

Effect of Double-Hyperconjugation on the Apparent Donor Ability of σ -Bonds: Insights from the Relative Stability of δ -Substituted Cyclohexyl Cations

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A combination of electronic, structural, and energetic analyses shows that a somewhat larger intrinsic donor ability of the C–H bonds compared to that of C–C bonds can be overshadowed by cooperative hyperconjugative interactions with participation of remote substituents (double hyperconjugation or through-bond interaction). The importance of double hyperconjugation was investigated computationally using two independent criteria: (a) relative total energies and geometries of two conformers (“hyperconjomers”) of δ -substituted cyclohexyl cations (b) and natural bond orbital (NBO) analysis of electronic structure and orbital interactions in these molecules. Both criteria clearly show that the *apparent* donor ability of C–C bonds can vary over a wide range, and the relative order of donor ability of C–H and C–C bonds can be easily inverted depending on molecular connectivity and environment. In general, relative donor abilities of σ bonds can be changed by their through-bond communication with remote substituents and by greater polarizability of C–X bonds toward heavier elements. These computational results can be confirmed by experimental studies of conformational equilibrium of δ -substituted cyclohexyl cations.

Introduction

Hyperconjugation, or delocalization which involves σ bonds, manifests itself in numerous stereoelectronic effects controlling organic structure and reactivity.^{1,2} In particular, such interactions can deliver electron density to electron-deficient centers and, thus, are often suggested to determine stereoselectivity of organic reactions where the transition states for stereodivergent pathways are characterized by different relative arrangements of donor and acceptor orbitals.

It is well established that donors such as C–Si, C–Ge, and C–Sn bonds are capable of providing significant stabilization to a developing positive charge.³ However,

the relative ability of many common σ donors, including the most ubiquitous case of C–H vs C–C bonds, is still widely debated.⁴ An often discussed example involves stereoelectronic control in nucleophilic addition to cyclohexanones and related compounds. A widely discussed model proposed by Cieplak suggests that the decisive stereoelectronic factor determining axial approach of nucleophilic attack on the C=O group involves electron donation from axial C–H bonds to the antibonding orbital associated with the incipient (forming) bond between incoming nucleophile (Nu) and the carbonyl carbon. In this model, the axial approach is favored because the above stabilizing interaction is more efficient than the analogous interaction with C–C-bonds during the equatorial approach of Nu (Figure 1).⁵ The larger donor ability

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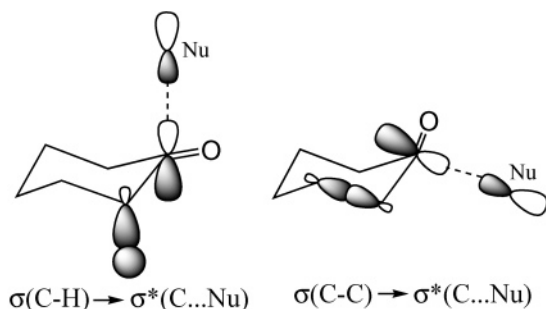


FIGURE 1. Most important transition-state-stabilizing hyperconjugative interactions for axial and equatorial nucleophilic addition to cyclohexanone according to Cieplak's model.

of C–H bonds compared to that of σ C–C bonds is the cornerstone of this model.⁶ This suggestion stimulated many experimental⁷ and theoretical⁸ studies, some of which questioned the order of relative donor abilities of σ C–C and C–H bonds.

The uncertainty of relative donor abilities of C–H and C–C bonds is not surprising because the difference between these two bonds is not large in ground-state neutral molecules. For example, a careful low-temperature X-ray structural study by Spinello and White found that the differences in donor ability of C–C and C–H bonds toward $\sigma(\text{C}=\text{O})$ acceptors of variable electronic demand are comparable to the experimental uncertainty of measurements.⁴ Two recent computational studies also found that the differences are small. Natural bond orbital (NBO) analysis indicates that C–H bonds are slightly better donors than σ C–C bonds in cyclohexane and related molecules.⁹ A similar conclusion was made by Rablen and co-workers in a theoretical study on the origin of gauche effects in substituted fluoroethanes.¹⁰ Note, however, that the small differences in neutral molecules do not prevent these effects from becoming significant in species with increased electron demand.¹¹

This importance has been well-recognized but also debated for quite a long time. For example, Nathan and Baker reported that a Me group provides more stabilization to the developing positive charge at the *p*-benzylic position than Et, *i*-Pr, and *t*-Bu groups in solvolysis of *p*-alkyl-substituted benzyl bromides (Me > Et > *i*-Pr > *t*-Bu)¹² and attributed this order of reactivity to the

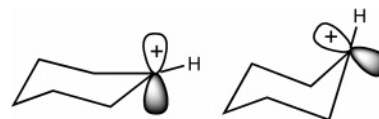


FIGURE 2. Axial and equatorial “hyperconjugomers” of cyclohexyl cations.

greater donating ability of C–H bonds compared to that of C–C bonds. Although these results are consistent with the trends in ¹³C NMR chemical shifts of the β -carbon in β -substituted styrenes in solvents of different polarity,¹³ the opposite trend found in the gas-phase pyrolysis of 1-arylethyl acetates cast a shadow of doubt at the original interpretation of the Nathan–Baker effect.¹⁴ To complicate the matter even further, a recent study of two conformers of cyclohexyl cations with two distinctly different patterns of hyperconjugative interactions (“hyperconjugomers”, Figure 2) found that a switch in the order of the apparent donor ability of C–H and C–C bonds in solution vs the gas phase occurs in the opposite direction.¹⁵ Although the isomer stabilized preferentially by $\sigma(\text{C-H}) \rightarrow n(\text{C}^+)$ hyperconjugation is more stable according to the gas-phase computations, the opposite order of stability was observed in experimental studies in solution and in computations including solvation effects (vide infra).

Taking into account the fundamental importance of this question and conflicting literature results, we decided to determine the intrinsic order of donor ability of C–H and C–C σ bonds in systems where the differences in donor ability of σ bonds may be significantly large to lead to experimentally observable consequences. Our choice of the model systems was inspired by the above elegant recent study of Rauk and co-workers¹⁵ who reported the dramatic effect of hyperconjugation on two isomeric chair conformers of 1-Me-1-cyclohexyl cation¹⁶ differing in having the carbocation *p*-orbital oriented either “axially” or “equatorially”. These conformers have distinctly different modes of hyperconjugative stabilization.¹⁵ The axial cationic orbital in the first hyperconjugomer interacts strongly with the adjacent axial C–H bonds whereas the equatorial vacant *p*-orbital in the second cation interacts most strongly with the anti-periplanar C–C bonds (Figure 2).

The contrasting nature of dominant hyperconjugative interactions in the two cyclohexyl cation conformers raises an intriguing question of whether the relative stability of these experimentally observable species can be taken as a measure of the relative donor ability of C–H and C–C bonds toward a carbocationic center. If this assumption is warranted, the greater stability of the “equatorial” conformer (ca. 0.6 kcal/mol according to B3LYP/6-31G*+ZPVE gas-phase calculations) could be taken as evidence that C–C bonds are slightly better

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(16) It was suggested originally that the “twist-boat” and “chair” conformers were in equilibrium but further studies confirmed the existence of two isomeric chair cations.

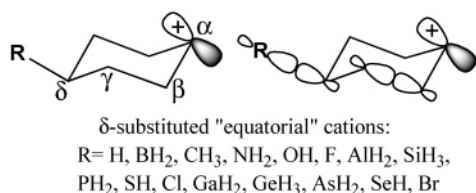


FIGURE 3. δ -Substituted cyclohexyl cations: choice of substituents and nature of orbital interactions.

donors than C–H bonds. Unfortunately, the situation is far from being simple because the “axial” conformer is experimentally ca. 1 kcal/mol more stable in solution—the effect which is accurately reproduced by computations including solvation effects.¹⁵ Interestingly, the effect of preferential solvation in this system is opposite to that observed in the Nathan/Baker¹² and Glyde/Taylor¹⁴ experiments discussed above! The seeming discrepancy in the estimates of the relative donor ability of C–H and C–C bonds in these cationic systems with theoretical predictions based on neutral molecules^{9,10} calls for a more detailed analysis of hyperconjugative interactions in these molecules which we will provide in the first part of this paper.

Another difference between the donor C–C and C–H orbitals is that, unlike β -C–H bonds in the axial cation, β, γ -C–C bonds in cyclohexyl cations are antiperiplanar not only to the equatorial cationic p-orbital but also to an equatorial δ -C–R bond (Figure 3). In the second part of this paper, we analyze whether the presence of this more extended hyperconjugative pattern is important in determining the apparent order of donor ability of C–C and C–H bonds. We will focus on whether the “second sphere” hyperconjugative interactions with the remote donor δ -C–R orbitals are capable of positive charge stabilization via through-bond communication with the vacant p-orbital—an effect also known as “double hyperconjugation”.^{17,18} We will investigate to what extent double hyperconjugation is translated into electronic and structural changes and whether this effect is capable of changing the *apparent* order of C–H and C–C donor ability and whether these effects should be experimentally observable as different relative stabilities of “equatorial” cations.

In this analysis, we employ two complementary criteria—effects of δ -substituents at the relative energies and structures of cyclohexyl cations (vide infra) and dissection of orbital interactions using natural bond orbital (NBO) analysis.¹⁹ This combination will provide

a way to correlate computational analysis with potentially experimentally observable equilibrium changes in substituted cyclohexyl cations which are common intermediates in solvolysis reactions.^{20,21}

Computational Details

All cyclohexyl cation geometries were fully optimized at the B3LYP/6-31G** and B3LYP/6-311++G** levels using the Gaussian 98 program.²² Electronic properties of model compounds were studied using the natural bond orbital (NBO) 4.0²³ program implemented in Gaussian. Detailed descriptions of the NBO calculations are available in the literature²⁴ and in the Supporting Information.

