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Direct Estimate of the Strength of Conjugation and Hyperconjugation by the Energy Decomposition Analysis Method

Israel Fernández and Gernot Frenking*[a]

Abstract: The intrinsic strength of π interactions in conjugated and hyperconjugated molecules has been calculated using density functional theory by energy decomposition analysis (EDA) of the interaction energy between the conjugating fragments. The results of the EDA of the *trans*-polyenes $H_2C{=}CH{-}(HC{=}CH)_n{-}CH{=}CH_2$ ($n = 1$–3) show that the strength of π conjugation for each C=C moiety is higher than in *trans*-1,3-butadiene. The absolute values for the conjugation between Si=Si π bonds are around two-thirds of the conjugation between C=C bonds but the relative contributions of ΔE_π to ΔE_{orb} in the all-silicon systems are higher than in the carbon compounds. The π conjugation between C=C and C=O or C=NH bonds in $H_2C{=}CH{-}C(H){=}O$ and $H_2C{=}CH{-}C(H){=}NH$ is comparable to the strength of the conjugation between C=C bonds. The π conjugation in $H_2C{=}CH{-}C(R){=}O$ decreases when R = Me, OH, and NH_2 while it increases when R = halogen. The hyperconjugation in ethane is around a quarter as strong as the π conjugation in ethyne. Very strong hyperconjugation is found in the central C−C bonds in cubylcubane and tetrahedranyltetrahedrane. The hyperconjugation in substituted ethanes $X_3C{-}CY_3$ (X,Y = Me, SiH_3, F, Cl) is stronger than in the parent compound particularly when X,Y = SiH_3 and Cl. The hyperconjugation in donor–acceptor-substituted ethanes may be very strong; the largest ΔE_π value was calculated for $(SiH_3)_3C{-}CCl_3$ in which the hyperconjugation is stronger than the conjugation in ethene. The breakdown of the hyperconjugation in $X_3C{-}CY_3$ shows that donation of the donor-substituted moiety to the acceptor group is as expected the most important contribution but the reverse interaction is not negligible. The relative strengths of the π interactions between two C=C double bonds, one C=C double bond and CH_3 or CMe_3 substituents, and between two CH_3 or CMe_3 groups, which are separated by one C−C single bond, are in a ratio of 4:2:1. Very strong hyperconjugation is found in $HC{\equiv}C{-}C(SiH_3)_3$ and $HC{\equiv}C{-}CCl_3$. The extra stabilization of alkenes and alkynes with central multiple bonds over their terminal isomers coming from hyperconjugation is bigger than the total energy difference between the isomeric species. The hyperconjugation in $Me{-}C(R){=}O$ is half as strong as the conjugation in $H_2C{=}CH{-}C(R){=}O$ and shows the same trend for different substituents R. Bond energies and lengths should not be used as indicators of the strength of hyperconjugation because the effect of σ interactions and electrostatic forces may compensate for the hyperconjugative effect.

Keywords: bonding analysis · conjugation · density functional calculations · energy decomposition · hyperconjugation

Introduction

Compounds with double bonds that are separated by one single bond are usually more stable than bond-shifted isomers in which the double bonds are isolated from each other by more than one single bond. The effect is called conjugation which is explained in MO theory by π–π* interactions while the same phenomenon is explained in VB theory in terms of resonance structures. Conjugative interactions play an important role in explaining the geometries and reactivities of molecules particularly in organic chemistry. The remarkably short C−C single bond distance in 1,3-butadiene is a structural manifestation of conjugation while 1,4-addition to enones is an example of the effect of conjugation on the reactivity of molecules. It is important, however, to recognize that conjugation is just a bonding model and therefore conjugative stabilization is only a virtual thermodynamic quantity that cannot be measured experimental-

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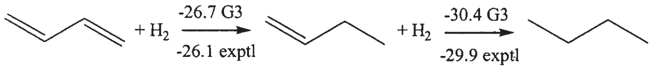
ly. The strength of conjugative interactions can only be determined with respect to a reference system. Although the choice of the reference system is somewhat arbitrary, a plausible and well-defined system can be helpful in establishing a relative scale for the strength of conjugative interactions.

Conjugation also leads to the delocalization of electronic charge which has been the topic of intensive theoretical and experimental research.[1] This work, however, is concerned with the energetic consequences of conjugative interactions. The most common approach to the estimation of conjugative stabilization is based on the initial suggestion of Kistiakowsky and co-workers[2] in 1936 to correlate stabilization with reaction energies. For example, the conjugative stabilization in 1,3-butadiene may be estimated as the difference between the first and second hydrogenation energies [Reaction (1)].

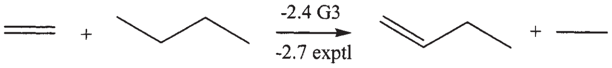


(1)

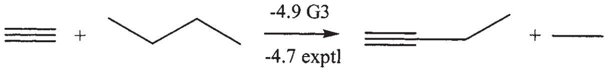
The first step of the hydrogenation reaction (1) is less exothermic than the second step[3] because in the latter process there is no loss of π conjugation. There are two problems with the above definition of conjugative stabilization. First, the products and educts in reaction (1) differ not only as a result of the π interactions between the double bonds but also because the σ bonds change during the reaction. Secondly, although there are no conjugating double bonds in 1-butene there are π interactions between the C=C π bond and the π orbitals of the ethyl group and this effect is known as hyperconjugation. The latter interaction is often neglected but it can significantly influence the structures and reaction energies of molecules. A recent example is the heat of hydrogenation of 1,3-butadiyne [reaction (2)].

(2)

The two steps of this hydrogenation reaction have nearly identical energies which led to the suggestion that there is no conjugation in 1,3-butadiyne.[4] This statement is not justified. It has been shown that as expected π conjugation in 1,3-butadiyne is even larger than in 1,3-butadiene when hyperconjugation is included in the analysis of the π interactions.[5] This can be done for example by using isodesmic reactions (3) and (4) to estimate thermodynamic stabilization through hyperconjugation in 1-butene and 1-butyne.



(3)



(4)

However, the latter approach has the same problem as the use of reactions (1) and (2) for estimating the strength of the π conjugation in 1,3-butadiene and 1,3-butadiyne because the σ bonds of the products and educts are not the same. It would be helpful if a reference system could be chosen which makes it possible to directly estimate the strength of π interactions, that is, conjugation and hyperconjugation, in molecules that are not considerably different from the investigated species. Energy decomposition analysis (EDA), which was developed by Ziegler and Rauk[6] following a similar procedure suggested by Morokuma,[7] is a method that uses only the π orbitals of the interacting fragments in the geometry of the molecule for estimating π interactions.

EDA[8] has proven a powerful tool for improving the understanding of the nature of the bonding in main-group[9] and transition-metal compounds.[10] Since the method has been discussed in detail previously[8–10] we shall describe the concept only briefly. In EDA, bond formation between the interacting fragments is divided into three steps that can be interpreted in a plausible way. In the first step the fragments, which are calculated using the frozen geometry of the entire molecule, are superimposed without electronic relaxation to yield the quasiclassical electrostatic attraction $\Delta E_{\mathrm{elstat}}$. In the second step the product wave function is antisymmetrized and renormalized, which gives the repulsive term $\Delta E_{\mathrm{Pauli}}$, termed the Pauli repulsion. In the third step the molecular orbitals relax to their final form to yield the stabilizing orbital interaction ΔE_{orb}. The latter term can be divided into contributions of orbitals with different symmetry. This third step is crucial for the present study. The sum of the three terms $\Delta E_{\mathrm{elstat}}+\Delta E_{\mathrm{Pauli}}+\Delta E_{\mathrm{orb}}$ gives the total interaction energy ΔE_{int}. Note that the latter is not the same as the bond dissociation energy because the relaxation of the fragments is not considered in ΔE_{int}. The interaction energy, ΔE_{int}, together with the term ΔE_{prep}, which is the energy necessary to promote the fragments from their equilibrium geometry to the geometry in the compounds, can be used to calculate the bond dissociation energy, $-D_e = \Delta E_{\mathrm{prep}}+\Delta E_{\mathrm{int}}$. Further details about EDA can be found in the literature.[8]

In recent communications we reported on the energy decomposition analysis of the π interactions in 1,3-butadiene, 1,3-butadiyne, and related systems[11] and we compared the calculated strength of the π conjugation in *meta*- and *para*-substituted benzylic cations and anions by using Hammett σ parameters.[12] Herein we report on a systematic study of the strength of the π conjugation and hyperconjugation in a variety of acyclic molecules. (Related work in which we analyze conjugation and hyperconjugation in cyclic molecules is in progress.) We analyze the π conjugation in the homologous series of four conjugated polyenes from *trans*-1,3-butadiene to all-*trans*-1,3,5,7,9-decapentaene. The π conjugation between C=C, Si=C, and Si=Si is compared through analysis of the EDA data for 1,3-butadiene and its mono-, di- and tetrasila analogues. We have also calculated the strength of the π conjugation between C=C and C=O bonds in the enone systems $H_2C{=}CH{-}C(R){=}O$, where R = H, Me, OH, NH_2, F, Cl, Br, and I, and in $H_2C{=}CH{-}C(H){=}NH$. Hyperconjugation has been analyzed in symmetrically and unsymmetrically substituted ethane molecules $X_3C{-}CY_3$, where X,Y = H, Me, SiH_3, F, and Cl. The strength of the π interactions in $H_2C{=}C(H){-}CX_3$ and $HC{\equiv}C{-}CX_3$ has been calculated for X = H, Me, SiH_3, F, and Cl. Finally we present the EDA results for the hyperconjugation between the methyl group and the C=O π bond in the carbonyl compounds $Me{-}C(R){=}O$, where R = H, Me, OH, NH_2, F, Cl, Br, and I, and for the hyperconjugation in $Me{-}C(H){=}NH$. The interacting fragments used in the EDA calculations are the open-shell species that result from cleavage of the σ bond(s) between them.

