^*_{\text{C-H}}$ interaction in propane indicate that $\sigma_{\text{C-H}}$ orbital is a slightly better donor. Note, however, that the difference is not large, and it is likely that donor substitution can change this pattern

(64) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677. White, J. M.; Robertson, G. B. *J. Org. Chem.* **1992**, *57*, 4638. Kuan, Y. L.; White, J. M. *J. Chem. Soc., Chem. Commun.* **1994**, 1195. Green, A. J.; Kuan, Y. L.; White, J. M. *J. Org. Chem.* **1995**, *60*, 2734. Chan, V. Y.; Clark, C.; Giordano, J.; Green, A. J.; Karalis, A.; White, J. M. *J. Org. Chem.* **1996**, *61*, 5227. Lambert, J. B.; Wang, G. T.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 9, 7838. Nguyen, K. A.; Gordon, M. S.; Wang, G.-T.; Lambert, J. B. *Organometallics* **1991**, *10*, 2798.

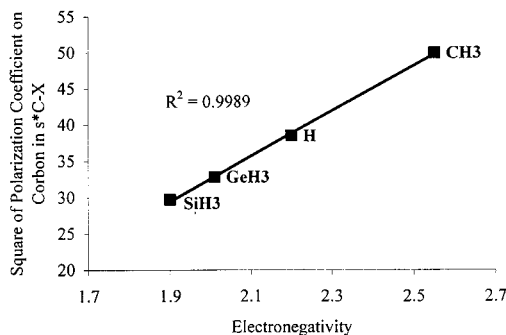


Figure 16. Correlation of polarization of C–H, C–C, C–Si, and C–Ge σ bonds with electronegativity. (See Figure 5 for the general correlation.)

and make a C–C bond a better donor than a C–H bond. Hence, the question of relative donor ability of C–C and C–H bonds has to be reexamined in every specific case when it is important.

Because of the lower energy of the $\sigma^*_{\text{C-Si}}$ orbital, a $\sigma_{\text{C-Si(H3)}}$ bond despite being a slightly better donor than a $\sigma_{\text{C-H}}$ bond is, at the same time, a slightly better acceptor. We will see another manifestation of this phenomenon in acceptor ability for C–P bonds (vide infra). These results are in a good agreement with the results of Hargittai et al.,⁶⁵ who suggested that the surprisingly similar Si–C bond length in tetramethylsilane and tetraphenyl silane arises from “a delicate balance of subtle stereoelectronic effects” and that Si–C is a slightly stronger acceptor than donor toward the antiperiplanar C–H bond.⁶⁶

Germanium is more electronegative than silicon (Pauling electronegativities of 2.01 vs 1.9). It is one of a few examples when an element from the IVth period is more electronegative than its analogue from the IIIrd period. It is remarkable how accurately this effect is reflected in the NBO analysis of polarization of the corresponding σ bonds (Figure 16). This is yet another example of the high reliability of the NBO method in the analysis of molecular structures.

We also compared the acceptor abilities of C–C bonds when the γ -carbon is primary, secondary, tertiary, or quaternary. For simplicity, we have considered only the C_s conformers of the model compounds (Table 5). The changes in acceptor ability are noticeable—methyl substitution increases the acceptor ability of the C–C bonds although not monotonically. This dependence is consistent with the observation that methyl is an inductively withdrawing group relative to hydrogen.⁶⁷ The changing hybridization of the γ -carbon is also significant. Finally, introduction of electronegative substituents at the γ -carbon increases the acceptor ability of the C–C bond, but the difference is surprisingly small.

Group Va. C–X bonds in this group are noticeably better acceptors than those discussed earlier mainly due to the increased bond polarization (increase in the F_{ij} term). Discussion of acceptor properties of C–X bonds where X is a group Va element is complicated by the presence of two conformers with either gauche- or anti-orientation of the heteroatom lone pair relative to the C–C bond. We will refer to these conformations as “gauche” and “anti”.⁶⁸ For ethylamine, the latter conformation is 0.5 kcal/mol more stable due to the larger energy of the $n_{\text{N}} \rightarrow \sigma^*_{\text{C-C}}$ interaction vs the energy of $n_{\text{N}} \rightarrow \sigma^*_{\text{C-H}}$ interaction

(65) Campanelli, A. R.; Ramondo, F.; Domenicano, A.; Hargittai, I. *J. Phys. Chem. A* **2001**, *105*, 5933.

(66) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434.

(67) Coolidge, M. B.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 2298.