Results and Discussion

1. NBO Dissection of Hyperconjugative Contributions to the Relative Stability of the Two Parent Cyclohexyl Cations. To understand the nature of delocalization effects involved in the two parent cyclohexyl cations, we carried out a detailed NBO analysis of the electronic structures of these species which is summarized in Figure 4. As suggested earlier by Rauk et al. for 1-Me-cyclohexyl cations,¹⁵ we found that $\sigma(\text{C}–\text{C}) \rightarrow n(\text{C}_1)$ and $\sigma(\text{C}–\text{H})_{\text{ax}} \rightarrow n(\text{C}_1)$ interactions play the dominant roles in stabilizing the equatorial and axial “hyperconjomers”. Interestingly, the $\sigma(\text{C}–\text{C}) \rightarrow n(\text{C}_1)$ interaction is larger than the $\sigma(\text{C}–\text{H})_{\text{ax}} \rightarrow n(\text{C}_1)$ effect in contrast to the $\sigma(\text{C}–\text{H})_{\text{ax}} \rightarrow \sigma^*(\text{C}–\text{H})'_{\text{ax}} > \sigma(\text{C}–\text{H})_{\text{eq}} \rightarrow \sigma^*(\text{C}–\text{C})$ order in neutral cyclohexane.⁹ This observation does not indicate inversion of the relative donor ability of C–H/C–C bonds—its real origin lies a nonperfect overlap of the vacant orbital with the “axial” C2–H bond as a result of planarization at C1. On the other hand, planarization

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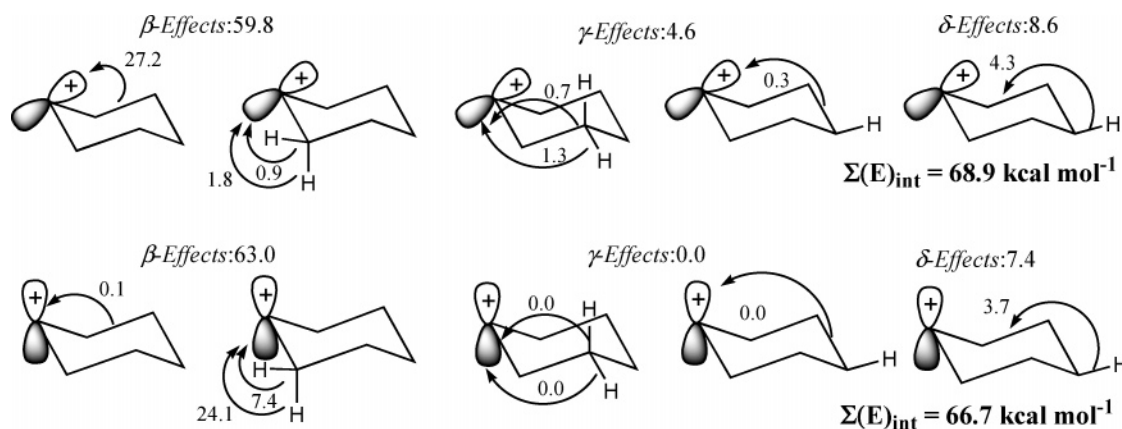


FIGURE 4. Second-order perturbation NBO energies in kcal/mol for important hyperconjugative interactions in axial and equatorial cyclohexyl cations (B3LYP/6-31G**).

also increases the overlap of the positive center with the “equatorial” C2–H bond, thus allowing the cation to benefit from the hyperconjugative interaction with two donors at the same time. Although the energy of combined $\sigma(\text{C–H})_{\text{ax}} \rightarrow n(\text{C}_1)$ and $\sigma(\text{C–H})_{\text{eq}} \rightarrow n(\text{C}_1)$ interactions in the “axial” conformer is greater than that of $\sigma(\text{C–C}) \rightarrow n(\text{C}_1)$ interactions in the “equatorial conformer” (31.5 vs 27.2 kcal mol^{−1}), the balance of hyperconjugative effects is tipped in favor of the “equatorial” conformer by subtle effects involving remote donor moieties: $\gamma\text{-}\sigma(\text{C–H})_{\text{eq}} \rightarrow n(\text{C}_1)$ homohyperconjugation with through space participation of $\gamma\text{-C–H}$ bonds^{25–27} and an increase in the $\delta\text{-}\sigma(\text{C–H})_{\text{eq}} \rightarrow \sigma^*(\text{C–C})$ interaction which can be taken as a manifestation of double hyperconjugation (orbital interaction through a bridge bond, *vide infra*).²⁸

Even though the close correspondence of the relative energies of combined hyperconjugative interactions in Figure 4 with the ca. 2 kcal mol^{−1} total energy differences between two cations may be fortuitous (numerical results of the NBO perturbative analysis for strongly delocalized systems should be taken with caution), this picture is qualitatively correct in illustrating the rather complex interplay of different hyperconjugative interactions. Importantly, this complexity precludes simply taking the difference between the two “axial” and “equatorial” cyclohexyl cations as a direct measure of relative donor abilities of C–H and C–C bonds.

On the other hand, the $\delta\text{-}\sigma(\text{C–H})_{\text{eq}} \rightarrow \sigma^*(\text{C–C})$ interaction in the equatorial cation is noticeably increased in comparison to the analogous interaction in the axial

cation (4.3 vs 3.7 kcal/mol) and neutral cyclohexanes (3.1 kcal/mol, R = H; 3.2 kcal/mol, R = F_{eq}). In fact, one can argue that such an increase in $\sigma(\text{C}_4\text{–H})_{\text{eq}} \rightarrow \sigma^*(\text{C}_3\text{–C}_2)$ interaction in the parent system (which is estimated as ca. $2[4.3 - 3.7] = 1.2$ kcal/mol provides a noticeable part of the larger stability of the equatorial cyclohexyl cation (1.9 kcal/mol) relative to that of the axial conformer. This observation provides evidence for extended charge delocalization through double hyperconjugation mechanism.^{17,29,30} It also suggests that if stability of the equatorial vs the axial cation is taken as a measure of the apparent donor ability of σ bridge C–C bonds toward the acceptor p -orbital at the cationic center, in systems shown in Figure 3, this stability should depend on the nature of equatorial substituent at the δ -position of cyclohexyl cation. It also implies that, at least in some cases, apparently greater donor ability of C–C bonds can be a result of higher order hyperconjugative interactions with remote orbitals. Although, somewhat ironically, in the case of the two hyperconjugomers of unsubstituted cyclohexyl cation this remote donor is a C–H bond, one can envision that other substituents may have a similar or even larger effect. If this assumption is correct, modulation of apparent donor ability of C–C bonds should be even more important in the case of stronger σ -donor δ -substituents. We will analyze these effects on geometries, electronic structure, and energies in the following sections.

2. δ -Substituted Cyclohexyl Cations. A. Substituent Effects at the Positive Charge Stabilization in Axial and Equatorial Cyclohexyl Cations. In this section, we will investigate the extent to which the presence of δ -substituents affects energies of cyclohexyl cations. If only the “first sphere” effects or differences in the intrinsic donor ability of C–H and C–C bonds are important, one would expect the relative energies of axial and equatorial “hyperconjugomers” to be independent of the δ -equatorial substituent R and only reflect the intrinsic difference between $\sigma(\text{C–H}) \rightarrow n(\text{C})$ and $\sigma(\text{C–C}) \rightarrow n(\text{C})$ interactions. On the other hand, if the “second sphere”

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(27) Homoconjugation is well established in chemistry of carbocations. Winstein, S.; Adams, R. *J. Am. Chem. Soc.* **1948**, *70*, 838. Sunko, D. E.; Hirsle-Starcevic, S.; Pollack, S. K.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 6163 and references therein and all vast literature on nonclassical carbocations.

(28) This phenomenon is important for C–Si and C–Sn bonds and has been called the δ effect: (a) Lambert, J. B.; Salvador, L. A.; So, J.-H. *Organometallics* **1993**, *12*, 697. (b) Adcock, W.; Coope, J.; Shiner, V. J., Jr.; Trout, N. A. *J. Org. Chem.* **1990**, *55*, 1411. (c) Adcock, W.; Kristic, A. R.; Duggan, P. J.; Shiner, V. J., Jr.; Coope, J.; Ensinger, M. W. *J. Am. Chem. Soc.* **1990**, *112*, 3140. (d) Lambert, J. B.; Salvador, L. A. *Tetrahedron Lett.* **1990**, *31*, 3841. (e) Green, A. J.; Van, V.; White, J. M. *Austr. J. Chem.* **1998**, *51*, 555.

(29) This is consistent with the unexpectedly large D isotope effects in solvolysis in a topologically similar bicyclo[2.2.2]octane system reported by Adcock and co-workers in ref 28c.

(30) For effects of Si and Sn in additions of nucleophiles to adamantyl systems, see: Adcock, W.; Cotton, J.; Trout, N. A. *J. Org. Chem.* **1994**, *59*, 1867. Adcock, W.; Head, N. J.; Lokan, N. R.; Trout, N. A. *J. Org. Chem.* **1997**, *62*, 6177.