Computational Details

The geometries of the molecules were optimized at the nonlocal DFT level of theory using Becke's exchange functional[13] in conjunction with Perdew's correlation functional[14] (BP86). Uncontracted Slater-type orbitals (STOs) were employed as basis functions in SCF calculations.[15] Triple-ζ-quality basis sets were used which were augmented by two sets of polarization functions, that is, p and d functions for the hydrogen atom and d and f functions for the other atoms. This level of theory is denoted as BP86/TZ2P. Most of our previous work was carried out at the BP86/TZ2P level of theory and may therefore be used to estimate the performance of the level of theory.[9–12] An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.[16] All structures were verified as minima on the potential-energy surface by calculating the Hessian matrices. The calculations were carried out using the ADF-(2003.1) program package.[8b]

The open-shell fragments for the EDA can only be calculated with the ADF program by using the restricted formalism while for the optimization of the fragments the unrestricted formalism is used. The energy differences between the restricted and unrestricted calculations were always <1 kcal mol^{-1} and are incorporated into the ΔE_{prep} values.

Results and Discussion

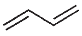
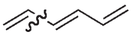
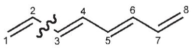
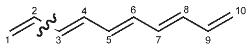
Conjugation: Table 1 gives the EDA results for an homologous series of four conjugated polyenes, *trans*-1,3-butadiene to all-*trans*-1,3,5,7,9-decapentaene, in which one terminal vinyl fragment interacts with the rest of the species. The interacting fragments were calculated in all cases in the electronic doublet state with the unpaired electron in a σ orbital. The calculated energies exhibit a smooth trend with the absolute values of the interaction energy ΔE_{int} and of the contributing energy terms ΔE_{elstat}, ΔE_{Pauli}, and ΔE_{orb} increasing with longer chain length in agreement with the shortening of the C2–C3 bond. The σ and π contributions to the orbital interactions also increase from left to right. The increase in the energy contribution is strongest when the number of conjugating double bonds increases from one to two while it falls off as the number of conjugating moieties becomes larger. Note that the relative contribution of ΔE_π to ΔE_{orb} also increases from 8.6% in 1,3-butadiene to 10.0% in all-*trans*-1,3,5,7,9-decapentaene. Note also that the increase in ΔE_π is very similar to the increase in the overall interaction energy ΔE_{int} although the absolute values of the former are much smaller than those of ΔE_{int} and the other terms. This provides a hint as to why many properties such as the excitation energy and absorption spectra of conjugated polyenes can be modeled by considering only the π electrons.[17]

We also investigated the π conjugation in the four polyenes using the conjugating C=C moieties as fragments when they simultaneously interact with each other. The terminal $\cdot HC{=}CH_2$ fragments were calculated in the electronic doublet state (with the unpaired electron in a formally sp^2-hybridized orbital) while the central $\cdot HC{=}CH\cdot$ fragments were calculated as open-shell triplets. The EDA results are given in Table 2.

As expected, the absolute values of the energy terms increase as the number of conjugating moieties rises from $n=2$ (*trans*-1,3-butadiene) to $n=5$ (all-*trans*-1,3,5,7,9-decapentaene). However, analysis of the calculated numbers reveals some interesting trends. The interaction energies rise more than just linearly as *n* increases. The polyenes experience an extra stabilization which is given by the ΔE_{int}(extra) values shown in Table 2. What is striking is the finding that the increase in the extra stabilization is very similar to the increase in the π conjugation which is given by the $\Delta\Delta E_\pi$ values. Note that the ΔE_π values contribute only 8.6–10.2% to the orbital interactions ΔE_{orb} which in turn provide only ~56% of the attractive interactions. Although the π-orbital interactions are only a minor contributor to the total binding they correlate very strongly with the overall trend shown by ΔE_{int}.

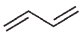
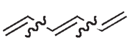
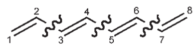
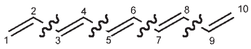
Next we investigated the strength of the π conjugation in the silicon analogues of 1,3-butadiene in which up to four of the carbon atoms are substituted by silicon. The conjugation

Table 1. EDA results for alkenes using two fragments.[a]

				
symmetry	C_{2h}	C_{2h}	C_{2h}	C_{2h}
ΔE_{int}	−128.5	−132.1	−133.0	−133.4
$\Delta\Delta E_{int}$[b]		−3.6	−0.9	−0.4
ΔE_{Pauli}	268.4	271.3	272.4	273.0
ΔE_{elstat}[c]	−169.9 (42.8%)	−172.4 (42.7%)	−173.0 (42.7%)	−173.4 (42.7%)
ΔE_{orb}[c]	−227.5 (57.2%)	−231.1 (57.3%)	−232.3 (57.3%)	−233.0 (57.3%)
ΔE_σ[d]	−207.5 (91.4%)	−209.0 (90.5%)	−209.4 (90.1%)	−209.6 (90.0%)
ΔE_π[d]	−19.5 (8.6%)	−22.0 (9.5%)	−23.0 (9.9%)	−23.4 (10.0%)
$\Delta\Delta E_\pi$[b]		−2.5	−1.0	−0.4
ΔE_{prep}	13.0	13.4	13.6	13.7
ΔE $(=-D_e)$	−115.5	−118.7	−119.4	−119.7
r(C2–C3) [Å]	1.453	1.444	1.441	1.439

[a] Energy values in kcal mol^{-1}. [b] The $\Delta\Delta E$ values give the difference in energy with the preceding molecule. [c] The percentage values in parentheses give the contribution to the total attractive interactions, $\Delta E_{elstat}+\Delta E_{orb}$. [d] The percentage values in parentheses give the contribution to the total orbital interactions, ΔE_{orb}.

Table 2. EDA results for alkenes using nC$_2$ fragments (n = 2– 5).[a]

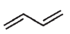
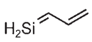
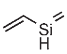
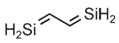
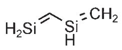
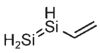
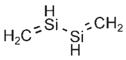
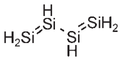
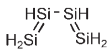
				
symmetry	C_{2h}	C_{2h}	C_{2h}	C_{2h}
ΔE_{int}	−128.5	−278.9	−429.9	−581.3
ΔE_{int}(extra)[b]	–	−21.9	−22.5	−22.9
ΔE_{Pauli}	268.4	501.0	737.2	976.1
ΔE_{elstat}[c]	−169.9 (42.8 %)	−340.2 (43.6 %)	−512.5 (43.9 %)	−686.0 (44.0 %)
ΔE_{orb}[c]	−227.5 (57.2 %)	−439.7 (56.4 %)	−654.6 (56.1 %)	−871.4 (56.0 %)
ΔE_{σ}[d]	−207.5 (91.4 %)	−398.3 (90.6 %)	−589.8 (90.1 %)	−782.1 (89.7 %)
ΔE_{π}[d]	−19.5 (8.6 %)	−41.4 (9.4 %)	−64.9 (9.9 %)	−89.3 (10.2 %)
$\Delta\Delta E_{\pi}$[e]	−19.5	−21.9	−23.5	−24.4
ΔE_{prep}	13.0	17.4	22.7	27.8
ΔE (= $-D_e$)	−115.5	−261.1	−407.2	−553.5
r(C−C)[f] [Å]	1.453	1.444	C2−C3: 1.441 C4−C5: 1.432	C2−C3: 1.439 C4−C5: 1.428

[a] Energy values in kcal mol^{-1}. [b] Extra stabilization with respect to the sum of the ΔE_{int} values of the preceding molecule and 1,3-butadiene. [c] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{elstat}+\Delta E_{orb}$. [d] The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb}. [e] Increase of ΔE_{π} with respect to the preceding molecule. [f] Length of the conjugating C−C bond.