(8.3 vs 7.7 kcal/mol, B3LYP/6-31G**, NBO E(2) energy). For ethylphosphine, the difference between the two conformations is essentially the same (0.6 kcal), and the energies of $n_P \rightarrow \sigma^*_{C-C}$ and $n_P \rightarrow \sigma^*_{C-H}$ interactions in the two conformers are 3.2 and 2.3 kcal/mol, respectively.

The lengths of the C–C, C–X, and C–H bonds (antiperiplanar to the C–X bonds) in the two conformers are quite different. The C–X bonds are shorter for the anticonformer in accord with the higher importance of $n_X \rightarrow \sigma^*_{C-C}$ interactions increasing double bond character in the C–X moiety. The C–H bonds antiperiplanar to the C–X bonds are slightly longer for the anticonformer. Interestingly, the relative order of C–C bond lengths in the two conformers is changed when going from N to P; the C–C bond is longer in the anticonformer in ethylamine but, it is shorter in the anticonformer of ethylphosphine. This difference can be attributed to the lesser importance of the $n_X \rightarrow \sigma^*_{C-C}$ interaction for phosphorus—a consequence of the phosphorus lone pair being a poor donor as compared with a nitrogen lone pair. Noteworthy are the recent similar conclusions of Carballeira et al. about the donor ability of phosphorus lone pairs.⁶⁹

Interestingly, the $\sigma_{C-H} \rightarrow \sigma^*_{C-X}$ interaction is 0.5–0.6 kcal/mol stronger in the conformation with antiorientation of the lone pair. This difference results from the larger value of the F_{ij} term for the “anti” conformation (note, however, that the C–X bond polarization in the two conformers remains almost the same). Interestingly, a similar conformational dependence of acceptor ability of C–X bonds is observed for carbon–chalcogen bonds. These observations have important implications for the analysis of conformationally flexible systems where the different acceptor ability of σ_{C-X} bonds in different conformers has to be taken into consideration.

The comparison of $\sigma_{C-H} \rightarrow \sigma^*_{C-P}$ and $\sigma_{C-P} \rightarrow \sigma^*_{C-H}$ interactions is quite interesting since phosphorus⁷⁰ has essentially the same electronegativity as hydrogen. As the result, polarization and donor ability of the C–PH₂ bond are essentially the same as that of the C–H bond. Despite this fact, the σ_{C-PH_2} bond is a noticeably better σ acceptor because of the lower energy of σ^*_{C-P} orbital.

Obviously, the acceptor ability of C–X bonds can be modified by changing the nature of functional group associated with atom X. For example, the C–N₂⁺ bond is a very strong acceptor, stronger than C–Hal bonds (Table 1).

Group VIa. The high acceptor ability of C–O bonds is well-known. It was extensively discussed as part of the stereo-electronic rationale for the anomeric effect (preference for an electronegative substituent to occupy an axial position at an anomeric carbon). The question of acceptor ability of C–S bonds is less well understood despite several intriguing reports. For example, in a thorough NBO study comparing the group 16 CH₂(XH)₂ (X = O, S, Se, and Te) systems, Salzner and Schleyer¹⁸ found that the $p_y(X) \rightarrow \sigma^*_{C-X}$ interactions make the largest contributions (among many) and decrease in the O > S > Se > Te order. However, this change might be due to a

decrease in the p-donating ability of the lone pairs or to a decrease in the acceptor ability of the σ^*_{C-X} orbitals, or both, and this has not been elucidated explicitly. Nevertheless, the decrease in acceptor ability was implicated by later work of the Schleyer group,⁷¹ which showed that the π donation of the heavier elements is not less effective than from their first row counterparts.

The order of acceptor ability of C–X bonds in chalcogens does not show such a monotonic increase when going down the group as in the case of C–halogen bonds. The reason for this is that the unfavorable changes in the F_{ij} elements are too large for C–Se bond. As a result, although the acceptor ability of C–S and C–Se bonds is almost the same, the C–S bond is a (marginally) better acceptor.

As in the case of carbon–nitrogen bonds, the acceptor ability of C–chalcogen bonds strongly depends on the relative orientation of the lone pairs. The discussion of aliphatic oxygen-containing compounds is complicated by the complex mixture of $n_O \rightarrow \sigma^*$ interactions with participation of both of the lone pairs and C–C and C–H bonds. The situation is simpler in the vinyl analogues where the p-lone pair on oxygen is parallel to the π -system and, thus, there are only two conformations that differ in the orientation of the in-plane sp^y lone pair. The differing acceptor abilities of the σ^*_{C-O} orbital in the two conformers can be explained by changes in molecular geometry and electron density at the carbon and oxygen atoms due to the “anomeric” $n_O \rightarrow \sigma^*_{C-C}$ interaction in the anti-conformer. This trend is general for all substituents on oxygen that we have studied including R = H, Me, CF₃, OCOF₃, and OCOCH₃.