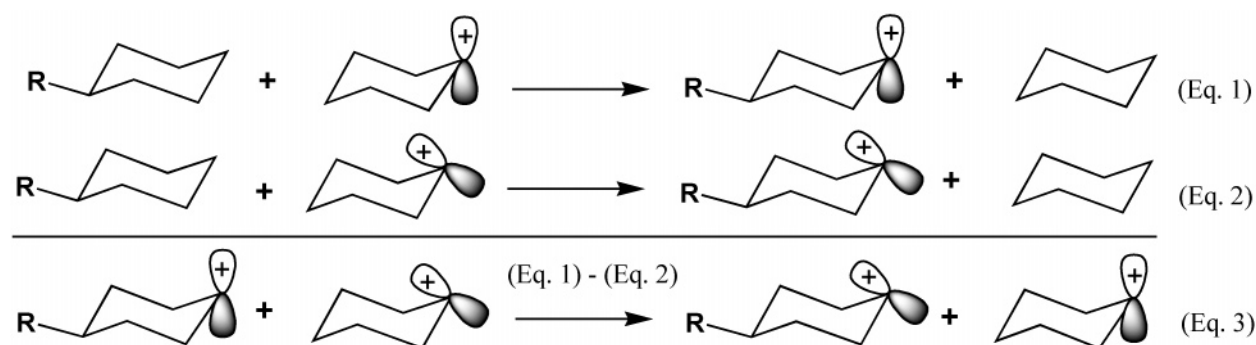


FIGURE 5. Three isodesmic equations used to calculate substituent stabilization energies (SEs) in the equatorial and axial cyclohexyl cations.

TABLE 1. Substituent Stabilization Energies (SEs) in the Equatorial (SE_{eq}) and Axial (SE_{ax}) Cyclohexyl Cations (kcal/mol) and Difference between Them ($\Delta SE_{eq-ax} = SE_{eq} - SE_{ax}$) Computed at the B3LYP/6-31G and B3LYP/6-311+G** Levels (Negative Values Indicate Stabilization Relative to the Parent Cation)**

R	SE_{eq}^a	SE_{ax}^a	ΔSE_{eq-ax}^a	SE_{eq}^b	SE_{ax}^b	ΔSE_{eq-ax}^b
H	0.00	0.00	0.00	0.00	0.00	0.00
BH ₂	-0.95	0.28	-1.23	-0.89	0.29	-1.18
AlH ₂	-9.11	NA ^c	NA ^c	-9.12	NA ^c	NA ^c
GaH ₂	-7.41	NA ^c	NA ^c	-8.83	NA ^c	NA ^c
CH ₃	-0.25	-0.73	0.48	-0.21	-0.72	0.51
SiH ₃	-2.49	0.66	-3.15	-2.50	0.64	-3.14
GeH ₃ ³⁴	-2.74	0.79	-3.53	-3.73	0.33	-4.06
NH ₂	2.71	0.73	1.98	3.37	1.28	2.09
PH ₂	0.63	2.28	-1.65	0.55	2.24	-1.69
AsH ₂	-1.31	1.64	-2.95	-1.89	1.42	-3.31
OH	5.56	2.68	2.88	6.66	3.66	3.00
SH ³⁵	5.63	4.91	0.72	5.51	4.85	0.66
SeH	3.67	4.07	-0.40	3.90	4.43	-0.53
F	11.53	7.27	4.26	13.09	8.74	4.35
Cl	11.20	8.62	2.58	11.18	8.63	2.55
Br	9.50	8.04	1.46	9.88	8.37	1.51

^a B3LYP/6-31G** level. ^b B3LYP/6-311++G** level. ^c The axial conformers were transformed into their equatorial isomers upon geometry optimization.

hyperconjugation is relevant, substituent effects on stability of the axial and equatorial cations should be noticeable.

These effects are estimated by the three isodesmic reactions given in Figure 5. The stabilization energies provided by these isodesmic reactions give different information (Table 1). Effects of substituents in axial cations which are described by eq 1 include a complicated

interplay of many factors such as hybridization²⁶ and inductive and field effects, which are still present in these species even when double hyperconjugation is minimized. Interestingly, most of the δ -substituents are destabilizing when compared to the unsubstituted “axial” cation (even such donors as Si, As, Ge).³¹ In the case of the two strongest σ donors (AlH₂ and GaH₂), the axial cations transform into more stable equatorial cations “in silico”, upon geometry optimization.

In sharp contrast with the situation in “axial” cations, many substituents have a stabilizing effect on the “equatorial” cations (eq 2). Such effects can be rather large, indicating that δ -C–X bonds are capable of efficient interaction with the cation p-orbital as long as all orbitals participating in the double hyperconjugation interaction relay overlap efficiently. For the same reason, the destabilizing effects of σ acceptors such as C-halogen bonds are also more pronounced in equatorial cations. Thus, the above “equatorial” stabilization energies (SE_{eq}) include stabilization or destabilization provided by σ C–X donors through the double hyperconjugation mechanism. They also include a number of other effects including those mentioned in the previous paragraph.

Subtraction of axial (SE_{ax}) from equatorial (SE_{eq}) stabilization energies provides the last isodesmic equation of Figure 5 where the contributions of the above non-hyperconjugative (inductive, field, etc.) effects are partially compensated. Although this compensation is not perfect, the ΔSE_{eq-ax} values give an improved estimate of the hyperconjugative stabilization of “equatorial” cations which has its source in the increase in double-hyperconjugative stabilization.

Although none of three types of stabilization energies isolates hyperconjugative donation in its pure form, these energies are directly derived from experimentally obtainable measurements and are defined in a way which makes them important from a practical point of view. In the later sections of the paper, we will analyze relative trends for these energies for elements of groups III–VII of the first three rows and compare these energies with quantum-mechanical estimates of hyperconjugative donor ability of σ bonds.

Although all of the above stabilization energies correlate with the electronegativity of the respective sub-

(31) The only notable exclusions are the cases of the strongest σ donors—AlH₂ and GaH₂ groups where axial cations are transformed during the geometry optimization in the respective equatorial isomers stabilized by double hyperconjugation.

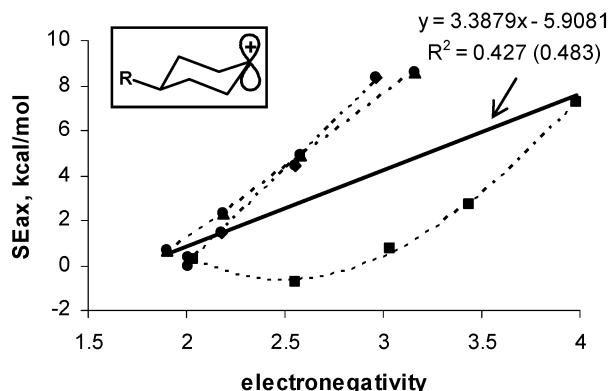
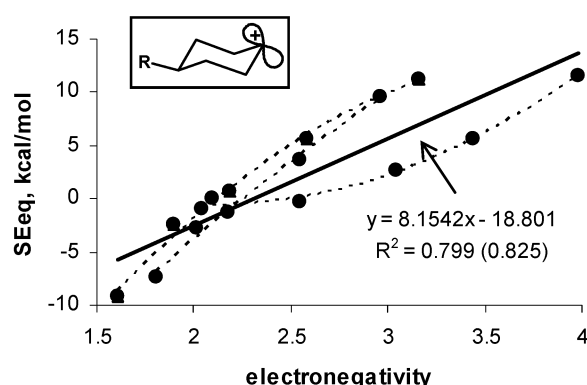


FIGURE 6. Correlations of substituent stabilization energies (SEs) in the “equatorial” (SE_{eq} , left) and “axial” (SE_{ax} , right) cyclohexyl cations [B3LYP/6-31G** (B3LYP/6-311++G**)] with electronegativity of substituents R. Individual correlations for each period are shown in dashed lines.

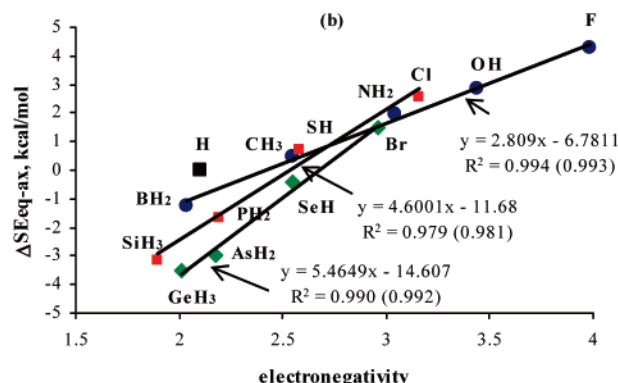
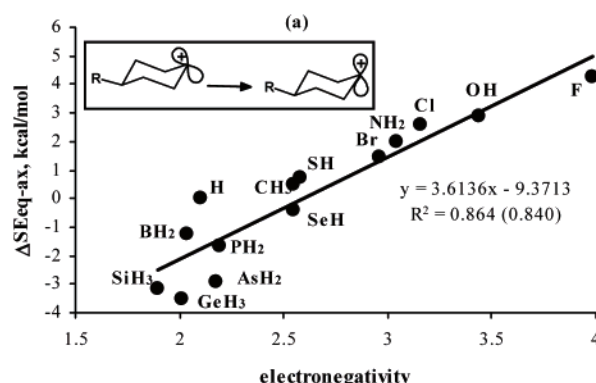


FIGURE 7. Two correlations between the differences in stabilization energies of δ - XH_n substituents in the equatorial and axial cyclohexyl cations (Figure 5) and electronegativity of the X. The top plot (a) corresponds to the general correlation; the bottom plot (b) gives separate correlations for each row. Calculations were performed at the B3LYP/6-31G** (B3LYP/6-311++G**) level (see Figure S2 in the Supporting Information for the correlation involving other electronegativity scales).

stituents, especially for the second and third rows (see the Supporting Information), Figure 6 reflects the absence of a *general* correlation for SE_{ax} values for elements from different rows. The combined correlation for SE_{eq} values is better but still noticeably scattered as a result of a rather complex interplay of different factors contributing to the effects of substituents.^{32,33} Not surprisingly, sensitivity of stabilization energies to electronegativity

(32) In general, nonmetals from the second and third rows are weaker “net” donors than one would expect from their electronegativity. On the other hand, the correlation slopes in Figure 6 become steeper for the heavier elements indicating that more polarizable C–R bonds are more sensitive to introduction of a positive charge. Stabilization energies for the first period are not only significantly less sensitive to the electronegativity but also more scattered compared to the case of SEs for the heavier elements which show almost perfect linear correlations with electronegativity. The strongest deviation is observed for the δ - BH_2 substituent and can be attributed to the p-acceptor properties of boron atom. Due to the presence of the empty p-orbital on boron, the BH_2 moiety provides very little stabilization to the equatorial cation and slightly destabilizes the axial cation.

