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# A COMPARISON OF THE RELATIVE MAGNITUDES OF THE INTERACTION ENERGIES BETWEEN FUNCTIONAL GROUPS WITH ZERO, ONE AND TWO INTERVENING 2p AOs ON CARBON, AND SUBSTITUENT EFFECTS ON THE RELATIVE GROUND-STATE ENERGIES OF *E*-1,2-DISUBSTITUTED ETHENES

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**_Ab initio_ theoretical calculations have been carried out on directly bonded donor–acceptor ($\ddot{X}$–Y) species and on variously substituted _E_-1,2-disubstituted ethanes, and $\pi$ interaction energies have been estimated. In conjunction with the previously calculated radical stabilization energies of mono- and disubstituted methyl radicals, a comparison is made of the relative magnitudes of the $\pi$ interaction energies between groups with zero, one and two intervening 2p AOs on carbon atoms. It is concluded that the stabilizing effect of the $\pi$ interaction between directly bonded donor $\ddot{X}$ and acceptor Y groups (zero intervening 2p AOs) is approximately 2·1 times that in the disubstituted methyl radicals (one intervening 2p AO), while in the _E_-1,2-disubstituted ethenes (two intervening 2p AOs) the stabilizing effect is ~0·7 of that calculated for the disubstituted methyl radicals for both acceptor–donor and acceptor–acceptor disubstituted systems. No correlation is observed with the $\pi$ stabilization energies of the 'cross-conjugated' 1,1-disubstituted ethenes.**

## INTRODUCTION

Organic chemists have long been interested in the effects of the interactions between functional groups, and the transmission of such effects through $\pi$ systems. Prior theoretical studies by the author have focused on the effect of various substituents on the relative stability of mono-[1] and disubstituted[2] methyl radicals, and 1,1-disubstituted ethenes.[3] Except for the extremely electronegative groups such as $R_3N^+$–, $R_2S^+$–, $R_3P^+$– and fluorine substituents, all other functional groups, both electron donating and electron withdrawing, stabilize a radical center relative to the hydrogen atom.[1] The calculated radical stabilization energies (RSEs) of substituted methyl radicals are in very good agreement with the results of various experimental studies carried out by Bordwell and coworkers.[4] The results of the calculations on the disubstituted methyl radicals strongly suggest that the 'captodative effect' concept[5] is not universally valid; some acceptor–donor (**AD**) combinations provide an extra stabilization over the sum of the stabilizations provided by the individual substituents, while other **AD** combinations result in net destabilization.[2] Furthermore, the results of the calculations indicate that certain diacceptor (**AA**) disubstituted methyl radicals derive net extra stabilization, in contrast to the suggestion of the captodative effect concept.[5] Didonor (**DD**) disubstituted methyl radicals suffer substantial net destabilization.[2] The more recent calculations on 1,1-disubstituted ethenes indicate that **AD** and **AA** 1,1-disubstitution results in significant ground state destabilization (and enhanced reactivity toward radical addition), while the effect of **DD** 1,1-disubstitution varied considerably, from providing a high degree of ground state stabilization to a high degree of ground state destabilization.[3] A reasonably good linear correlation between the rates of addition of free radicals with the $E_{\mathrm{LUMO}}$ of substituted alkenes was observed.[3] In the present article are reported the results of theoretical calculations on directly bonded donor ($\ddot{X}$) and acceptor (Y) groups and on variously substituted 1,2-disubstituted ethenes, which allows for a comparison to be made of the relative magnitudes of the $\pi$ interaction energies between $\ddot{X}$ and Y groups with zero, one and two intervening 2p AOs on carbon.

The present calculations have been carried out at the 4-31G basis-set level with full geometry optimization using the GAUSSIAN86 package of programs.[6]

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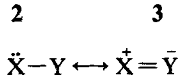
Although it must be recognized that, ideally, polarization functions should be included in the basis set for these heteroatom-containing systems, the 4-31G basis set was chosen for this study in order to be able to make comparisons with the results of the earlier theoretical studies[1,2] carried out at the 4-31G level. The 4-31G basis set was originally dictated (1984) by the large number of species ultimately included in those studies (a total of 209 mono- and disubstituted methyl radicals and disubstituted methanes) and the computing capabilities available at the initiation of the studies. Although one may question the accuracy of the results, qualitative trends are readily apparent, and the comparison of the calculated radical stabilization energies with experimental values is excellent.[4] It would not be realistic to try to carry out calculations at a higher basis-set level on all of the species required for the analysis presented in this article.