between the Si=C and C=C π bonds in 1-sila- and 2-sila-1,3-butadiene has already been addressed in a theoretical study by Trinquier and Malrieu.[18] These workers compared the π conjugation in the silabutadienes with that in the parent compound 1,3-butadiene but it was not clear if the former compounds have stronger or weaker π interactions than the latter. They used a model proposed by Daudey et al.[19] in which the Hartree–Fock π orbitals of the dienes are replaced by appropriate nonresonating localized π MOs in the field of the σ SCF distributions. This method gave resonance energies of 10.3 kcal mol^{-1} for 1,3-butadiene, 13.7 kcal mol^{-1} for 1-sila-1,3-butadiene and 28.3 kcal mol^{-1} for 2-sila-1,3-butadiene. Isodesmic reactions of these three compounds yielded a completely different order for the strength of the conjugation which was estimated as 11.6 kcal mol^{-1} for 1,3-butadiene, 5.7 kcal mol^{-1} for 1-sila-1,3-butadiene and only 0.2 kcal mol^{-1} for 2-sila-1,3-butadiene.[18] We decided to tackle the unresolved question about the strength of the π conjugation and we extended the scope of the study to di-, tri-, and tetrasila-1,3-butadiene. A substituted derivative of tetrasila-1,3-butadiene with bulky Tip groups (Tip = 2,4,6-triisopropylphenyl) has been synthesized and structurally characterized by X-ray diffraction by Weidenbruch et al.[20] but the other silicon homologs are only known as unstable intermediates.[21] Interestingly, the tetrasila-1,3-butadiene adopts an s-*gauche* geometry rather than the *trans* form which is found for most analogous carbon compounds.[20]

Table 3 gives the EDA results for 1,3-butadiene and its silicon analogues. We calculated the planar *cis* and *trans* forms of 1,3-butadiene. The calculated data indicate that the π conjugation in *trans*-1,3-butadiene (19.5 kcal mol^{-1}) is slightly stronger than in *cis*-1,3-butadiene (17.2 kcal mol^{-1}) which can be explained by the shorter C2−C3 bond length of the latter species. Note that planar *cis*-1,3-butadiene is not a minimum on the PES. Steric repulsion between the terminal methylene groups leads to twisting about the central C2−C3 bond yielding an s-*gauche* form that is 0.31 kcal mol^{-1} lower in energy than the planar *cis* form but 3.70 kcal mol^{-1} less stable than the planar *trans* form. This is in agreement with experimental results[22] and with previous theoretical

Table 3. EDA results for sila-1,3-butadienes. The interacting fragments are the terminal C=C, C=Si, or Si=Si species.[a]

											
	trans	*cis*	**1**	**2**	**3**	**3′**	**4**	**5**	**6**	*trans*-**7**	*cis*-**7**
symmetry	C_{2h}	C_{2v}	C_s	C_s	C_{2h}		C_s	C_s	C_{2h}	C_{2h}	C_{2v}
ΔE_{int}	−128.5	−125.7	−131.3	−102.5	−135.7	−134.6	−110.8	−98.8	−79.5	−79.0	−77.8
ΔE_{Pauli}	268.4	257.4	263.8	176.9	263.9	244.0	177.5	172.4	107.2	109.3	105.6
ΔE_{elstat}[b]	−169.9 (42.8 %)	−163.1 (42.6 %)	−160.4 (40.6 %)	−128.5 (46.0 %)	−152.9 (38.3 %)	−144.0 (38.0 %)	−125.6 (43.6 %)	−120.9 (44.6 %)	−88.8 (47.5 %)	−81.9 (43.5 %)	−78.6 (42.9 %)
ΔE_{orb}[b]	−227.5 (57.2 %)	−220.0 (57.4 %)	−234.6 (59.4 %)	−150.9 (54.0 %)	−246.7 (61.7 %)	−234.6 (62.0 %)	−162.7 (56.4 %)	−150.3 (55.4 %)	−98.0 (52.5 %)	−106.4 (56.5 %)	−104.8 (57.1 %)
ΔE_{σ}[c]	−207.5 (91.4 %)	−202.7 (92.2 %)	−209.9 (89.5 %)	−138.9 (92.1 %)	−213.9 (86.7 %)	−205.1 (87.4 %)	−146.4 (89.9 %)	−136.9 (91.1 %)	−89.2 (91.0 %)	−93.7 (88.1 %)	−93.0 (88.7 %)
ΔE_{π}[c]	−19.5 (8.6 %)	−17.2 (7.8 %)	−24.8 (10.5 %)	−12.0 (7.9 %)	−32.8 (13.3 %)	−29.5 (12.6 %)	−16.4 (10.1 %)	−13.4 (8.9 %)	−8.8 (9.0 %)	−12.6 (11.9 %)	−11.8 (11.3 %)
ΔE_{prep}	13.0	14.2	17.7	8.2	2.6	21.9	11.5	8.3	2.9	3.1	3.3
ΔE (= $-D_e$)	−115.5	−111.5	−113.6	−94.3	−133.1	−112.7	−99.3	−90.5	−76.6	−75.9	−74.5
r(X−X′) [Å][d]	1.453	1.469	1.442	1.844	1.424	1.453	1.817	1.845	2.299	2.274	2.284

[a] Energy values in kcal mol^{-1}. [b] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{elstat}+\Delta E_{orb}$. [c] The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb}. [d] Interatomic distance between the central atoms X and X′.

work.[23] The *gauche* form has C_2 symmetry and therefore σ–π mixing takes place. The calculated π conjugation in the planar *cis* form may be used as a reference value which serves as an upper limit of the conjugation in the s-*gauche* form.

The strength of the π conjugation in *trans*-1-sila-1,3-butadiene (**1**) is clearly larger (24.8 kcal mol^{-1}) than in *trans*-1,3-butadiene while the π conjugation in *trans*-2-sila-1,3-butadiene (**2**) (12.0 kcal mol^{-1}) is significantly weaker than in both *trans*-1,3-butadiene and **2**. The change in the π conjugation can be explained by the polarization of the C=Si π bond towards the more electronegative carbon atom which yields a stronger π interaction when the C=Si π bond is bonded with the carbon end next to the C=C π bond rather than with the silicon end and by the shorter (longer) central bond in **1** (**2**). The EDA data for the strength of the π conjugation ΔE_π in **1** and **2** are at variance with the trends predicted by Trinquier and Malrieu.[18] We think that the present values are more reasonable when one considers the polarization of the π orbitals.

The change in the central bond length and the polarization of the C=Si π bond also accounts for the EDA data for the π conjugation in *trans*-disila-1,3-butadienes **3**–**6**. *trans*-1,4-Disila-1,3-butadiene (**3**) has the largest ΔE_π value (32.8 kcal mol^{-1}) of the series while its isomer *trans*-2,3-disila-1,3-butadiene (**6**) has the smallest ΔE_π value (8.8 kcal mol^{-1}). We calculated the π conjugation in compound **3′** which was optimized using the same C2−C3 bond length as that in *trans*-1,3-butadiene in order to address the question of how much of the increase in the strength of the π conjugation comes from the shorter carbon−carbon bond in **3**. The data in Table 3 show that the stronger π conjugation in the latter compound comes mainly from the substitution of the terminal carbon atoms by silicon which yields an increase of 10.0 kcal mol^{-1} when one goes from *trans*-1,3-butadiene (19.5 kcal mol^{-1}) to **3′** (29.5 kcal mol^{-1}). The shortening of the central carbon−carbon bond from **3′** to **3** enhances the π conjugation by only 3.3 kcal mol^{-1}. It follows that the nature of the terminal groups in the homologs of 1,3-butadiene is more important for the strength of the π conjugation than the central bond length. The same conclusion comes from a comparison of the ΔE_π values of **2** and **5**. The latter compound has stronger π conjugation (13.4 kcal mol^{-1}) than the former (12.0 kcal mol^{-1}) although the central bond in **5** (1.845 Å) is a little longer than that in **2** (1.844 Å).

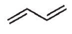
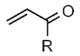
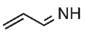
As expected, substitution of the terminal carbon atoms in **6** by silicon atoms to yield **7** enhances the π conjugation. The π conjugation in the tetrasila-1,3-butadiene species *cis*-**7** (11.8 kcal mol^{-1}) is slightly weaker than in *trans*-**7** (12.6 kcal mol^{-1}), as was found in the parent carbon system. The absolute ΔE_π values for the all-silicon systems *cis*-**7** and *trans*-**7** are about two-thirds of the values for 1,3-butadiene. Note that the relative contribution of the π conjugation to the total orbital interactions, which is given by the percentage values of ΔE_π, is higher for tetrasila-1,3-butadiene than for 1,3-butadiene. Thus, π conjugation plays an as important role in the silicon analogues of 1,3-butadiene as in the parent system. The same conclusion was drawn from the experimental data for hexaaryl-substituted *cis*-tetrasila-1,3-butadiene. The electronic spectrum of the latter compound exhibits a significant bathochromic shift compared with persilylated disilenes and the central (terminal) Si−Si bonds are shorter (longer) than typical silicon–silicon single (double) bonds.[20]

The *trans* form of tetrasila-1,3-butadiene is 1.39 kcal mol^{-1} lower in energy than the *cis* form which is less than the difference in energy between *trans*- and *cis*-1,3-butadiene (4.01 kcal mol^{-1}). Relaxation of the C_{2v} geometry constraints to yield the s-*gauche* energy minima showed that the latter form is lower in energy than the *cis* form of 1,3-butadiene by 0.31 kcal mol^{-1} and 1.64 kcal mol^{-1} lower than the *trans* isomer of tetrasila-1,3-butadiene. This means that the s-*gauche* form becomes the global energy minimum of the latter species while it remains higher in energy than the *trans* form of 1,3-butadiene.