(33) The observation that SE_{eq} and SE_{ax} follow slightly different trends in different periods (see the Supporting Information) is not surprising—its origin can be traced back to the trends in *acceptor* ability of σ bonds. In C–X σ bonds, this ability 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 σ^*C-X orbitals. Alabugin I. V.; Zeidan, T. A. *J. Am. Chem. Soc.* **2002**, *124*, 3175.

is increased in the “equatorial” cations where cationic orbitals communicate better with the $\sigma(C-R)$ bonds.

Although the ΔSE_{eq-ax} values from all periods are reasonably well described by a single correlation (Figure 7) suggesting that the ΔSE_{eq-ax} values indeed provide a better estimate of the relative trends in hyperconjugative donor ability of C–R bonds,³⁶ the δ -substituents cluster into three groups. As shown in Figure 7a, the first group displays positive ΔSE_{eq-ax} values and consists of cation-destabilizing strongly electronegative acceptors with Pauling electronegativity of ≥ 3 . The second group includes elements of intermediate electronegativity (ca. 2.5) which form C–R bonds with donor abilities close to that of C–H bonds (CH_3 , SH , and SeH). The final group ($R = BH_2$, PH_2 , AsH_2 , SiH_3 , GeH_3) includes relatively electropositive substituents with negative ΔSE_{eq-ax} values. In this group, the ΔSE_{eq-ax} values are scattered and electronegativity is not a good indicator of donor ability

(34) The relative trend for H, Si and Ge are qualitatively consistent with the relative values of kinetic δ -effect for H/Si/Ge of $1.0/10^4/10^5$.²⁸

(35) For a recent analysis of the competition between anchimeric assistance and hyperconjugation in the interaction of a carbocationic center with S-, Se-, and Te-containing moieties, see: White, J. M.; Lambert, J. B.; Spiniello, M.; Jones, S. A.; Gable, R. W. *Chem. Eur. J.* **2002**, *8*, 2799. The results were consistent with the presence of strong donation from the C–S and C–Se bonds without angular distortion.

(36) Although the correlation coefficient is moderate, the R^2 value for the correlation increases to 0.92 when the most deviating H and BH_2 groups are excluded.

toward the δ -cationic center. The scattering may be partially due to a nonperfect compensation of the non-hyperconjugative effects but also is related to the differences in polarizabilities of C–R bonds in different periods as shown in Figure 7b.³⁷ The divergence of the curves for different periods is caused by the fact that the more polarizable C–R bonds with heavier elements are more sensitive to the introduction of a positive charge at the remote position even when electronegativities of the respective elements is close (note H vs B and B vs Ge). The differences in polarizability between the elements of the first and second rows are especially pronounced.

B. Effect on Geometries. In this section, we discuss the effect which double hyperconjugation imposes on the geometries of substituted cyclohexyl cations. In general, both of the two parent cation conformers are distorted from the ideal chair geometry and considerable changes in certain bond lengths are observed relative to the respective neutral molecules. These changes reflect delocalizing interactions needed to stabilize the positive charge. In the equatorial cation, the vacant p-orbital is tilted inside the ring with the simultaneous ring puckering. In the axial cation, the cationic carbon is almost planar—the C₂–C₁(+)-H–C₆ torsion angle is ca. 175° whereas in the equatorial cations this torsion angle is close to 165°. Direct hyperconjugation weakens and lengthens the C₂–C₃ and C₅–C₆ bonds (ca. 1.613–1.686 Å) parallel to the vacant p-orbital in the equatorial cation and the C₂–H_{ax} and C₅–H_{ax} bonds (ca. 1.120–1.22 Å) in the axial cation (Table S7, Supporting Information). The bridge C–C bond is ca. 0.1 Å shorter in the respective axial cations again illustrating the difference in the two major delocalizing modes (C–C vs C–H hyperconjugations).³⁹ These structural changes are similar to those reported by Hrovat and Borden in an earlier theoretical study of substituent effects in 4-substituted bicycle[2.2.2]-oct-1-yl cations.⁴⁰

When donor δ -substituents are introduced in the equatorial cation, the bridge C–C bond bond elongates. Introduction of σ -acceptors has an opposite effect (Table S7 (Supporting Information), Figure 8). These structural changes are closely associated with electronic properties and energies of equatorial cations as illustrated by Figure 9, which shows that the length of the bridge C–C bonds correlates well with the population of σ (C–C) bridge orbitals (Figure 9a) and with the relative stabilities (Figure 9b) of equatorial and axial cations. In contrast, the C–H_{eq} bond length in the axial cations is nearly independent of the nature of the remote substituents (Table S7, Supporting Information).

C. NBO Analysis of Electronic Structure. (a) Substituent Effects on Distribution of Electron Density in δ -Substituted Cyclohexyl Cations. The

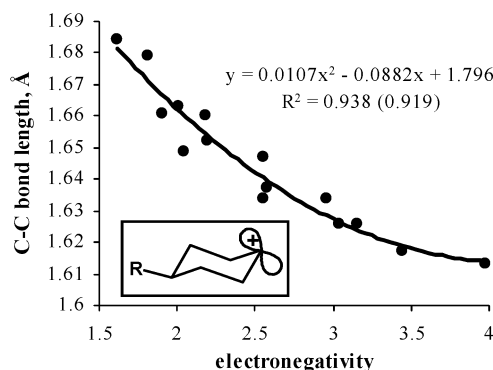


FIGURE 8. Correlation of the average C₂–C₃/C₅–C₆ bond lengths with electronegativity of substituents in the equatorial cyclohexyl cations at the B3LYP/6-31G** (B3LYP/6-311++G**) level.

correlations given in Figure 9 already provided a hint at the close connection between structures, energies, and electronic structures of δ -substituted cyclohexyl cations. In the following sections, we will use NBO analysis to gain a better understanding of electronic effects responsible for the observed trends in substituted cations. We will begin this discussion with a brief analysis of hyperconjugation in equatorially substituted *neutral* cyclohexanes. In general, presence of σ (C–C) \rightarrow σ^* (C–R) interaction decreases population of the bridge σ (C–C) NBOs from the ideal population of 2.0 electrons. In a similar way, σ (C–R) \rightarrow σ^* (C–C) interaction increases the population of σ^* (C–C) orbitals which are empty in the idealized Lewis approximation. Figure 10 clearly shows that population of bridge σ (C–C) bonds in neutral cyclohexanes correlates with σ (C–C) \rightarrow σ^* (C–R) hyperconjugative interactions. As R becomes a stronger acceptor, population of σ (C–C) orbitals decreases due to partial transfer of electron density to the acceptor σ^* (C–R) orbitals. Increased acceptor ability of σ C–R bonds from second and third rows is due to the lowering of the respective σ^* (C–R) energies.³³

When the positive charge is introduced, the slope of the correlation of σ (C–C) population with electronegativity of substituents changes its direction (Figure 11). This change indicates reversal in the direction of prevailing hyperconjugative effect. In other words, influence of δ -C–R bonds is dominated by their *acceptor* ability in neutral cyclohexanes and by their *donor* ability in the respective cations. This change is consistent with the dramatically increased role of σ (C–R) \rightarrow σ^* (C–C) interaction. This interaction is coupled with the strong σ (C–C) \rightarrow n(C) hyperconjugation providing a mechanism for positive charge delocalization in these saturated molecules. The partial transfer of electron density from the donor orbitals to the vacant p-orbital of the cationic carbon atom through this mechanism is readily traced in the changes in electronic population of the donor and the acceptor orbitals. Whereas orbital populations in the axial cations are insensitive to the presence of a δ -substituent (σ (C–H)_{ax}, 1.849–1.862 e; n_{C1}, 0.403–0.431 e; Table 3), populations of σ (C₂–C₃) (1.805–1.846 e) and especially of n_{C1} (0.406–0.578 e) in the equatorial cations show considerable variations (Table 3). These effects clearly result from orbital interactions rather than from field effects because the respective changes in the popu-

(37) For a discussion of the role of polarizability of in donor ability, see: Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, 16, 1. Exner, O.; Böhm, S. *J. Chem. Soc.* **1997**, 1235.

(38) See the Supporting Information for the complete geometries of all calculated species.