## DIRECTLY BONDED X AND Y GROUPS

In this article we will consider only the interactions between the donor groups HO— and $H_2N$—($\ddot{X}$) and the acceptor groups $H_2B$—and—CHO (Y) in the directly bonded systems ($\ddot{X}$—Y) for reasons that will become apparent later. For the evaluation of the $\pi$ interactions between $\ddot{X}$ and Y groups structures **1**–**4** were selected for study. (The various conformations of **1**–**4** have been the subject of prior theoretical studies which will not be documented here.) In **1** and **2** the major resonance contributing structures are shown in equation (1), in which structure **6** is the major contributor to the $\pi$ interaction between the two groups. The contribution of **6** to the resonance hybrid of **1** and **2** contributes to the 'double bond character' between the $\ddot{X}$ and Y groups and the $\pi$ charge density on the $\ddot{X}$ and Y groups as indicated by the $\pi$ Mulliken populations and charges. In **3** and **4** the resonance interaction illustrated in structure **8** [equation (2)] similarly imparts 'double bond character' between the $\ddot{X}$ and Y groups.

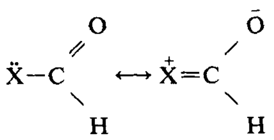
The resonance delocalization between the $\ddot{X}$ and Y groups illustrated in resonance structures **6** and **8** can only be present when the local planes of symmetry in the $\ddot{X}$ and Y groups are coincident, and will not be present when the internal planes are perpendicular. (This precludes the inclusion of the —C≡N and —C≡C—R groups in this study because of the presence of two equivalent orthogonal $\pi$ systems.) *Ab initio* calculations have been carried out on the all-planar conformations of **1**–**4** and on the perpendicular conformations maintaining the bond distances and bond angles the same as in the optimized all-planar conformations, and also with full geometry optimization. In the case of **1** and **3**, calculations have been carried out maintaining the nitrogen atom planar and also allowing for pyramidalization. The total energies of all of the structures of **1**–**4** are given in Table 1, and the $\pi$ charges and Mulliken populations of the planar species **1**–**4** are given in Table 2. The $\pi$ Mulliken populations and $\pi$ charges calculated for **1** and **2** indicate an extensive 'double-bond character' to the $\ddot{X}$–Y bond (the $\pi$ Mulliken population of ethene is ~0·26).

$H_2N{-}BH_2$ $HO{-}BH_2$ $H_2N{-}CHO$ $HO{-}CHO$
**1** **2** **3** **4**



$$\ddot{X}{-}Y \longleftrightarrow \overset{+}{X}{=}\overset{-}{Y} \quad (1)$$

**5** **6**



(2)

**7** **8**

A critical question that must be answered is, how does one quantitatively assess the stabilization afforded a species by the functional group interactions implied in the resonance contributing structures **6** and **8**? It is, in fact, strictly not possible to do. Calculations have been carried out on the all-planar and perpendicular structures of **1**–**4**; the perpendicular structures not allowing

Table 1. Total energies for the planar and perpendicular conformations of structures 1–4

| Structure | $E_{tot}$ (au) |
|---|---|
| $H_2N{-}BH_2$ | −81·37858 |
| $H_2N{-}BH_2$ (pno)[a] | −81·32048 |
| $H_2N{-}BH_2$ (p)[b] | −81·32492 |
| $H_2N{-}BH_2$ (npp)[c] | −81·32492 |
| $HO{-}BH_2$ | −101·17676 |
| $HO{-}BH_2$ (pno)[a] | −101·15541 |
| $HO{-}BH_2$ (po)[d] | −101·15902 |
| $H_2N{-}CHO$ | −168·68159 |
| $H_2N{-}CHO$ (pno)[a] | −168·64383 |
| $H_2N{-}CHO$ (po)[b] | −168·64730 |
| $H_2N{-}CHO$ (npp)[c] | −168·64978 |
| $HO{-}CHO$[e] | −188·47562 |
| $HO{-}CHO$[f] | −188·45633 |
| $HO{-}CHO$ (pno)[a] | −188·45474 |
| $HO{-}CHO$ (po)[d] | −188·45633 |

[a] Perpendicular, non-optimized structure having the bond distances and angles the same as in the planar, optimized structure.
[b] Perpendicular, optimized structure with planar nitrogen.
[c] Perpendicular, optimized structure with paramadilized nitrogen.
[d] Perpendicular optimized structure.
[e] *Z-anti*-conformation.
[f] *E-anti*-conformation.