The remaining EDA data for 1,3-butadiene and its silicon homologs in Table 3 give further useful information about the nature of the central bond. Although this paper focuses on π conjugation we will briefly discuss the results in the context of this bond. Note that the nature of the central bond changes very little when one compares 1,3-butadiene with tetrasila-1,3-butadiene. The relative contributions of the quasiclassical electrostatic $\Delta E_{\mathrm{elstat}}$ and orbital ΔE_{orb} terms to the attractive interactions are nearly the same while the π conjugation is slightly greater in the latter system. The orbital interactions are enhanced while the electrostatic attraction is weakened when one goes from *trans*-1,3-butadiene to *trans*-1,4-disila-1,3-butadiene (**3**) which is mainly due to the increase in the π conjugation (Table 3). But π conjugation is not always the most important factor that explains the change in the bonding interactions. Compounds **4** and **5** have a central Si−C bond in which conjugation takes place either between a Si=Si bond and a C=C bond (**5**) or between two Si=C bonds (**4**). Table 3 shows that the stronger overall attraction in the latter compound ($\Delta E_{\mathrm{int}} = -110.8$ kcal mol^{-1}) relative to the former species ($\Delta E_{\mathrm{int}} = -98.8$ kcal mol^{-1}) comes mainly from the σ interactions which increase by 9.5 kcal mol^{-1} and not from the π interactions which increase by only 3.0 kcal mol^{-1}.

Next we discuss the EDA results for the enone and enimine compounds given in Table 4. The π conjugation in the parent enone system 2-propenal is slightly stronger (20.5 kcal mol^{-1}) than in *trans*-1,3-butadiene (19.5 kcal mol^{-1}) although the bond length of the conjugating C2−C3 bond in the former compound is longer (1.474 Å) than in the latter (1.453 Å). Substitution of the α hydrogen atom in the former molecule by methyl, hydroxy, or amine groups leads to slightly weaker π conjugation for vinyl methyl ketone (18.0 kcal mol^{-1}), propenoic acid (18.4 kcal mol^{-1}), and propenamide (15.6 kcal mol^{-1}). It follows that α-hydrogen substitution in 2-propenal by the π-donor ligands OH and NH_2 weakens the π conjugation in the parent enone system. This is not the case for substitution with halogen atoms F, Cl, Br, and I, which are also π-donor ligands. Table 4 shows that the

Table 4. EDA results for enone and enimine compounds. The interacting fragments are the terminal C=C and C=O (C=N) moieties.[a]

										
		R = H	R = Me	R=OH	R = NH_2	R = F	R = Cl	R = Br	R = I	
symmetry	C_{2h}	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s
ΔE_{int}	−128.5	−104.9	−101.4	−111.7	−102.4	−114.0	−104.8	−101.1	−95.3	−111.7
ΔE_{Pauli}	268.4	324.3	317.8	296.2	302.7	295.4	310.1	316.8	327.1	316.3
ΔE_{elstat}[b]	−169.9	−186.9	−186.1	−176.6	−178.7	−173.6	−171.5	−168.3	−167.2	−187.6
	(42.8%)	(43.5%)	(44.4%)	(43.3%)	(44.1%)	(42.4%)	(41.3%)	(40.3%)	(39.6%)	(43.8%)
ΔE_{orb}[b]	−227.5	−242.3	−233.2	−231.3	−226.4	−235.7	−243.3	−249.6	−255.2	−240.4
	(57.2%)	(56.5%)	(55.6%)	(56.7%)	(55.9%)	(57.6%)	(58.7%)	(59.7%)	(60.4%)	(56.2%)
ΔE_σ[c]	−207.5	−221.8	−215.1	−212.9	−210.8	−215.1	−222.2	−228.2	−233.8	−220.3
	(91.4%)	(91.6%)	(92.3%)	(92.1%)	(93.1%)	(91.3%)	(91.3%)	(91.4%)	(91.6%)	(91.7%)
ΔE_π[c]	−19.5	−20.5	−18.0	−18.4	−15.6	−20.6	−21.1	−21.4	−21.4	−20.1
	(8.6%)	(8.4%)	(7.7%)	(7.9%)	(6.9%)	(8.7%)	(8.7%)	(8.6%)	(8.4%)	(8.3%)
ΔE_{prep}	13.0	7.6	9.0	9.1	9.1	8.7	9.1	9.4	10.3	10.2
ΔE (=$-D_e$)	−115.5	−97.2	−92.4	−102.6	−93.3	−105.3	−95.7	−91.7	−85.1	−101.5
r(C2−C3) [Å][d]	1.453	1.474	1.489	1.480	1.495	1.471	1.474	1.474	1.475	1.465

[a] Energy values in kcal mol^{-1}. [b] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{elstat}+\Delta E_{orb}$. [c] The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb}. [d] Length of the conjugating C−C bond.

π conjugation in propenoyl fluoride (20.6 kcal mol^{-1}) and particularly in the analogous compounds with heavier halogen atoms [chlorine (21.1 kcal mol^{-1}), bromine (21.4 kcal mol^{-1}), and iodine (21.4 kcal mol^{-1})] is stronger than in 2-propenal. The change in π conjugation that occurs with the halogenide atoms does not result from a change in the C2−C3 bond length of the conjugation bond which remains nearly the same as in the parent system. Table 4 also shows that the π conjugation in propenimine is stronger (20.1 kcal mol^{-1}) than in *trans*-1,3-butadiene (19.5 kcal mol^{-1}) but weaker than in 2-propenal (20.5 kcal mol^{-1}).

The ΔE_π data for the enone molecules $H_2C{=}CH{-}C(R){=}O$ provide a scale which shows how much a substituent R enhances or weakens the π conjugation between the C=C and C=O moieties. Another scale for estimating substituent effects on conjugation has been derived from experimental data by Hammett.[24] Hammett analyzed the rate of hydrolysis of benzoic acids carrying a substituent R in the *para* position. Hammett parameters are now widely used in organic chemistry.[25] We have recently shown that Hammett's σ_p parameters correlate very well with the ΔE_π values of benzylic cations and anions.[12] We were curious to find out whether there is also a correlation between Hammett's σ_p parameters and the ΔE_π data of the enone molecules $H_2C{=}CH{-}C(R){=}O$. Figure 1 shows that there is indeed a linear correlation (correlation coefficient −0.97 and standard deviation 0.54) which suggests that the electronic effect of the substituents R on π conjugation in homo- and heteroconjugated systems is similar and thus appears to be rather independent of the nature of the conjugating system.

Hyperconjugation: Hyperconjugation is the interaction between orbitals having π symmetry where at least one of the π orbitals is located at an atom that does not have a multiple bond. Figure 2a and b show the case in which the π orbital of a C=C double bond interacts with the π orbital of a CR_3 group. Hyperconjugation has two components, namely C=C→CR_3 donation (Figure 2a), which is also called positive hyperconjugation, and C=C←CR_3 back-donation (Figure 2b), which is usually called negative hyperconjugation.[26] The latter interaction is particularly important when the saturated donor group carries an electron lone-pair. Negative hyperconjugation is also very important for explaining the anomeric effect.[27]

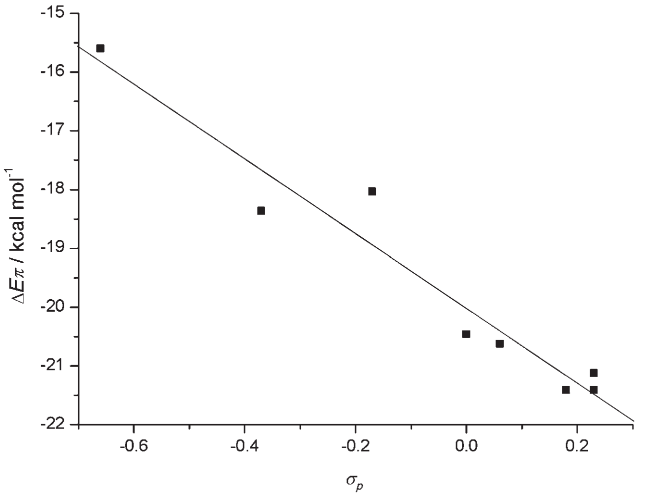


Figure 1. Plot of ΔE_π values versus Hammett σ_p constants.

Hyperconjugation also operates in saturated systems like ethane that have π orbitals (Figure 2c and d). Hyperconjugation may also take place between orbitals that have pseudo-π symmetry, as shown in Figure 2a′–d′. Figure 2a′ and b′ schematically show the relevant orbitals of C=C−CR_3 in which one of the C−R bonds is in the plane of the C=C orbital which now has only local π symmetry. The interacting acceptor and donor orbitals of the CR_3 group have σ* and σ symmetry, respectively. The hyperconjugation shown in Figure 2a′ is therefore named a π→σ* interaction while the situation shown in Figure 2b′ is called a σ→π* interac-

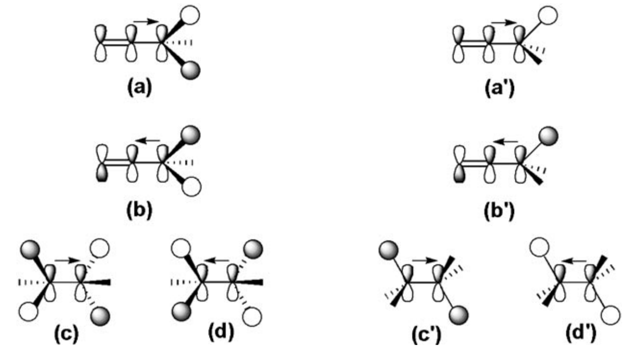


Figure 2. Schematic representation of hyperconjugation between a C=C double bond and a CR_3 group. Left: Hyperconjugation between π orbitals. a) C=C→CR_3 π donation; b) C=C←CR_3 π back-donation; c) and d) hyperconjugation in ethane-like molecules. Right: Hyperconjugation involving σ orbitals. a′) C=C→CR_3 donation from an occupied orbital having local π symmetry to a σ* orbital; b′) C=C←CR_3 back-donation from an occupied σ orbital to a vacant orbital which has local π* symmetry; c′) and d′) hyperconjugation between σ and σ* orbitals.