(39) For the same reason, elongation of the “equatorial” C–H bonds in the axial cations is smaller than that of the “axial” bonds even though the σ (C–H)_{ax} \rightarrow n(C+) interaction also provides some stabilization to the axial cation.

(40) Hrovat, D. A.; Borden, W. T. *J. Org. Chem.* **1992**, 57, 2519. This study showed the importance of electron correlation in describing double hyperconjugation and proved the deficiency of simple RHF treatment of such systems.

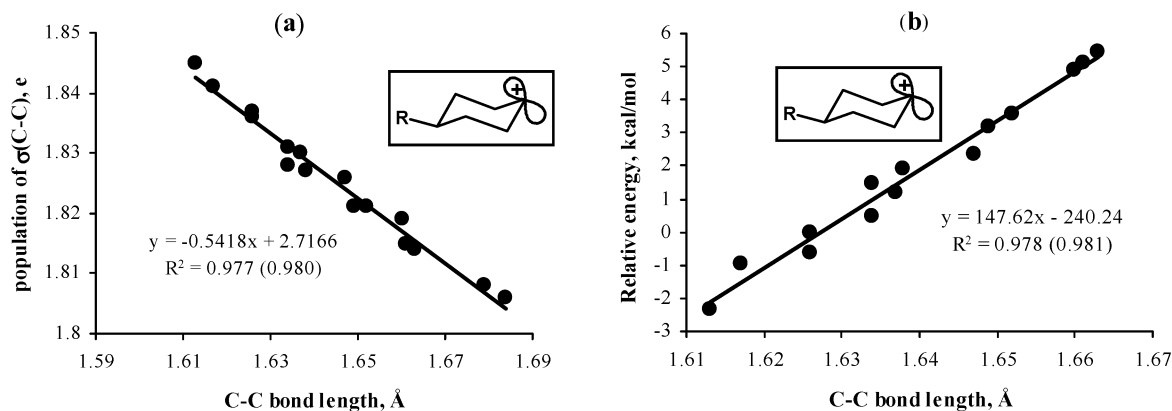


FIGURE 9. Correlations of the average C2–C3/C5–C6 bond lengths with (a) the average population of the corresponding $\sigma(\text{C-C})$ orbitals and with (b) the relative energies of equatorial and axial cyclohexyl cations calculated at the B3LYP/6-31G** (B3LYP/6-311++G**) level.

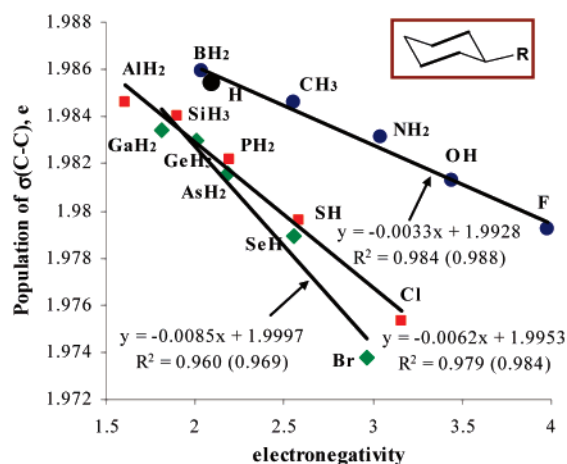


FIGURE 10. Correlations of the population of donor $\sigma(\text{C-C})$ orbitals with electronegativity of substituents from three different rows in equatorially substituted cyclohexanes at the B3LYP/6-31G** (B3LYP/6-311++G**) level (see Figure S3 (Supporting Information) for the correlations for $\sigma(\text{C-H})$ orbitals).

lation of C2–H_{ax} bond in equatorial cation (1.963–1.967e) and C2–C3 (1.974–1.982) in axial cation are almost negligible. Although these orbitals are vicinal to the positive centers, they do not overlap with the vacant

p-orbital, and thus, their population does not deviate considerably from the 2.0 e population of a perfectly localized σ bond (Tables 2 and 3).

In contrast, populations of the remote $\sigma(\text{C-R})$ orbitals (Table 2, Figure 11) in equatorial cations are considerably reduced compared to the respective neutral molecules. Interestingly, the population of the $\delta\text{-C-H}_{\text{eq}}$ orbital (1.946 e) is smaller than the population of the $\beta\text{-C-H}_{\text{ax}}$ orbital (1.965 e). Changes in the C–C and C–R bonds summarized in Figure 11 show that population of the bridge C–C bonds varies within 1.81–1.85 e whereas the population of C–R bonds spans the range of 1.786–1.989 e. Clearly, the C–R bonds undergo more dramatic changes despite being more distant from the vacant p-orbital. Together these observations illustrate again that in these systems spatial proximity and field effects are less important than correct orbital alignment (Table 2).

Another interesting observation is that the population of C–C bonds in equatorial cyclohexyl cations linearly responds to electronegativity of R whereas such correlation for the population of C–R bonds is nonlinear. The degree of nonlinearity and the extent of electron transfer from the C–R bonds to the cationic center increase noticeably for the more polarizable bonds involving heavier elements.

The extent of charge transfer from the remote donor substituents R to the acceptor p-orbital can also be

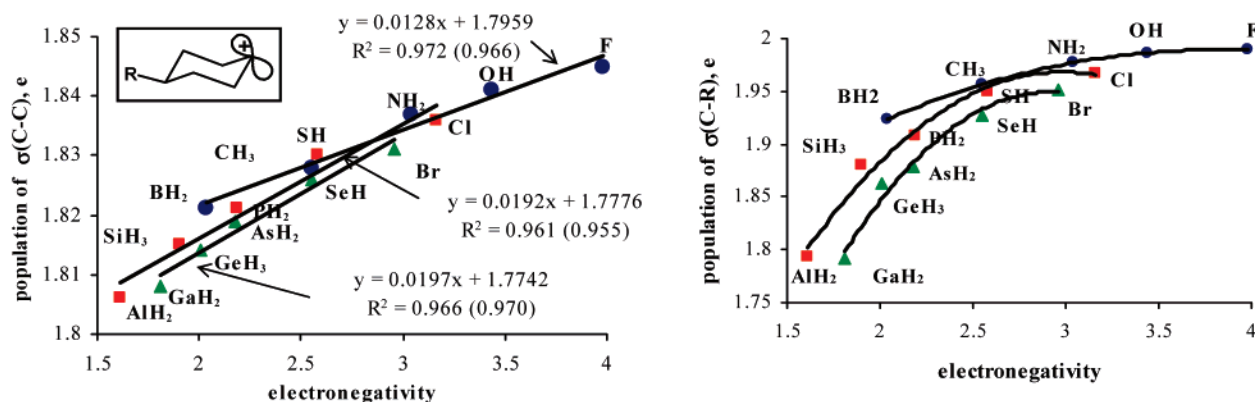
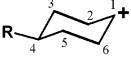
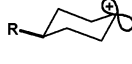
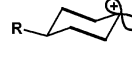
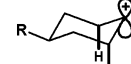
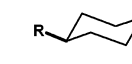
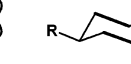


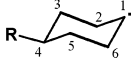

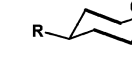


FIGURE 11. Correlations of the population of donor ($\sigma(\text{C-C})$ and $\sigma(\text{C-R})$) orbitals in the equatorial cyclohexyl cations with electronegativity of elements in periods [B3LYP/6-31G** (B3LYP/6-311++G**) level]. See the Supporting Information (Figure S4) for the combined correlation.

TABLE 2. Populations (in Electrons) of the $\sigma(\text{C}-\text{R})$, $\sigma(\text{C}-\text{C})$, $\Sigma(\text{C}-\text{H})_{\text{ax}}$, and $\sigma^*(\text{C}-\text{C})$ NBOs in Equatorial and Axial Cyclohexyl Cations Computed at the B3LYP/6-31G** (B3LYP/6-311++G**) Level (See the Tables in the Supporting Information for Further Details)

						
	pop $\sigma(\text{C}-\text{R})$	pop $\sigma^*(\text{C}-\text{C})^a$	pop $\sigma(\text{C}-\text{H})_{\text{ax}}^a$	pop $\sigma(\text{C}-\text{R})$	pop $\sigma^*(\text{C}-\text{C})^a$	pop $\sigma(\text{C}-\text{C})^a$
H	1.948 (1.946)	0.019 (0.019)	1.968 (1.965)	1.976 (1.976)	0.017 (0.017)	1.982 (1.982)
BH ₂	1.924 (1.923)	0.026 (0.026)	1.968 (1.966)	1.967 (1.966)	0.020 (0.020)	1.981 (1.981)
CH ₃	1.956 (1.955)	0.017 (0.017)	1.967 (1.965)	1.980 (1.978)	0.016 (0.016)	1.982 (1.981)
SiH ₃	1.879 (1.879)	0.035 (0.034)	1.968 (1.966)	1.953 (1.954)	0.022 (0.021)	1.979 (1.979)
NH ₂	1.978 (1.978)	0.018 (0.017)	1.969 (1.964)	1.989 (1.988)	0.018 (0.018)	1.981 (1.981)
PH ₂	1.908 (1.905)	0.033 (0.034)	1.967 (1.964)	1.965 (1.963)	0.022 (0.022)	1.978 (1.977)
OH	1.986 (1.986)	0.014 (0.013)	1.969 (1.964)	1.992 (1.991)	0.017 (0.016)	1.981 (1.981)
SH	1.949 (1.946)	0.026 (0.026)	1.967 (1.963)	1.977 (1.974)	0.021 (0.021)	1.978 (1.978)
F	1.989 (1.989)	0.013 (0.011)	1.966 (1.963)	1.994 (1.993)	0.016 (0.015)	1.980 (1.980)
Cl	1.968 (1.966)	0.020 (0.020)	1.966 (1.963)	1.983 (1.982)	0.020 (0.020)	1.977 (1.977)

^a The average values for the population of $\sigma^*(\text{C}_2-\text{C}_3)/\sigma^*(\text{C}_5-\text{C}_6)$ and $\sigma(\text{C}_3-\text{H}_{\text{ax}})/\sigma(\text{C}_5-\text{H}_{\text{ax}})$ pairs of orbitals are given.