Similar effects were found for C–S bonds. Interestingly, although C–S(H) is a better acceptor than C–O(H), when electronegativity of substituents on the chalcogen atoms is increasing, the role of F_{ij} term increases also, and the relative acceptor ability of C–O(R) and C–S(R) bonds may change.

The other interesting feature of C–S bonds is that their σ acceptor ability is anisotropic; it is important which end of a C–S bond participates in a hyperconjugative interaction. Earlier, we have found this effect in 1,3-dithiane, where the C3–S2 bond is an excellent acceptor in the direction of C5 but a poor acceptor in the direction of C1 (Figure 1).^{72,73} We have attributed this effect to distortion of the chair conformation by long C–S bonds. In this paper, we have investigated this effect in acyclic model compounds: methyl ethyl ether, methyl ethyl sulfide, and methyl ethyl selenide. Remarkably, although the effect is weakened, it does not disappear (Figure 19). The difference is smallest for oxygen although, even in this case, the C–O bond is a still noticeably better acceptor than the O–C bond. In this case, the difference can be explained readily by the higher electronegativity of oxygen resulting in polarization of the σ^*_{C-O} orbital toward carbon which increases the acceptor properties on the carbon end. On the other hand, the difference becomes

(68) The “anti” conformation is, in fact, a syn conformation if positions of the N–H bonds is considered. However, we will use the “anti” notation to stress that this is the orientation of the lone pair which is controlling the relative energies of the two conformers.

(69) For analysis of anomeric effect in CH₂(XH₂)(2) (X = N, P, As) compounds, see: Carballeira, L.; Perez-Juste, I. *J. Phys. Chem. A* **2000**, *104*, 9362.

(70) For the role of hyperconjugation in breaking and formation of C–P bonds, see: Graczyk, P. P.; Mikolajczyk, M. *J. Org. Chem.* **1996**, *61*, 2995.

(71) Kapp, J.; Schade, C.; El-Nahas, A.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2236.

(72) This effect can explain the observation of proton loss at C5 position in 1,3-dithiane in gas phase and formation of fragmentation products. Bartmess, J. E.; Hays, R. L.; Khatri, Misra, R. N.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 4746. Fisher, C. L.; Kahn, S. D.; Hehre, W. J.; Caserio, M. C. *J. Am. Chem. Soc.* **1989**, *111*, 7379.

(73) For an important seminal contribution to the role of acceptor ability of C–S bonds in stabilizing carbanions where anisotropic properties of the C–S bonds were considered, see: Borden, W. T.; Davidson, E. R.; Andersen, N. H.; Denniston, A. D.; Epiotis, N. D. *J. Am. Chem. Soc.* **1978**, *100*, 1604.

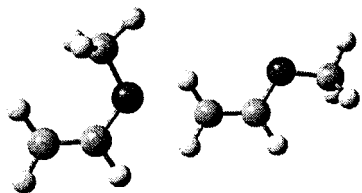


Figure 17. Two conformations of methyl vinyl ether.

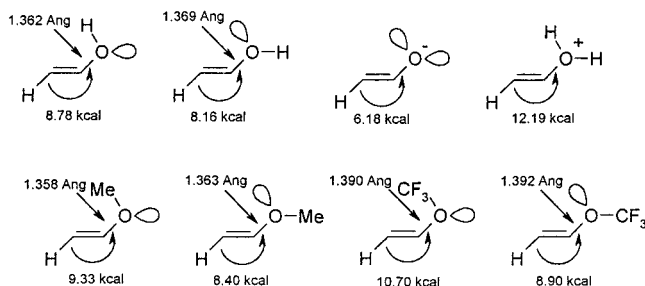


Figure 18. Substitutional and conformational effects on the energy $\sigma_{C-H} \rightarrow \sigma^*_{C-O}$ interaction in enols, vinyl ethers, and related compounds (p lone pair is perpendicular to the molecular plane and is not shown for clarity).

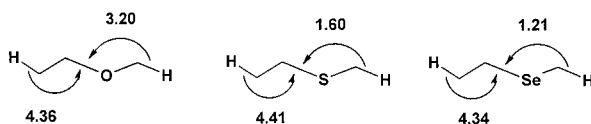


Figure 19. Comparison of acceptor ability (E_{del} energies) of C–X bonds in different directions.

very large for carbon–sulfur bonds where a remarkable anisotropic pattern of acceptor ability is found. The C–S bonds can be regarded as a one-directional acceptor. The energy of the $\sigma_{C-H} \rightarrow \sigma^*_{S-C}$ interaction is almost the same as the $\sigma_{S-C} \rightarrow \sigma^*_{C-H}$ interaction and, thus, the net donor/acceptor ability of S–C bond on its sulfur end is almost zero. The trend for carbon–chalcogen bonds to be good acceptors at their carbon end but poor acceptors at their chalcogen (X) end is further increased for selenium.