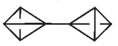
tion. The latter description becomes important, for example, in systems that exhibit strong negative hyperconjugation such as CH_3CH_2X, where X is a particularly strong donor such as an electron lone-pair or a lithium atom.[28] In our work we studied only the hyperconjugation that results from genuine π interactions.

The strength of the hyperconjugation in ethane was the topic of a recent controversy.[29] It has been suggested that the staggered geometry of ethane is caused by hyperconjugation rather than steric repulsion.[29a,c] Although this view was rejected by other workers[29b,d] there was agreement that hyperconjugation even in saturated systems is important. Therefore we carried out a systematic EDA of the strength of hyperconjugation in saturated and unsaturated compounds.

We first discuss the EDA results for the ethane compounds $X_3C{-}CX_3$, where X = H, Me, SiH_3, F, and Cl, which are given in Table 5. The EDA data suggest that the orbital interactions provide 52–58 % of the attractive C−C interactions while the electrostatic bonding contributes between 42–48 %. Note that the relaxation of the CX_3 fragments after breaking the $X_3C{-}CX_3$ bond varies between 5.3 and 39.7 kcal mol^{-1} which means that the bond dissociation energy (BDE) may not correlate well with the intrinsic carbon–carbon interactions. For example, the ΔE_{int} values for $Me_3C{-}CMe_3$ (−93.2 kcal mol^{-1}) and $F_3C{-}CF_3$ (−92.4 kcal mol^{-1}) are very similar but the BDE value of the latter molecule (87.1 kcal mol^{-1}) is much higher than that of the former (63.0 kcal mol^{-1}) because C_2F_6 has a very small ΔE_{prep} value (Table 5).

The $X_3C{-}CX_3$ molecules were optimized with D_{3d} symmetry. The EDA was carried out with C_{3v} symmetry which means that there are orbitals with $a_1(\sigma)$, $a_2(\delta)$, and $e(\pi)$ symmetry. The small contribution of δ to the substituted ethylenes, which comes from the d polarization functions, can be neglected. Table 5 shows that the hyperconjugation in ethane is −10.0 kcal mol^{-1} which is 5.4 % of the total orbital interactions. Comparison with the calculated strength of the conjugation in *trans*-1,3-butadiene (−19.5 kcal mol^{-1}) indicates that hyperconjugation is as expected weaker but not negligible. Note that the hyperconjugation in ethane comes from two components of the degenerate e(π) orbital. Only one component is shown in Figure 2c. A quantitative comparison of the hyperconjugation in ethane should therefore be made with 1,3-butadiyne. The EDA of the latter compound gives a value of $\Delta E_{\pi} = -45.0$ kcal mol^{-1} for the strength of the conjugation.[11] This result and the value of ΔE_{π} for ethane indicate that the strength of the hyperconjugative interactions between C−H bonds is about a quarter of the strength of the conjugation between C=C π bonds.

Table 5. EDA results of symmetrically substituted ethanes $X_3C{-}CX_3$.[a]

	X = H	X = CH_3	X = SiH_3	X = F	X = Cl	X = C(cubyl) 	X = C(tetrahedryl) 
symmetry[b]	D_{3d}	D_{3d}	D_{3d}	D_{3d}	D_{3d}	D_{3d}	D_{3d}
ΔE_{int}	−114.8	−93.2	−89.0	−92.4	−70.2	−105.2	−142.6
ΔE_{Pauli}	200.8	253.6	226.0	254.9	296.3	344.1	225.2
ΔE_{elstat}[c]	−131.3	−163.5	−131.4	−151.3	−157.0	−206.9	−144.0
	(41.6 %)	(47.2 %)	(41.7 %)	(43.6 %)	(42.8 %)	(46.1 %)	(39.2 %)
ΔE_{orb}[c]	−184.2	−183.2	−183.6	−196.1	−209.5	−242.3	−223.8
	(58.4 %)	(52.8 %)	(58.3 %)	(56.4 %)	(57.2 %)	(53.9 %)	(60.8 %)
$\Delta E_{\sigma}(a_1)$[d]	−174.3	−170.9	−165.6	−183.0	−188.2	−221.6	−196.7
	(94.6 %)	(93.3 %)	(90.2 %)	(93.4 %)	(89.8 %)	(91.5 %)	(87.9 %)
$\Delta E_{\delta}(a_2)$[d]	0.0	−0.6	−0.5	−0.2	−0.4	−0.2	0.0
	(0.0 %)	(0.3 %)	(0.3 %)	(0.1 %)	(0.2 %)	(0.1 %)	(0.0 %)
$\Delta E_{\pi}(e)$[d]	−10.0	−11.6	−17.5	−12.9	−20.9	−20.5	−27.1
	(5.4 %)	(6.4 %)	(9.5 %)	(6.6 %)	(10.0 %)	(8.5 %)	(12.1 %)
ΔE_{prep}	21.8	30.2	39.7	5.3	17.2	7.8	6.4
$\Delta E\ (=-D_e)$	−93.8	−63.0	−49.3	−87.1	−53.0	−97.4	−136.2
r(C−C) [Å]	1.532	1.591	1.612	1.565	1.593	1.476	1.425

[a] Energy values in kcal mol^{-1}. [b] The EDA was carried out using C_{3v} symmetry. [c] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{elstat}+\Delta E_{orb}$. [d] The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb}.

Table 5 shows that the hyperconjugation in the substituted ethanes $X_3C{-}CX_3$ (X = Me, SiH_3, F, Cl) is stronger than in the parent compound particularly for X = SiH_3 and Cl. It is generally assumed that silyl groups exhibit strong hyperconjugative interactions which makes them suitable protecting groups for multiple bonds.[30] The data in Table 5 suggest that the hyperconjugation of C−Cl bonds is even stronger than that of $C{-}SiH_3$ bonds. Unlike C−Cl bonds, the latter group can additionally protect a multiple bond through steric shielding by bulky R groups in $C{-}SiR_3$. Please note that the hyperconjugation in substituted ethanes $X_3C{-}CX_3$ is stronger than in $H_3C{-}CH_3$ although the C−C bonds in the former compounds are clearly longer than in ethane. The compounds with the strongest hyperconjugation, $(SiH_3)_3C{-}C(SiH_3)_3$ and $Cl_3C{-}CCl_3$, actually have the longest C−C bonds. This is an important result because a short bond is often taken as evidence for hyperconjugation. The hyperconjugation in $Cl_3C{-}CCl_3$ ($-20.9\,\mathrm{kcal\,mol^{-1}}$) is more than twice as strong as in ethane. It follows from comparison with the ΔE_π value calculated for ethyne that the hyperconjugation between CR_3 groups across a C−C bond may be half as strong as the conjugation between C≡C π bonds. If both π components of the CR_3 group are active the total hyperconjugation can be as strong as a single C≡C π bond.

Particularly interesting examples of strong hyperconjugation across C−C single bonds have been calculated between two cubyl moieties in cubylcubane and between two tetrahedranyl fragments in tetrahedranyltetrahedrane (Table 5). Cubylcubane was synthesized in 1988 by Eaton and coworkers.[31] The experimentally observed short C−C distance of the central bond (1.458 Å) is reproduced by the BP86/TZ2P calculations which give a value of 1.476 Å. An even shorter bond is predicted by BP86/TZ2P calculations on tetrahedranyltetrahedrane (1.425 Å, Table 5), which is in agreement with earlier calculations by Xie and Schaefer.[32] Very recently, the hexakis(trimethylsilyl)-substituted derivative of the latter compound was synthesized by Tanaka and Sekiguchi[33] which was the first example of a tetrahedranyltetrahedrane molecule. The experimental value for the central C−C distance (1.436 Å) is in excellent agreement with the theoretical values. The authors explained the short distance in terms of the high percentage s character of the carbon−carbon bond orbital of the central bond.[33] Note that the skeletal bonds of the central carbon atoms in the above compound are also rather short (1.483–1.484 Å). Table 5 shows that the short central C−C bonds in cubylcubane and tetrahedranyltetrahedrane can also be explained by unusually strong hyperconjugation. The $\Delta E_\pi(e)$ values for cubylcubane ($-20.5\,\mathrm{kcal\,mol^{-1}}$) and tetrahedranyltetrahedrane ($-27.1\,\mathrm{kcal\,mol^{-1}}$) are much higher than for $Me_3C{-}CMe_3$ ($-11.6\,\mathrm{kcal\,mol^{-1}}$). We think that the short central bonds of cubylcubane and tetrahedranyltetrahedrane are at least partially caused by π-bonding contributions.