TABLE 3. Natural Charge (Electron) on C1 in Cyclohexyl Cations; Populations (Electron) of Acceptor $n(\text{C}_1)$ NBOs and of Donor $\sigma(\text{C}-\text{C})$ and $\sigma(\text{C}-\text{H})_{\text{ax}}$ NBOs in the Equatorial and Axial Cations, Respectively (at the B3LYP/6-311++G** Level)

						
	$q(\text{C}_1)$	pop $\sigma(\text{C}-\text{C})^a$	pop $n(\text{C}_1)$	$q(\text{C}_1)$	pop $\sigma(\text{C}-\text{H}_{\text{ax}})^a$	pop $n(\text{C}_1)$
H	0.232 (0.308)	1.827 (1.827)	0.458 (0.460)	0.295 (0.375)	1.855 (1.852)	0.407 (0.419)
BH ₂	0.214 (0.288)	1.821 (1.821)	0.482 (0.484)	0.294 (0.374)	1.853 (1.850)	0.409 (0.420)
CH ₃	0.237 (0.313)	1.828 (1.829)	0.453 (0.455)	0.296 (0.377)	1.856 (1.852)	0.407 (0.419)
SiH ₃	0.191 (0.259)	1.815 (1.815)	0.512 (0.516)	0.295 (0.375)	1.853 (1.849)	0.407 (0.418)
NH ₂	0.251 (0.331)	1.837 (1.837)	0.436 (0.436)	0.296 (0.376)	1.856 (1.853)	0.408 (0.419)
PH ₂	0.202 (0.272)	1.821 (1.822)	0.499 (0.503)	0.294 (0.374)	1.853 (1.849)	0.409 (0.420)
OH	0.266 (0.347)	1.841 (1.842)	0.416 (0.418)	0.297 (0.377)	1.860 (1.856)	0.407 (0.419)
SH	0.234 (0.307)	1.830 (1.829)	0.458 (0.463)	0.295 (0.375)	1.854 (1.850)	0.408 (0.418)
F	0.275 (0.357)	1.845 (1.846)	0.405 (0.406)	0.298 (0.378)	1.862 (1.858)	0.405 (0.416)
Cl	0.258 (0.336)	1.836 (1.836)	0.426 (0.430)	0.298 (0.378)	1.859 (1.855)	0.403 (0.415)

^a The average values for the population of $\sigma(\text{C}_2-\text{C}_3)/\sigma(\text{C}_5-\text{C}_6)$ and $\sigma(\text{C}_3-\text{H}_{\text{ax}})/\sigma(\text{C}_5-\text{H}_{\text{ax}})$ pairs of orbitals are given.

estimated from the NBO population of formally vacant p-orbital at the cationic center. Figure 12 shows contrasting behavior of the respective equatorial and axial cations which further illustrates the efficiency of double hyperconjugation. In equatorial cations, electron donor δ -substituents efficiently transfer electron density to the electron deficient carbon. Not surprisingly, electron ac-

ceptors have the opposite effect. Again, higher polarizability of the C-R bonds of higher periods leads to a stronger hyperconjugative response to the presence of a cationic center and deviations from the simple linear correlations.

Despite the complexity of the above correlations, the differences in populations of both n_{C_1} and $\sigma(\text{C}-\text{R})$ orbitals

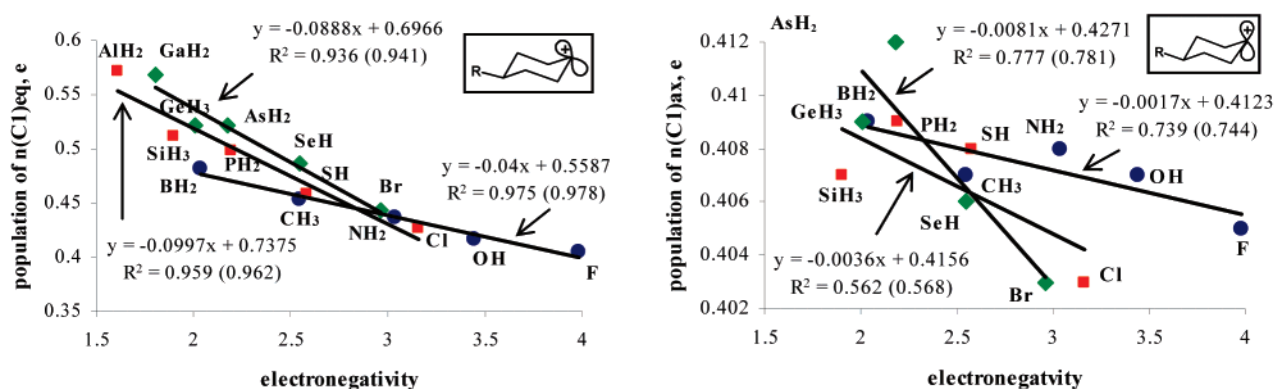


FIGURE 12. Contrasting correlations of the population of cationic p-orbital with electronegativity of δ -substituents in equatorial (left) and axial (right) cyclohexyl cations at the B3LYP/6-31G** (B3LYP/6-311++G**) level. See Figure S5 (Supporting Information) for the correlation of charge C1 with population of $n(C1)$.

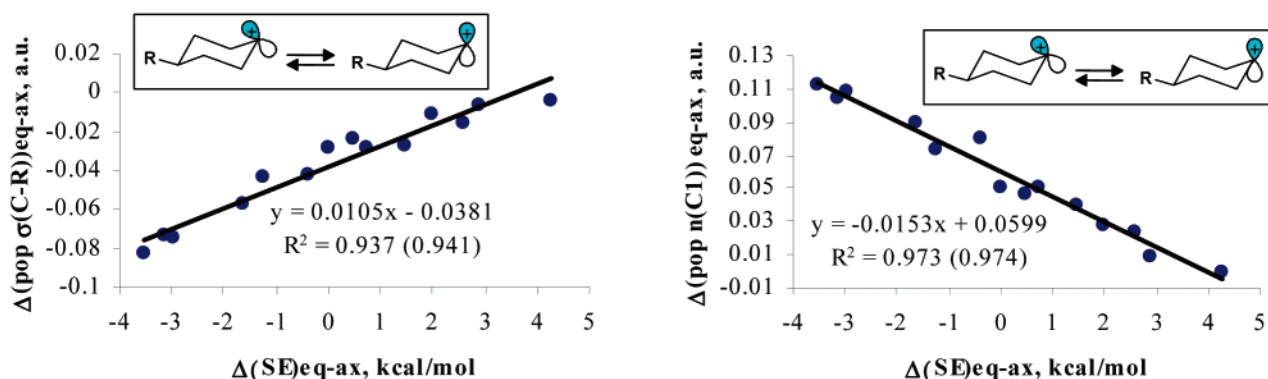


FIGURE 13. Correlations of changes of populations of $\sigma(C-R)$ and $n(C1)$ orbitals between axial and equatorial cations with ΔSE_{eq-ax} values [B3LYP/6-31G** (B3LYP/6-311++G**) level].

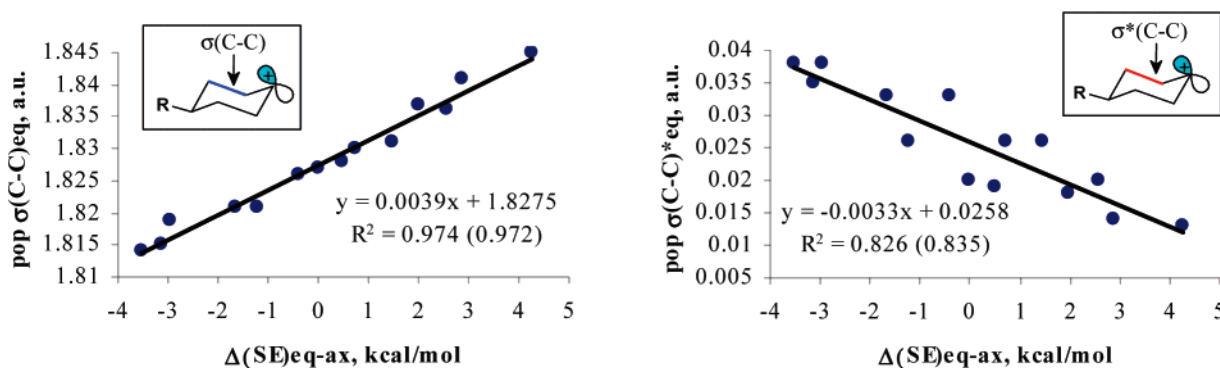


FIGURE 14. Correlations of populations of $\sigma(C-C)$ and $\sigma^*(C-C)$ bridge orbitals with ΔSE_{eq-ax} values at B3LYP/6-31G** (B3LYP/6-311++G**) level.

between the axial and equatorial cations correlate very well with ΔSE_{eq-ax} values (Figure 13) illustrating internal consistency of these parameters in description of the same physical phenomenon—double hyperconjugation.