Table 2. Total π charges and π Mulliken populations for the planar structures of **1**–**4**

| Structure | π Charge[a] X | π Charge[a] Y | π Mulliken population |
|---|---|---|---|
| $H_2N-BH_2$ (**1**) | +0·240 | −0·240 | 0·130 |
| $HO-BH_2$ (**2**) | +0·183 | −0·183 | 0·100 |
| $H_2N-CHO$ (**3**) | +0·186 | +0·279[b] | 0·051 |
| $HO-CHO$[c] (**4**) | +0·133 | +0·291[b] | 0·039 |

[a] Based on gross orbital populations.
[b] For the carbon atom of the CHO group.
[c] For the lowest-energy *Z-anti*-conformation.

for the π delocalization implied in structures **6** and **8**. In going from the all-planar to the perpendicular structures, the π overlap between the $\ddot{X}$ and Y groups is destroyed. However, the lower-lying σ MOs have also undergone a significant decrease in delocalization, i.e. the σ MOs of the planar structures are more delocalized than in the perpendicular structures. While the non-bonding pairs of electrons on the $\ddot{X}$ groups are delocalized by interaction with the vacant 2p AO on the boron atom or the C=O π bond in the all-planar species, in the perpendicular structures the non-bonded pairs of electrons are delocalized by mixing with the π-type σ group orbitals, resulting in a stabilizing effect. In the present analysis it will be assumed that the various σ effects cancel, and that the energy difference between the all-planar and perpendicular structures will closely represent the π interaction energy, $\Delta E_\pi$. The values of the calculated $\Delta E_\pi$s are given in Table 3. The magnitudes of the $\Delta E_\pi$s vary considerably, decreasing with increasing electronegativity of the donor $\ddot{X}$ group, and decreasing with increased charge separation.

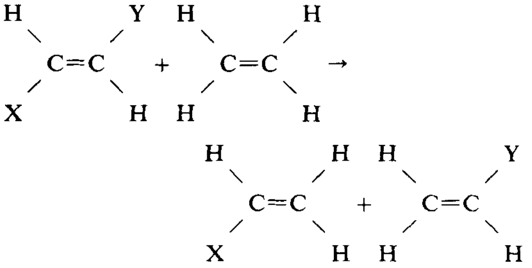
Table 3. $\Delta E_\pi$s for structures **1**–**4**

| Structure | $\Delta E_\pi$ (kcal mol$^{-1}$) |
|---|---|
| **1**[a] | 36·46 |
| **1**[b] | 33·67 |
| **1**[c] | 33·67 |
| **2**[a] | 13·40 |
| **2**[b] | 11·13 |
| **3**[a] | 23·69 |
| **3**[b] | 21·52 |
| **3**[c] | 19·96 |
| **4**[a,d] | 13·10 |
| **4**[b] | 12·10 |

[a] Based on perpendicular, non-optimized structure with planar nitrogen.
[b] Based on perpendicular, optimized structure with planar nitrogen.
[c] Based on perpendicular, optimized structure with non-planar nitrogen.
[d] Based on the *Z-anti*-conformation of the planar structure.

## 1,2-DISUBSTITUTED ETHENES

Calculations have also been carried out on a number of **AD**, **AA** and **DD** *E*-1,2-disubstituted ethenes. (Calculations have not been carried out on the *Z*-1,2-disubstituted ethenes in order to avoid long-range interactions between the $\ddot{X}$ and Y groups which might contribute to the total energies of the systems and make it more difficult to determine the π stabilization energies. Calculations were carried out only on the *anti* conformations of the HO-containing systems and the *s-trans* conformation of the CHO-containing systems.) The $E_{tot}$s, $\pi E_{HOMO}$s, $\pi E_{LUMO}$s and the $c_i$s at $C_1$ and $C_2$ in the π HOMOs and LUMOs are given in Table 4. The corresponding data for the monosubstituted ethenes appears in reference 3. The $\Delta E_{12}$s for the overall change in total energy for the isodesmic reaction shown in equation (3) are given in Table 5. The $\Delta E_{12}$s are taken as a measure of the π interaction energy between the $\ddot{X}$ and Y groups that is transmitted through the C=C π system.