Table 6 gives EDA data for unsymmetrically substituted ethane systems $X_3C{-}CY_3$ (X,Y = Me, SiH_3, F, Cl). Note that the orbital term of the molecules $H_3C{-}CF_3$ and $H_3C{-}CCl_3$, which have the most polar C−C bonds, make significantly higher relative and absolute contributions to the total interaction energy than the other compounds. The EDA data also indicate that through a favorable combination of donor and acceptor groups the overall hyperconjugation can be significantly stronger in asymmetric systems than in symmetric systems. The strongest hyperconjugation is calculated for $(SiH_3)_3C{-}CCl_3$, which has a ΔE_π value of $-29.7\,\mathrm{kcal\,mol^{-1}}$. It is not only the absolute value but also the relative contribution (12.5 %) of the hyperconjugation to the total orbital interactions that are higher in the latter compound than in the parent systems $(SiH_3)_3C{-}C(SiH_3)_3$ and $Cl_3C{-}CCl_3$. Please note that the hyperconjugation in $(SiH_3)_3C{-}CCl_3$ is even stronger than in tetrahedranyltetrahedrane although the latter compound has a much shorter central C−C bond (1.425 Å) than the former (1.523 Å).

It is reasonable to assume that the strong hyperconjugation in $(SiH_3)_3C{-}CCl_3$ comes mainly from $(SiH_3)_3C \rightarrow CCl_3$ π

Table 6. EDA results for unsymmetrically substituted ethanes $X_3C{-}CY_3$.[a]

	X = H Y = CH_3	X = H Y = SiH_3	X = H Y = F	X = H Y = Cl	X = CH_3 Y = SiH_3	X = CH_3 Y = F	X = CH_3 Y = Cl	X = SiH_3 Y = F	X = SiH_3 Y = Cl	X = F Y = Cl
symmetry[b]	T_d	C_{3v}	C_{3v}	C_{3v}	C_{3v}	C_{3v}	C_{3v}	C_{3v}	C_{3v}	C_{3v}
ΔE_{int}	−104.6	−100.9	−113.4	−100.2	−91.6	−103.4	−91.9	−102.2	−91.3	−81.7
$\Delta E_{\mathrm{Pauli}}$	243.8	228.7	444.0	418.6	243.0	282.2	299.4	288.2	319.9	285.3
$\Delta E_{\mathrm{elstat}}$[c]	−156.8 (45.0 %)	−139.2 (42.2 %)	−160.0 (28.7 %)	−165.1 (31.8 %)	−149.7 (44.7 %)	−177.4 (45.9 %)	−174.3 (44.5 %)	−168.7 (43.2 %)	−173.1 (42.1 %)	−157.7 (43.0 %)
ΔE_{orb}[c]	−191.6 (55.0 %)	−190.4 (57.8 %)	−397.4 (71.3 %)	−353.7 (68.2 %)	−184.9 (55.3 %)	−208.9 (54.1 %)	−217.1 (55.5 %)	−221.7 (56.8 %)	−238.1 (57.9 %)	−209.2 (57.0 %)
$\Delta E_\sigma(a_1)$[d]	−180.2 (94.1 %)	−176.4 (92.7 %)	−382.7 (96.3 %)	−336.5 (95.1 %)	−169.6 (91.7 %)	−191.8 (91.8 %)	−197.2 (90.8 %)	−197.3 (89.0 %)	−207.9 (87.3 %)	−192.0 (91.8 %)
$\Delta E_\delta(a_2)$[d]	< −0.1	< −0.1	< −0.1	< −0.1	−0.6 (0.3 %)	−0.3 (0.1 %)	−0.5 (0.2 %)	−0.3 (0.1 %)	−0.5 (0.2 %)	−0.2 (0.1 %)
$\Delta E_\pi(e)$[d]	−11.3 (5.9 %)	−13.9 (7.3 %)	−14.6 (3.7 %)	−17.2 (4.9 %)	−14.7 (8.0 %)	−16.8 (8.0 %)	−19.5 (9.0 %)	−24.1 (10.9 %)	−29.7 (12.5 %)	−17.0 (8.1 %)
ΔE_{prep}	22.3	23.3	14.1	18.6	33.0	16.6	24.9	21.9	31.8	10.1
$\Delta E\ (=-D_e)$	−82.3	−77.6	−99.3	−81.6	−58.6	−86.8	−67.0	−80.3	−59.5	−71.6
r(C−C) [Å]	1.539	1.562	1.504	1.515	1.601	1.534	1.563	1.512	1.523	1.570

[a] Energy values in $\mathrm{kcal\,mol^{-1}}$. [b] The EDA was carried out using C_{3v} symmetry. [c] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{orb}}$. [d] The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb}.

donation and less from $Cl_3C{\rightarrow}C(SiH_3)_3$ π donation because the silyl group is a good donor. We estimated the strengths of the donor contributions $X_3C{\rightarrow}CY_3$ and $Y_3C{\rightarrow}CX_3$ to the total hyperconjugation through EDA calculations of $X_3C{-}CY_3$ in which the π* orbital of the CY_3 fragment was deleted. Table 7 gives the ΔE_π values for the symmetric and unsymmetrical systems $X_3C{-}CY_3$. The data in parentheses below the ΔE_π values correspond to the $X_3C{\rightarrow}CY_3$ (first value) and $Y_3C{\rightarrow}CX_3$ donation (second value). The sum of the two values in parentheses do not exactly give the total ΔE_π value because deletion of the π* orbital affects all the other orbitals in the calculations which means that the remaining interacting orbitals in the deletion calculation are not the same as in the undeleted one. However, the deletion procedure may be used to estimate the relative strengths of $X_3C{\rightarrow}CY_3$ and $Y_3C{\rightarrow}CX_3$ donation to the total hyperconjugation.

Table 7. Calculated total and partial ΔE_π(e) values for ethanes $X_3C{-}CY_3$.[a,b]

X/Y	H	CH_3	SiH_3	F	Cl
H	−10.0 (−5.6)	−11.3 (−6.4; −6.7)	−13.9 (−8.2; −7.7)	−14.6 (−5.9; −11.2)	−17.2 (−7.3; −12.2)
CH_3		−11.6 (−6.8)	−14.7 (−8.7; −8.3)	−16.8 (−8.2; −11.7)	−19.5 (−9.3; −13.1)
SiH_3			−17.5 (−9.8)	−24.1 (−10.4; −17.4)	−29.7 (−12.6; −20.8)
F				−12.9 (−7.9)	−17.0 (−10.1; −10.2)
Cl					−20.9 (−12.1)

[a] The first value in parentheses is an estimate of the $\pi(X_3C){\rightarrow}\pi^*(CY_3)$ π donation after deleting the π*(e) orbitals in CX_3. The second value in parentheses is an estimate of the $\pi(Y_3C){\rightarrow}\pi^*(CX_3)$ π donation after deleting the π*(e) orbitals in CY_3. [b] Energy values in kcal mol^{-1}.

Table 7 shows that the major contribution to the hyperconjugation in $(SiH_3)_3C{-}CCl_3$ indeed comes mainly from $(SiH_3)_3C{\rightarrow}CCl_3$ π donation (−20.8 kcal mol^{-1}) and less from $Cl_3C{\rightarrow}C(SiH_3)_3$ π donation (−12.6 kcal mol^{-1}). The relative contributions to the hyperconjugation in the other unsymmetrical systems $X_3C{-}CY_3$ generally agree with chemical expectations but there are some points worthy of note. For example, hyperconjugation in $Me_3C{-}CMe_3$ is stronger (−11.6 kcal mol^{-1}) than in $H_3C{-}CH_3$ (−10.6 kcal mol^{-1}) but the π donor strength of the CMe_3 group in the mixed compound $Me_3C{-}CH_3$ is slightly smaller (−6.4 kcal mol^{-1}) than that of the CH_3 group (−6.7 kcal mol^{-1}) which means that C−H bonds are slightly better π donors than C−C bonds when they interact directly with each other. In all other systems $Me_3C{-}CY_3$ and $H_3C{-}CY_3$ (Y = SiH_3, F, Cl) it is found that the π donation $Me_3C{\rightarrow}CY_3$ is bigger than $H_3C{\rightarrow}CY_3$ (Table 7) which means that in these compounds C−C bonds are better π donors than C−H bonds. The EDA data indicate that the relative π donor strengths of two groups may be inverted depending on the acceptor moiety. The same conclusion has been drawn by Alabugin and Manoharan[34] who analyzed hyperconjugation in cyclohexyl cations. Note also that hyperconjugation involving the CCl_3 group in $Cl_3C{-}CY_3$ is clearly always stronger than in the corresponding fluorine systems $F_3C{-}CY_3$ but in $Cl_3C{-}CF_3$ the two components $Cl_3C{\rightarrow}CF_3$ (−10.1 kcal mol^{-1}) and $F_3C{\rightarrow}CCl_3$ (−10.2 kcal mol^{-1}) have nearly the same strength with CF_3 even being a slightly stronger π donor.