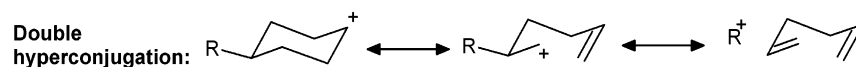
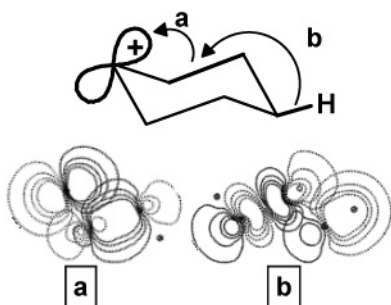
Based on these results, treatment of the bridge C–C bond is a simple “transmitter” of the interaction between the cationic center, and the C–R bond can be used only for the most general qualitative discussions. Although the sum of $\sigma(C-C)$ and $\sigma^*(C-C)$ populations remains almost constant and only a little charge is transferred from the bridge C–C moiety to the cationic center, electron acceptors (e.g., F, O, etc.) increase localization of the bridge C–C bonds preventing communication of

the two acceptors as indicated by increased population of $\sigma(C-C)$ orbitals and decreased population of $\sigma^*(C-C)$ (Table 2, Figure 14). Thus, the C–C bond is not a spectator but a dynamic gating factor capable of fine-tuning double hyperconjugation—shutting it off when a strong acceptor is present at the δ -position or opening it up when a strong donor at this position is available.

(b) Dissection of Hyperconjugative Interactions. The NBO analysis allows dissection of double hyperconjugation into components and gives further insight into its nature, e.g., the active role of the bridge C–C orbital in communication of the donor and acceptor moieties. In a possible scenario, electron density from the $\sigma(C-R)$

TABLE 4. Second-Order Perturbation Energies (kcal mol⁻¹) for the Major Interactions Involved in the Equatorial and Axial Cations of Various Cyclohexane Derivatives from NBO Computations at the B3LYP/6-31G** (B3LYP/6-311++G**) Level and the Average Energy Values of Any Pair of Interactions (See the Tables in the Supporting Information for Further Details)

R					
	$\sigma(\text{CC}) \rightarrow n(\text{C}_1)$	$\sigma(\text{CR}) \rightarrow \sigma^*(\text{CC})$	$\sigma(\text{CH}_{\text{ax}}) \rightarrow n(\text{C}_1)$	$\sigma(\text{CH}_{\text{eq}}) \rightarrow n(\text{C}_1)$	$\sigma(\text{CR}) \rightarrow \sigma^*(\text{CC})$
H	27.16 (27.54)	4.34 (4.14)	24.10 (24.30)	7.37 (8.03)	3.66 (3.32)
BH ₂	27.15 (27.50)	4.25 (3.98)	24.67 (24.91)	6.89 (7.57)	3.45 (3.04)
CH ₃	27.36 (27.67)	3.02 (2.87)	23.98 (24.21)	7.53 (8.19)	2.50 (2.24)
SiH ₃	26.59 (26.86)	5.76 (5.21)	24.81 (25.10)	6.55 (7.28)	4.47 (3.73)
GeH ₃	26.06 (26.42)	6.04 (5.60)	25.32 (25.34)	6.01 (6.88)	4.70 (4.03)
NH ₂	26.66 (27.17)	2.09 (1.93)	24.05 (24.27)	7.61 (8.27)	1.83 (1.60)
PH ₂	25.72 (26.14)	4.71 (4.46)	24.85 (25.21)	6.47 (7.16)	3.82 (3.35)
OH	26.60 (26.93)	1.96 (1.71)	22.92 (23.28)	8.29 (8.88)	1.74 (1.45)
SH	26.24 (26.65)	3.95 (3.62)	24.88 (25.22)	6.75 (7.41)	3.38 (2.89)
F	25.37 (25.74)	1.75 (1.45)	22.35 (22.81)	8.59 (9.10)	1.57 (1.23)
Cl	25.65 (25.95)	3.16 (2.82)	23.24 (23.76)	7.95 (8.43)	2.75 (2.32)

**FIGURE 15.** Resonance contributions to double hyperconjugation.¹⁷**FIGURE 16.** Overlap of donor and acceptor NBOs for the $\sigma(\text{C}-\text{C}) \rightarrow n(\text{C}^+)$ (a) and $\sigma(\text{C}-\text{H}) \rightarrow \sigma^*(\text{C}-\text{C})$ (b) interactions in the equatorial cyclohexyl cation.

donor is transmitted to the highly polarized and electron deficient bridge C–C bond in the first step. This increase in electron density makes the bridge orbital a better donor and allows it to transfer, in the second step, the acquired electron density further to the vacant p-orbital (Figure 16). In such a case, energies of respective $\sigma(\text{C}-\text{R}) \rightarrow \sigma^*(\text{C}-\text{C})$ and $\sigma(\text{C}-\text{C}) \rightarrow n(\text{C}_1)$ hyperconjugative interactions should increase as R becomes a better donor.

The NBO energies of $\sigma(\text{C}-\text{R}) \rightarrow \sigma^*(\text{C}-\text{C})$ and $\sigma(\text{C}-\text{C}) \rightarrow n(\text{C}^+)$ interactions in Tables 4 and 5 show that the magnitudes of *both* of these interactions respond strongly

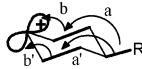
to the nature of δ -substituents and, thus, the σ bridge indeed plays an active role in positive charge delocalization. As expected, electropositive substituents increase energies of these hyperconjugative donations (Figure 17). These correlations are not perfectly linear—the presence of the most electropositive substituents leads to a steeper increase in the hyperconjugative energies which parallels enhanced polarizability of these bonds.^{41–43} Although the numerical accuracy of perturbative NBO analysis decreases in highly delocalized structures, and these energies should be taken only as a qualitative guide in the

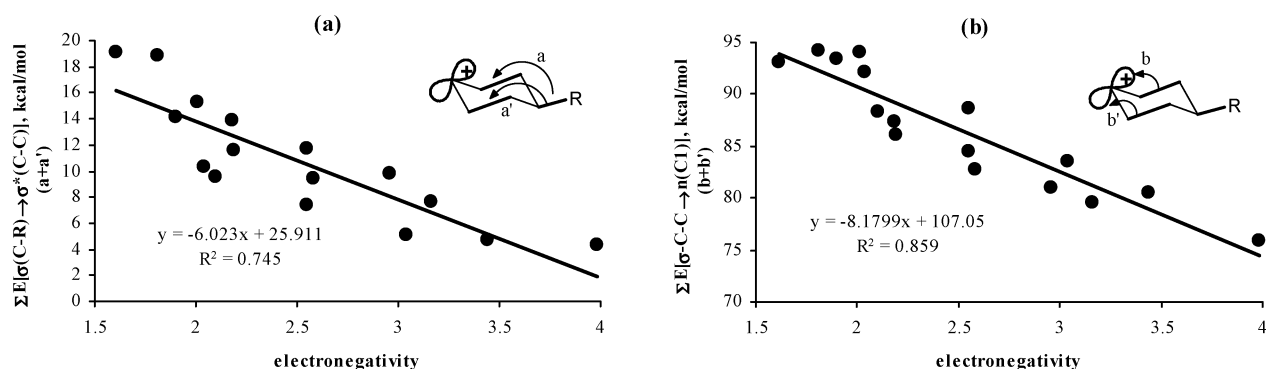
(41) Again, comparison of these effects with the axial cations given in Supporting Information provides a useful reference point. Clearly, sensitivity of $\sigma(\text{C}-\text{H}) \rightarrow n(\text{C})$ interaction in the axial cations to the nature of R is noticeably lower.

(42) Interestingly, the $\sigma(\text{C}-\text{R}) \rightarrow \sigma^*(\text{C}-\text{C})$ and $\sigma(\text{C}-\text{C}) \rightarrow n(\text{C})$ interactions are cooperative²⁶—the energies for two interactions together are larger than the sum of the individual energies obtained from the NBO deletion procedure. An interesting question is whether this cooperativity indicates that, in the case of strong σ donors, the strong through-bond interaction pattern gradually transforms into a 6e σ -aromatic system.

(43) It is interesting that these donor/acceptor interactions are topologically similar to theorbital interactions of two σ radicals through σ^* bridge orbitals which plays an important role in the chemistry of 1,4-diradicals. Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. Squires, R. R.; Cramer, C. J. *J. Phys. Chem. A* **1998**, *102*, 9072. Hoffner, J.; Schottelius, J.; Feichtinger, D.; Chen, P. *J. Am. Chem. Soc.* **1998**, *120*, 376. Kraka, E.; Cremer, D. *J. Am. Chem. Soc.* **2000**, *122*, 8245. Alabugin, I. V.; Manoharan, M. *J. Am. Chem. Soc.* **2003**, *125*, 4495.