The large difference in acceptor ability of C–X bonds on their X and C ends can explain the myth of lower acceptor ability of C–X bonds when X is an element from a higher period. Although remarkable, this effect is not unexpected since carbon and sulfur (selenium) ends of C–S(Se) bond display different overlap with antiperiplanar C–H orbitals (Figure 20).⁷⁴ We believe that this effect can find application in the design of electron-transfer bridges with fast electron transfer in one direction but slow transfer back in the back direction. Such systems can find applications in the design of molecular diodes (molecular rectifiers⁷⁵). We plan to investigate this phenomenon further in future work.

Conclusion

For the first time, the σ acceptor properties of a large set of C–X bonds where X is a main group element from groups IVA to VIIa of the first four periods were systematically studied using

(74) Another potentially important factor is that the bond dipoles of the C–S and S–C bonds are oriented in opposite directions. Juaristi, E.; Cuevas, G. *Tetrahedron Lett.* **1992**, *33*, 1847. Juaristi, E.; Cuevas, G.; Vela, A. *J. Am. Chem. Soc.* **1994**, *116*, 5796.

(75) Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* **1974**, *29*, 277. Scheib, S.; Cava, M. O.; Baldwin, J. W.; Metzger, R. M. *J. Org. Chem.* **1998**, *63*, 1198. Majumder, C.; Mizuseki, H.; Kawazoe, Y. *J. Phys. Chem. A* **2001**, *105*, 9454.

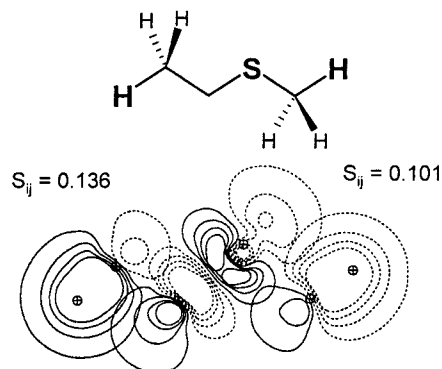


Figure 20. Different overlap (S_{ij}) of opposite ends of σ^*_{S-C} orbital with two antiperiplanar σ_{C-H} orbitals.

NBO analysis. The acceptor ability of σ bonds in monosubstituted ethanes increases when going to the end of a period and down the group. Enhancement of the acceptor ability of σ bonds within periods parallels the increase in electronegativity of X, whereas augmentation of acceptor ability in groups is opposite to the changes in electronegativity of X and is a consequence of the lowering of energy of σ^*_{C-X} orbitals.

The general trends in acceptor ability of σ bonds result from a rather complex combination of several effects which is well illustrated by different trends observed in monosubstituted ethenes. When the bridge carbon–carbon bond becomes shorter, the role of electronegativity of substituent X increases. As a result, the acceptor ability of σ bonds can be significantly modified by substitution and by presence of several conformers.

The stereoelectronic effects displayed by C–X bonds formed by X from the second and third rows are highly anisotropic. For example, C–chalcogen bonds are excellent σ acceptors at the carbon end but poor σ acceptors at the chalcogen end. We propose that this effect can be used for the design of σ -bridges with one-directional electron-transfer conductivity.

While the general trends determined in this work should be useful for qualitative reasoning, one should bear in mind that the magnitude of hyperconjugative effects is extremely sensitive to small variations in structure. This sensitivity and the fact that the differences in acceptor ability of C–X bonds in neutral molecules are rarely more than several kcal/mol stresses the need for an unambiguous and quantitative estimation of energy of hyperconjugative interactions associated with stereoelectronic effects. Otherwise, *caveat emptor!*

Acknowledgment. The authors thank Florida State University for the First Year Assistant Professor Award (to I.A.) and Professors W. Borden, P. v. R. Schleyer, F. Weinhold, J. Saltiel, and W. Herz for stimulating discussions.

Supporting Information Available: Total energies and Cartesian coordinates of substituted ethanes and ethenes. Selected properties of C–H, C–C, and C–X bonds in substituted ethanes at the B3LYP/6-31G** level. Correlation of overlap matrix element with square of the Fock matrix element in substituted ethanes. Correlation of energy of “antiperiplanar” σ_{C-H} orbitals with electronegativity of element X in substituted ethanes, CH_3-CH_2X . Computational results for haloethanes at the B3LYP/SDD level. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA012633Z