Hyperconjugation is frequently invoked in discussions on the interaction of a saturated substituent with an unsaturated double or triple bond. Therefore we analyzed the π interactions in the ethylene and acetylene systems $H_2C{=}CH{-}CX_3$ and $HC{\equiv}C{-}CX_3$ with the same groups as above (X = H, Me, SiH_3, F, Cl). The results are given in Table 8 and Table 9.

The EDA data show that the hyperconjugation in the alkyne parent compound $HC{\equiv}C{-}CH_3$ (−20.1 kcal mol^{-1}) is slightly more than twice as strong as in the alkene parent molecule $H_2C{=}CH{-}CH_3$ (−9.3 kcal mol^{-1}). The hyperconjugation in the former compound has two π components while only one in the latter. The C−C single bond in $HC{\equiv}C{-}CH_3$ is also shorter (1.456 Å) than that in $H_2C{=}CH{-}CH_3$

Table 8. EDA results for substituted alkenes $H_2C{=}CH{-}CX_3$. The interacting fragments are $H_2C{=}CH$ and CX_3.[a]

	X = H	X = CH_3	X = SiH_3	X = F	X = Cl
symmetry	C_s	C_s	C_s	C_s	C_s
ΔE_{int}	−119.4	−108.8	−107.9	−113.8	−102.7
ΔE_{Pauli}	229.0	267.9	269.2	272.3	314.0
ΔE_{elstat}[b]	−147.6 (42.4 %)	−171.8 (45.6 %)	−161.5 (42.8 %)	−170.1 (44.1 %)	−178.9 (42.9 %)
ΔE_{orb}[b]	−200.8 (57.6 %)	−204.9 (54.4 %)	−215.6 (57.2 %)	−215.9 (55.9 %)	−237.8 (57.1 %)
ΔE_σ(a′)[c]	−191.5 (95.4 %)	−195.4 (95.4 %)	−201.2 (93.3 %)	−204.3 (94.6 %)	−223.2 (93.8 %)
ΔE_π(a″)[c]	−9.3 (4.6 %)	−9.5 (4.6 %)	−14.4 (6.7 %)	−11.6 (5.4 %)	−14.7 (6.2 %)
ΔE_π(a″)[d]	−4.0	−4.3	−5.8	−7.6	−8.9
ΔE_π(a″)[e]	−6.0	−6.2	−9.7	−5.2	−6.9
ΔE_{prep}	17.2	18.8	20.1	10.4	15.6
ΔE (= $-D_e$)	−102.2	−90.0	−87.8	−103.4	−87.1
r(C−C) [Å]	1.500	1.516	1.512	1.496	1.496

[a] Energy values in kcal mol^{-1}. [b] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{elstat}+\Delta E_{orb}$. [c] The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb}. [d] Estimate of the $\pi(H_2C{=}CH){\rightarrow}\pi^*(CX_3)$ π donation after deleting the π*(a″) orbitals in $H_2C{=}CH$. [e] Estimate of the $\pi^*(H_2C{=}CH){\leftarrow}\pi(CX_3)$ π donation after deleting the π*(a″) orbitals in CX_3.

Table 9. EDA results of substituted alkynes HC≡C−CX_3. The interacting fragments are HC≡C and CX_3.[a]

	X = H	X = CH_3	X = SiH_3	X = F	X = Cl
symmetry	C_{3v}	C_{3v}	C_{3v}	C_{3v}	C_{3v}
ΔE_{int}	−143.6	−133.1	−133.6	−130.4	−120.8
$\Delta E_{\mathrm{Pauli}}$	176.5	219.1	239.1	218.1	281.8
$\Delta E_{\mathrm{elstat}}$[b]	−125.5	−151.8	−147.5	−140.6	−157.9
	(39.2 %)	(43.1 %)	(39.6 %)	(40.4 %)	(39.2 %)
ΔE_{orb}[b]	−194.6	−200.4	−225.2	−207.8	−244.7
	(60.8 %)	(56.9 %)	(60.4 %)	(59.6 %)	(60.8 %)
ΔE_{σ}[c]	−174.6	−179.8	−192.2	−184.4	−212.2
	(89.7 %)	(89.7 %)	(85.4 %)	(88.9 %)	(86.7 %)
ΔE_{π}[c]	−20.1	−20.6	−33.0	−23.0	−32.5
	(10.3 %)	(10.3 %)	(14.6 %)	(11.1 %)	(13.3 %)
ΔE_{π}[d]	−9.3	−10.4	−14.7	−17.2	−22.4
ΔE_{π}[e]	−12.8	−12.6	−21.4	−9.8	−14.4
ΔE_{prep}	13.1	14.5	16.1	7.5	12.7
ΔE (=$-D_e$)	−130.5	−118.6	−117.5	−122.9	−108.1
r(C−C) [Å]	1.456	1.469	1.446	1.456	1.435

[a] Energy values in kcal mol^{-1}. [b] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{\mathrm{elstat}}+\Delta E_{\mathrm{orb}}$. [c] The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb}. [d] Estimate of the π(HC≡C)→π^*(CX_3) π donation after deleting the π*(a″) orbitals in HC≡C. [e] Estimate of the π(HC≡C)←π(CX_3) π donation after deleting the π*(a″) orbitals in CX_3.

(1.500 Å). The intrinsic hyperconjugation of each component in propene and propyne thus has nearly the same strength. For both compounds the π donation from the methyl group to the multiple bond is stronger than the acceptance of the methyl group. Hyperconjugation in HC≡C−CH_3 is twice as strong as in H_3C−CH_3 (−10.0 kcal mol^{-1}).

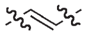
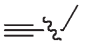
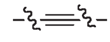
The hyperconjugation in the substituted systems H_2C=CH−CX_3 and HC≡C−CX_3 is stronger than in the parent compounds, particularly for X = SiH_3 and Cl. The methyl groups in H_2C=CH−CMe_3 and HC≡C−CMe_3 yield only slightly larger ΔE_{π} values than propene and propyne. Note that both π components H_2C=CH→CMe_3 and H_2C=CH←CMe_3 are stronger than those in propene while in the triply bonded system the HC≡C←CMe_3 π donation (−12.6 kcal mol^{-1}) is actually slightly weaker than the HC≡C←CH_3 π donation (−12.8 kcal mol^{-1}). Thus, the C−H bonds are better π donors than C−C when one compares HC≡C−CH_3 with HC≡C−CMe_3 while the opposite order is calculated for the compounds H_2C=CH−CH_3 and H_2C=CH−CMe_3. Analysis of the EDA data for the other systems H_2C=CH−CX_3 and HC≡C−CX_3 gives results that are in agreement with chemical intuition, that is, the C(SiH_3)$_3$ group is a stronger π donor than π acceptor while CF_3 and CCl_3 are stronger π acceptors than π donors when they interact with a carbon–carbon multiple bond (Table 8 and Table 9).

A very important conclusion that can be drawn from the data given in Table 8 and Table 9 concerns the correlation between the calculated strength of hyperconjugation given by the ΔE_{π} values and the theoretically predicted C−CX_3 bond lengths and energies. Short single bonds are often used as criteria for strong hyperconjugation. It could also be assumed that large ΔE_{π} values should yield stronger bonds. The data in Table 8 and Table 9 show that there is no clear correlation between the C−CX_3 bond lengths and the ΔE_{π} values. For example, the H_2CCH−CX_3 distances for X = F and Cl are equally short (1.496 Å) while the bond length for X = SiH_3 is longer (1.512 Å) although the hyperconjugation in the fluorine compound is weaker than in the silicon compound. The HCC−C(SiH_3)$_3$ bond (1.446 Å) is longer than the HCC−CCl_3 bond (1.435 Å) but the hyperconjugation in the former molecule is slightly larger than in the latter. Other effects such as the influence of the electronegativity of the substituent on the σ bonding and the electrostatic interaction play a role that hamper a direct correlation between hyperconjugation and bond distance. The same holds for the effect of hyperconjugation on bond strength. Such a correlation might be expected between the values calculated for ΔE_{int} and ΔE_{π}. Table 8 and Table 9 show that the interaction energies are significantly higher for H_2CCH−CH_3 and HCC−CH_3 than for H_2CCH−CMe_3 and HCC−CMe_3, respectively. The hyperconjugation in the methyl-substituted systems is slightly larger, however, than in the parent compounds.

The EDA makes it possible to investigate the question why alkenes and alkynes with terminal multiple bonds are less stable than those with internal π bonds. In general, more substituted alkenes are energetically lower-lying than less substituted species. The textbook explanation is that hyperconjugation is partly responsible for the lower energy of the more substituted alkenes.[25] Table 10 gives the EDA results for 1-butene, 2-butene, 1-butyne, and 2-butyne. The calculations show that the "internal" isomers 2-butene and 2-butyne are electronically more stable than the terminal isomers by 3.7 and 7.0 kcal mol^{-1}, respectively. The EDA data indicate that the contribution of the hyperconjugation to the higher stability of 2-butene over 1-butene is 7.8 kcal mol^{-1}, which is about twice as much as the total energy difference between the two isomers. The difference between the ΔE_{π} values of 1-butyne and 2-butyne is even greater (9.2 kcal mol^{-1}). Note that the stabilization of the latter comes from only one π component of the hyperconjugation in 2-butyne. The contribution of the total hyperconjugation in 2-butyne can be estimated to yield an extra stabilization of 18.5 kcal mol^{-1} compared with 1-butyne.[35] Thus, the hyperconjugative stabilization of terminal alkenes and alkynes compared with their internal isomers is larger than the total energy difference.