TABLE 5. NBO Deletion Energies (kcal mol⁻¹) for the Major Interactions Involved in the Equatorial and Axial Cyclohexyl Cations at the B3LYP/6-31G** Level (See the Supporting Information for Further Details)

R									
	a	a'	b	b'	a+a'	b+b'	a+b	a'+b'	a+a'+b+b'
H	4.66	4.66	34.15	34.15	9.59	88.25	39.40	39.40	102.97
BH ₂	4.95	4.95	34.42	34.42	10.37	92.13	40.34	40.34	109.73
CH ₃	3.57	3.57	34.57	34.57	7.37	88.68	38.67	38.67	99.98
SiH ₃	6.73	6.73	33.66	33.66	14.17	93.48	41.83	41.83	120.67
NH ₂	2.56	2.33	27.42	39.36	5.04	83.57	30.19	42.05	91.02
PH ₂	5.34	5.67	25.63	39.79	11.61	86.10	31.89	47.25	110.59
OH	2.48	2.19	31.06	35.00	4.76	80.53	33.77	37.41	86.80
SH	4.48	4.71	24.68	41.73	9.48	82.74	29.58	47.37	95.52
F	2.13	2.13	31.52	31.52	4.34	75.83	33.86	33.86	81.49
Cl	3.71	3.71	32.07	32.07	7.63	79.50	36.25	36.25	90.31

**FIGURE 17.** Correlations of NBO deletion energies (B3LYP/6-31G**) corresponding to the pairs of $\sigma(\text{C-R}) \rightarrow \sigma^*(\text{C-C})$ interactions (a) and $\sigma(\text{C-C}) \rightarrow n(\text{C}_1)$ interactions (b) with the electronegativity of the corresponding elements of substituent (see Figures S7 and S8 (Supporting Information) for more details).

estimate of *relative* importance of $\sigma(\text{C-R}) \rightarrow \sigma^*(\text{C-C})$ and $\sigma(\text{C-C}) \rightarrow n(\text{C}^+)$ interactions, it is clear that the cooperative effects of these interactions are sufficiently large to overshadow the relatively small intrinsic differences in the donating ability of C–C and C–H bonds.

On the General Order of Donor Ability of σ Bonds. Although the main topic of this paper involves energetic, structural, and electronic consequences of double hyperconjugation, the results pose an intriguing question. Can one take the relative order of substituents effects on the relative stabilities of “equatorial” cations as an experimentally verifiable general scale of donor ability of σ C–R bonds? An advantage in developing such a scale based on these systems would be that the donor and acceptor sites are not *directly* connected.⁴⁴ Ideally, when *local* steric and electrostatic effects are minimized, the hyperconjugative contributions to the observable experimental values should become more obvious. Indeed,

we have shown that even though one cannot expect hyperconjugative donor ability to be the only determining factor in these systems, structural, electronic, and energy contributions from double hyperconjugation combine in a highly consistent picture.

Since SE_{eq} values are defined as the apparent stabilizing effect of the substituent relative to unsubstituted cyclohexyl cation, they can be taken to represent “apparent” donor ability of substituent R as a whole. However, SE_{eq} include contributions from many effects in addition to pure σ donation and, thus, should not be confused with the donor ability of the respective $\sigma(\text{C-R})$ bond. These values change as follows: $\text{Al} > \text{Ga} \gg \text{Ge} \geq \text{Si} > \text{As} \geq \text{B} > \text{C} \geq \text{H} > \text{P} > \text{N} > \text{Se} > \text{O} \geq \text{S} > \text{Br} > \text{Cl} \geq \text{F}$. The $\Delta\text{SE}_{\text{eq-ax}}$ values (Table 1) provided by eq 3 give an estimate of σ donor ability which follows the order of $(\text{Al}, \text{Ga}) \gg \text{Ge} > \text{As} \geq \text{Si} > \text{P} > \text{B} > \text{Se} > \text{H} > \text{C} > \text{S} > \text{Br} > \text{N} > \text{Cl} > \text{O} > \text{F}$ (\geq means that difference is less than 0.5 kcal/mol, \gg stands for the difference more than 3 kcal/mol). Although this scale does not isolate hyperconjugation completely from other components, these

(44) Interestingly, group-transfer energies are dominated by the electronegativity effects in the case of directly connected atoms, e.g.: Wiberg, K. B. *Acc. Chem. Res.* **1999**, 32, 922.

stabilization energies are practically useful, chemically meaningful and can be verified experimentally as outlined recently by Rauk and co-workers.¹⁵

Not surprisingly, the two above scales of donor ability are different. Interestingly, the relative positions of carbon and hydrogen switch. According to SE_{eq} values ("apparent" donor ability of substituent R) the CH_3 group is a stronger donor than the H substituent, a trend which is reversed according to ΔSE_{eq-ax} values ("apparent" hyperconjugative donor ability of $\sigma(C-R)$ bond). In addition, similar switches are observed for a number of other pairs including potentially important combinations of other orbitals of similar donor ability (Cl/O, Br/O, S/O, B/P, C/P, N/Se etc.). To analyze to what extent the ΔSE_{eq-ax} scale is influenced by a nonperfect compensation of the nonhyperconjugative effects, one can also consider relative trends from more rigorous quantum-mechanical estimate provided by NBO analysis. Values of $\sigma(C-R) \rightarrow \sigma^*(C-C)$ energies (Table 5) which, in principle, should be the most straightforward criterion of donor ability) suggest that $Al > Ga \gg Ge > Si > As \gg Se > P > B > Br > H > S \gg Cl > C > N > O > F$. The "anomalous" positions of Br and Cl are not surprising because the polarizable C-Br and C-Cl bonds are indeed moderately strong donors. Unfortunately, $\sigma(C-R) \rightarrow \sigma^*(C-C)$ energies are influenced not only by the donor ability of σ bonds but also by the changing acceptor ability of $\sigma^*(C-C)$ bonds in different cyclohexyl cations which is, in turn, modified by the difference in the acceptor properties of the corresponding C-R antibonds (*vide infra*). Interestingly, when $\sigma(C-R) \rightarrow \sigma^*(C-C)$ and $\sigma(C-C) \rightarrow n(C_1)$ interactions (Table 5) are added to account for the second component in the double hyperconjugation array, the relative order approaches that given by the ΔSE_{eq-ax} scale: $Ga > Al > Ge > Si > As > P > B > H > C > Se > S > N > Br > Cl > O > F$. Populations of $\sigma(C-R)$ bonds (Table 2) in equatorial cyclohexyl cations give a similar order: $Al, Ga \gg Ge > As, Si > P > B, Se > H, S > C \gg Br > Cl > N > O > F$. Note that in all of the above trends the C-H bond remains a stronger donor than the C-C bond and that the donor abilities decrease when going from left to right in a period and from bottom to top in a group. However, differences arise when elements of different periods are compared. These differences suggest that one has to be careful in defining the criteria of donor ability. Since criteria that are based on the NBO dissection of the wave function are not directly measurable experimentally, the discussion of which of the above NBO criteria is the best from the purist point of view goes beyond the scope of this paper. On the other hand, even though the ΔSE_{eq-ax} criterion is not perfect, the ΔSE_{eq-ax} values can be determined experimentally. Moreover, they are based on physically and chemically meaningful phenomena and provide a useful estimate of the relative trends in donor ability of σ bonds.

Finally, we hope that the relative orders of the donor abilities reported above will be useful for qualitative reasoning but we would like to caution against their noncritical applications. One of important conclusions from this study is that the communication of σ bonds throughout the molecule has a large effect on the relative donor abilities of σ bonds even when donor and acceptor

sites are not directly connected. Other points one has to consider in developing a general scale of donor ability of σ bonds are the greater sensitivity of C-X bonds toward heavier elements to increased electronic demand (increased polarizability) and the active role of the σ bridge connecting donor and acceptor orbitals. In light of these findings, it would be very interesting to reexamine some of the literature controversies regarding the relative donor abilities of σ bonds and to determine whether some of them were fueled by similar differences in the definitions.⁴⁵

Conclusions

Importantly, the order of donor ability of σ bonds in organic molecules is not "set in stone" because bonds in carbon-based networks efficiently communicate with each other through double hyperconjugation and other "second sphere" effects. Such interactions can efficiently change the intrinsic order of donor ability of σ bonds as illustrated by the order of *apparent* donor ability of C-H and C-C bonds in δ -substituted cyclohexyl cations.

The systematic differences between elements from different periods such as the higher polarizability of σ bonds with heavier elements is another reason one has to be careful in developing a "truly general" trend in the donor ability of σ bonds. Even when two C-X and C-Y σ bonds, with X and Y from different rows, display similar donor ability in neutral molecules close to their energy minimum conformation, these bonds will respond differently to structural perturbation such as introduction of a cationic center.

Finally, σ bridge connecting the donor and acceptor moieties shows remarkable behavior. Although the net amount of charge is transferred from the bridge C-C moiety to the cationic center remains essentially constant, electron acceptors increase localization of the bridge C-C bonds preventing communication of the two acceptors. Thus, the C-C bond is not a spectator but a dynamic gating factor capable of fine-tuning double hyperconjugation—shutting it off when a strong acceptor is present or opening it up when a strong donor is available.

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Supporting Information Available: Correlations of substituent stabilization energies of the "equatorial" and "axial" cyclohexyl cations with electronegativity in different periods. Correlations of the populations of donor and acceptor orbitals in cyclohexanes and cyclohexyl cations with electronegativity. Correlations of NBO deletion energies of individual and

(45) Obviously, the differences in the donor abilities of a C-X σ donor bond depend on the nature of the acceptor, topology of interaction, contribution of electrostatic and steric effects and substitution on the X atom. We *expect* that such effects may (and most likely will) change the apparent donor ability of σ bonds in stereoelectronic effects and require computational reexamination of such effects every time a new system is subject to investigation.

combined hyperconjugative interactions with eneelectronegativity. Correlation of the relative energies of equatorial and axial cations with the hyperconjugative energies. The second-order perturbation as well as the NBO deletion energies of individual hyperconjugative interactions and the sum of the major hyperconjugative interactions involved in axial and

equatorial cyclohexyl cations. Cartesian coordinates of all optimized geometries computed at both B3LYP/6-31G** and B3LYP/6-311++G** levels. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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