(3)

An analysis of the data in Table 5 reveals a significant difference between the **AD** 1,2-disubstituted ('push–pull') systems and the **AA** and **DD** 1,2-disubstituted systems. The **AD** systems all enjoy significant ground-state stabilization (positive $\Delta E_{12}$s). The extent of the stabilization is quite dependent on the relative electronegativity of the acceptor and donor groups, decreasing with increased electronegativity of the donor group and increasing with increased electronegativity of the acceptor group. In contrast, both the **AA** and **DD** disubstituted systems suffer significant ground-state destabilization (negative $\Delta E_{12}$s).

An analysis of the data appearing in Table 4 shows that the π HOMOs become lower in energy in the sequence **DD** < **AD** < **AA**, while the π LUMOs become higher in energy in the sequence **AA** < **AD** < **DD**. The HOMO–LUMO energy gaps ($\Delta E_{HOMO-LUMO}$) are similar in the **AD** and **AA** systems (11·9–13·2 and 11·6–12·2 eV), and are considerably less than in the **DD** systems (13·6–14·6 eV). In the previous theoretical study on the 1,1-disubstituted ethenes, a reasonably

Table 4. $E_{tot}$s, $\pi E_{HOMO}$s, $\pi E_{LUMO}$s, $\Delta E_{(HOMO-LUMO)}$ and $\pi$ coefficients[a] for 1,2-disubstituted ethenes

| System | X | Y | $E_{tot}$ (au) | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) | $E_{HOMO-LUMO}$ | C1 | C2 |
|---|---|---|---|---|---|---|---|---|
| **AD** | $NH_2$ | $BH_2$ | −158·11047 | −8·6467 | +3·3008 | 11·9475 | 0·583<br>0·120 | 0·309<br>0·675 |
| | OH | $BH_2$ | −177·89580 | −9·7732 | +2·6295 | 12·4027 | 0·566<br>0·173 | 0·411<br>0·637 |
| | $NH_2$ | CN | −224·47737 | −8·8769 | +3·9027 | 12·7796 | 0·581<br>0·541 | 0·332<br>0·902 |
| | OH | CN | −244·26314 | −9·9892 | +3·2292 | 13·2184 | 0·502<br>0·585 | 0·407<br>0·855 |
| | $NH_2$ | CHO | −245·44249 | −8·8679 | +3·4099 | 12·2778 | 0·576<br>0·322 | 0·325<br>0·762 |
| | OH | CHO | −265·22677 | −10·0036 | +2·7906 | 12·7942 | 0·549<br>0·375 | 0·421<br>0·722 |
| **AA** | $BH_2$ | $BH_2$ | −128·35705 | −10·7310 | +0·9107 | 11·6417 | 0·513<br>0·362 | 0·513<br>0·362 |
| | $BH_2$ | CN | −194·73385 | −10·9816 | −0·8598 | 11·8414 | 0·461<br>0·546 | 0·480<br>0·364 |
| | $BH_2$ | CHO | −215·69725 | −11·0403 | +0·8375 | 11·8778 | 0·486<br>0·474 | 0·509<br>0·359 |
| | CN | CN | −261·10196 | −11·2322 | +0·9853 | 12·2175 | 0·449<br>0·641 | 0·449<br>0·641 |
| | CN | CHO | −282·06772 | −11·2477 | +0·8835 | 12·1312 | 0·460<br>0·522 | 0·465<br>0·588 |
| | CHO | CHO | −303·03293 | −11·2703 | +0·8443 | 12·1146 | 0·485<br>0·491 | 0·485<br>0·491 |
| **DD** | $NH_2$ | $NH_2$ | −187·81125 | −6·6163 | +7·0024 | 13·6187 | 0·475<br>0·977 | 0·475<br>0·977 |
| | OH | $NH_2$ | −207·61025 | −7·6029 | +6·4748 | 14·0777 | 0·424<br>1·003 | 0·543<br>0·917 |
| | OH | OH | −227·40579 | −8·7014 | +5·8776 | 14·5790 | 0·508<br>0·944 | 0·508<br>0·944 |

[a] Top row of coefficients are for the HOMO, second row are for the LUMO.