We finally investigated the strength of the hyperconjugation between a methyl group and a C=O double bond in carbonyl compounds Me−C(R)=O that carry the same substituents R as in the above analysis of the enone compounds H_2C=CH−C(R)=O. The results are shown in Table 11. The

Table 10. EDA results for isomers of butene and butyne. For 1-butene and 1-butyne the interactions between two fragments were calculated, while for 2-butene and 2-butyne three fragments were used as shown.[a]

				
symmetry	C_s	C_{2h}	C_s	D_{3d}[b]
ΔE_{int}	−115.8	−258.5	−140.1	−292.2
ΔE_{Pauli}	247.5	413.9	197.6	328.6
ΔE_{elstat}[c]	−158.8	−290.0	−138.8	−245.6
	(43.7 %)	(43.1 %)	(41.1 %)	(39.6 %)
ΔE_{orb}[c]	−204.6	−382.4	−198.8	−375.2
	(56.3 %)	(56.9 %)	(58.9 %)	(60.4 %)
ΔE_{σ}[d]	−194.7	−364.8	−188.4	−355.7
	(95.1 %)	(95.4 %)	(94.8 %)	(94.8 %)
ΔE_{π}[d]	−9.9	−17.7	−10.4	−19.6
	(4.9 %)	(4.6 %)	(5.2 %)	(5.2 %)
$\Delta\Delta E_{\pi}$	0.0	−7.8	0.0	−9.2
ΔE_{prep}	17.9	26.0	15.5	49.4
ΔE (=$-D_e$)	−97.9	−232.5	−124.6	−242.8
r(C−C) [Å]	1.506	1.501	1.460	1.458
E_{rel}	0.0	−3.7	0.0	−7.0

[a] Energy values in kcal mol^{-1}. [b] The EDA was carried out with C_s symmetry, that is, the ΔE_{π} value gives only one component of the π bonding. [c] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{elstat}+\Delta E_{orb}$. [d] The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb}.

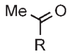
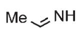
EDA data suggest that the investigated carbon−carbon bonds Me−C(R)=O are weaker but make a significantly larger contribution to the orbital term than the Me−CH=CH$_2$ single bond. The absolute value for the hyperconjugation ΔE_{π} in the carbonyl compounds Me−C(R)=O is slightly bigger than in Me−CH=CH$_2$ except for R = NH$_2$, but the relative contribution to ΔE_{orb} in the former compounds is less than in propene. Note that the hyperconjugation in Me−C(R)=O shows for the substituents R the same trend as the conjugation in H$_2$C=CH−C(R)=O (Table 4). The acetyl halogenides Me−C(X)=O (X = F, Cl, Br, I) possess stronger hyperconjugation than the parent acetaldehyde while acetic acid, acetamide, and dimethyl ketone have smaller ΔE_{π} values than Me−CH=O (Table 11). The calculated hyperconjugation in ethaneimine also agrees with the above trend.

Conclusion

The energy decomposition analysis of the chemical bond gives a quantitative insight into the nature of the bonding in terms of orbital interactions, coulombic attraction, and Pauli repulsion which can be interpreted in a physically meaningful way.[6–8] The orbital interaction term ΔE_{orb} gives for molecules that have mirror symmetry well-defined energy values ΔE_{π} which indicate the strength of the π interactions between molecular fragments. The results presented in this work show that the calculated ΔE_{π} values can be used as a scale to estimate the relative contributions of π interactions that come from the conjugation between multiple bonds or from the hyperconjugation arising from the interactions of saturated groups possessing π orbitals. The very good correlation between the ΔE_{π} values and Hammett's σ_p parameters indicates that the theoretical values are useful for explaining experimental observations that are related to π interactions.

The EDA results for the polyenes show that the strength of the π conjugation in each C=C moiety is higher than that in *trans*-1,3-butadiene. There is an increase in ΔE_{π}/C=C which converges towards a final value which appears to be reached after six to eight C=C moieties. The absolute values for the conjugation between Si=Si π bonds are about $^2/_3$ of the conjugation between C=C bonds, but the relative contributions of ΔE_{π} to ΔE_{orb} in the all-silicon systems are higher than in the carbon compounds. The π conjugation between C=C and C=O or C=NH bonds is comparable to the strength of the conjugation between C=C bonds; it is slightly stronger in 2-propenal than in *trans*-1,3-butadiene, it is

Table 11. EDA results for substituted carbonyl compounds Me−C(R)=O and ethaneimine.[a]

										
		R = H	R = Me	R = OH	R = NH$_2$	R = F	R = Cl	R = Br	R = I	
symmetry	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s
ΔE_{int}	−119.4	−97.8	−95.6	−107.2	−98.5	−109.4	−99.4	−95.4	−89.3	−104.0
ΔE_{Pauli}	228.9	439.4	434.2	435.6	427.4	440.9	416.3	405.6	394.4	439.4
ΔE_{elstat}[b]	−147.5	−167.5	−167.9	−159.3	−163.1	−156.9	−155.9	−153.3	−152.2	−166.1
	(42.4 %)	(31.2 %)	(31.7 %)	(29.4 %)	(31.0 %)	(28.5 %)	(30.2 %)	(30.6 %)	(31.6 %)	(30.6 %)
ΔE_{orb}[b]	−200.7	−369.6	−361.9	−383.3	−362.7	−393.4	−359.9	−347.8	−331.0	−377.3
	(57.6 %)	(68.8 %)	(68.3 %)	(70.6 %	(68.9 %)	(71.5 %)	(69.8 %)	(69.4 %)	(68.4 %)	(69.4 %)
ΔE_{σ}[c]	−191.5	−358.5	−351.9	−373.1	−354.0	−382.1	−348.1	−335.8	−318.9	−367.1
	(95.4 %)	(97.0 %)	(97.2 %)	(97.4)	(97.6 %)	(97.1 %)	(96.7 %)	(96.6 %)	(96.3 %)	(97.3 %)
ΔE_{π}[c]	−9.3	−11.1	−10.0	−10.1	−8.8	−11.3	−11.8	−12.0	−12.1	−10.2
	(4.6 %)	(3.0 %)	(2.8 %)	(2.6 %)	(2.4 %)	(2.9 %)	(3.3 %)	(3.4 %)	(3.7 %)	(2.7 %)
ΔE_{prep}	17.2	11.5	12.4	12.8	12.7	12.3	12.0	12.0	12.6	14.0
ΔE (=$-D_e$)	−102.2	−86.3	−83.2	−94.4	−85.5	−97.1	−87.4	−83.4	−76.7	−90.0
r(C−C)[d]	1.500	1.505	1.520	1.507	1.523	1.496	1.500	1.500	1.501	1.504

[a] Energy values in kcal mol^{-1}. [b] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{elstat}+\Delta E_{orb}$. [c] The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb}. [d] Length of the conjugating C−C bond in Å.

weaker in vinyl methyl ketone, propenoic acid, and particularly in propenamide, while it is enhanced in the propenoyl halogenides.

The strength of the hyperconjugation between the methyl groups in ethane is around $^1/_4$ as strong as the strength of the π conjugation in ethyne. Very strong hyperconjugation is found for the central C−C bonds in cubylcubane and tetrahedranyltetrahedrane. The hyperconjugation in substituted ethanes $X_3C{-}CY_3$, where X,Y = Me, SiH_3, F, and Cl, is stronger than in the parent compound. The strongest hyperconjugation in symmetrically substituted systems is found when X,Y = SiH_3 and Cl. The hyperconjugation in donor–acceptor-substituted ethanes may be very strong; the largest ΔE_π value is calculated for $(SiH_3)_3C{-}CCl_3$ for which the hyperconjugation is nearly thrice as strong as that in ethane. The breakdown of the hyperconjugation in $X_3C{-}CY_3$ shows that the donation of the donor-substituted moiety to the acceptor group is as expected the most important contribution but the reverse interaction is not negligible. The relative strengths of the π interactions between two C=C double bonds, one C=C double bond and CH_3 or CMe_3 substituents, and between two CH_3 or CMe_3 substituents, which are separated by one C−C single bond, are in a ratio of 4:2:1. The extra stabilization of alkenes and alkynes with central double or triple bonds over isomers with terminal π bonds coming from hyperconjugation is bigger than the energy difference between them. Very strong hyperconjugation is found in $HC{\equiv}C{-}C(SiH_3)_3$ and $HC{\equiv}C{-}CCl_3$. The hyperconjugation in Me−C(R)=O is half as strong as the conjugation in $H_2C{=}CH{-}C(R){=}O$ and shows the same trend for different substituents R. Bond energies and lengths should not be used as indicators of the strength of hyperconjugation because the effect of σ interactions and electrostatic forces may compensate for the hyperconjugative effect.

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