Table 5. $\Delta E_{tot}$s for the isodesmic reaction shown in equation (3)

| System | X | Y | $\Delta E_{tot}$ (kcal mol$^{-1}$) |
|---|---|---|---|
| **AD** | $NH_2$ | $BH_2$ | +9·69 |
| | OH | $BH_2$ | +5·45 |
| | $NH_2$ | CN | +5·27 |
| | OH | CN | +1·30 |
| | $NH_2$ | CHO | +6·04 |
| | OH | CHO | +1·13 |
| **AA** | $BH_2$ | $BH_2$ | −2·97 |
| | $BH_2$ | CN | −1·18 |
| | $BH_2$ | CHO | −1·49 |
| | CN | CN | −4·84 |
| | CN | CHO | −3·68 |
| | CHO | CHO | −2·85 |
| **DD** | $NH_2$ | $NH_2$ | −10·67 |
| | OH | $NH_2$ | −6·34 |
| | OH | OH | −4·19 |

good linear correlation between the relative rates of alkyl-free radical addition versus $E_{LUMO}$ of the combined **AD** and **AA** disubstituted ethenes was observed. With the 1,2-disubstituted ethenes there is insufficient experimental data with which to carry out such a comparison. However, one would anticipate that the **AA** and **DD** disubstituted systems would be more reactive than the **AD** disubstituted systems toward free-radical addition.

## COMPARISON OF $\pi$ INTERACTION ENERGIES BETWEEN GROUPS SEPARATED BY ZERO, ONE AND TWO INTERVENING 2p AOs

The discussion of the relative magnitudes of the $\pi$ interaction energies between the various functional groups will use as a reference point the radical stabilization energies (RSEs) of the disubstituted methyl radicals,[2] the RSEs being defined as the overall change in total

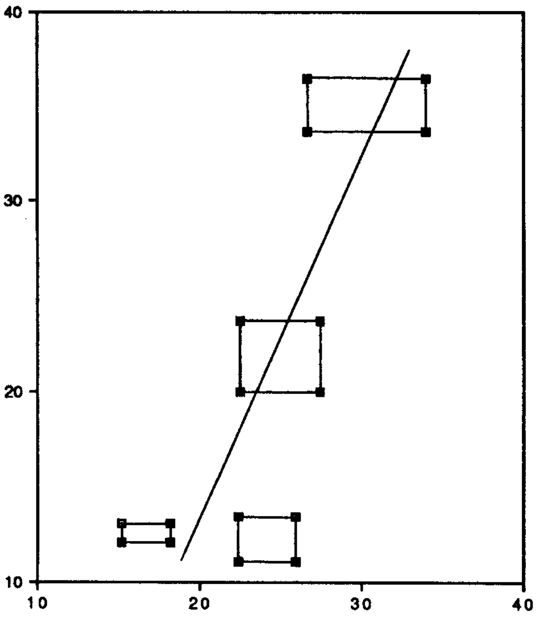


Figure 1. Plot of $\Delta E_\pi$ for the **AD** $\ddot{X}-Y$ species versus the radical stabilization energies (RSEs) of disubstituted methyl radical

energy of the species in equation (4):

$$\ddot{X}-\dot{C}H-Y + CH_4 \rightarrow \ddot{X}-CH_2-Y + \dot{C}H_3 \qquad (4)$$

The use of the RSEs as a focus for the comparison of the $\pi$ delocalization energies has been made on the basis of the greater number of disubstituted methyl radicals and 1,1- and 1,2-disubstituted ethenes for which calculational results are available.

Figure 1 displays the plot of $\Delta E_\pi$ versus RSE for structures **1**–**4**. The vertical ranges in $\Delta E_\pi$ represent the extremes for the values of $\Delta E_\pi$ for each structure given in Table 3. The horizontal ranges of the RSEs represent the extreme values of the RSEs calculated for the different conformations possible relating the kinetic and thermodynamic relationships between the conformations of the disubstituted methyl radicals and the disubstituted methanes.[2] The slope of the plot is ~2·1, indicating that the $\pi$ interaction in the directly bonded $\ddot{X}-Y$ species is roughly twice that in the disubstituted methyl radicals. Figure 2 displays the plot of the RSEs versus the $\Delta E_{12}$s. Again, the horizontal bars indicate the range of the RSEs as indicated above. (There are no ranges for the $\Delta E_{12}$s.) Interestingly, this plot shows very reasonable linearity including both **AD** and **AA** disubstituted systems. The slope of this plot is ~1·6, indicating that the effect of the $\pi$ interaction in the disubstituted methyl radicals is ~1·6 times more effec-

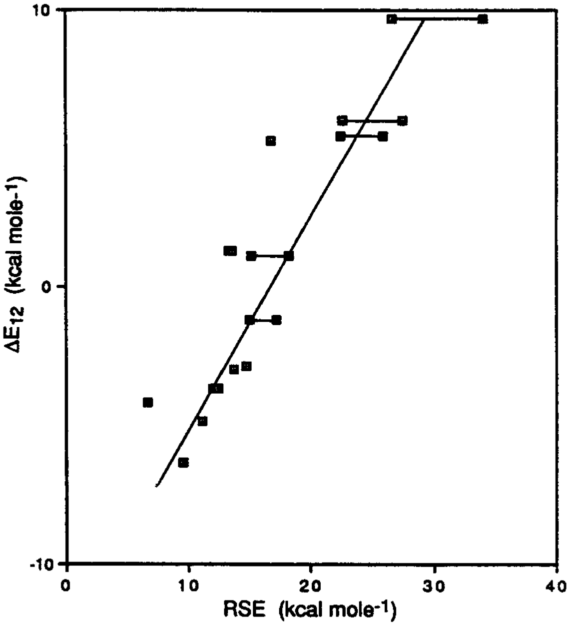


Figure 2. Plot of the radical stabilization energies (RSEs) of disubstituted methyl radicals versus $\Delta E_{12}$ of *E*-1,2-disubstituted ethenes

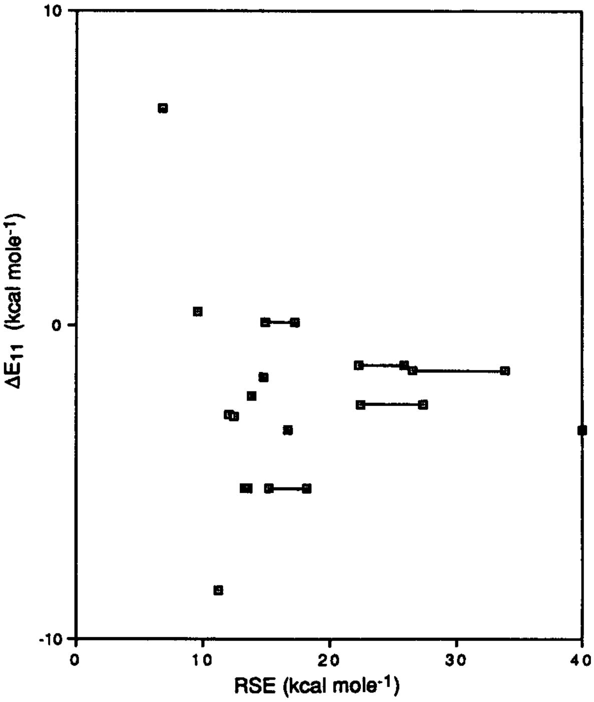


Figure 3. Plot of the radical stabilization energies (RSEs) of disubstituted methyl radicals versus $\Delta E_{11}$s for 1,1-disubstituted ethenes

tive than in the *E*-1,2-disubstituted ethenes, and that in the directly bonded species the $\pi$ delocalization is ~2·7 times more effective. This attenuation in the $\pi$ interactions must arise from a decrease in the extent of the contribution of the dipolar resonance contributing structures due to the increase in work expended to separate the charges in the bipolar structures. Figure 3 shows the plot of the RSEs versus the $\Delta E_{11}$s (the overall change in energy for the isodesmic reaction relating 1,1-disubstituted ethenes and ethene versus the monosubstituted ethenes).[3] There is obviously no correlation between the two systems. This is not at all surprising, because the $\pi$ systems in the directly bonded $\ddot{X}$–Ys, disubstituted methyl radicals and the *E*-1,2-disubstituted ethenes are 'through conjugated' systems, whereas the 1,1-disubstituted ethenes are 'cross conjugated' systems.

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