

Quantitative Nonempirical Analysis of the π -Conjugative Effects of Substituents

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Abstract: A quantitative nonempirical analysis of the π -conjugative effects of various substituents is presented. Ab initio SCF-MO computations implemented with a computational procedure that provides quantitative information about the effects associated with orbital interactions suggest that in $^+\text{CH}_2\text{-X}$ and $\text{BH}_2\text{-X}$, the overall π effect of the substituents OH, SH, F and Cl is stabilizing, while in $\text{CH}_2=\text{CH-X}$ the overall π effect of these substituents is destabilizing. The factors controlling the conjugative effects of these substituents are discussed in detail.

Introduction

Recently we have suggested² that substituent effects are dependent on the electronic nature of the parent substrate. In particular, we have found that in $^+\text{CH}_2\text{XH}$ systems ($\text{X} = \text{O}, \text{S}$) the second-row heteroatom is a better π donor, while in the systems $\text{CH}_2=\text{CHXH}$, $\text{CH}\equiv\text{CXH}$, and $\text{C}_6\text{H}_5\text{-XH}$ the trend reverses and the first-row heteroatom becomes the better π donor. The same is true for the comparison of F and Cl.

These results have been rationalized in terms of a qualitative one-electron molecular orbital (OEMO) analysis focusing on the stabilizing π MO interactions which obtain in the systems under comparison. Our previous discussion has been based on eq 1 and 2, where overlap is neglected and where SE represents the stabilization energy resulting from the interaction of a doubly occupied MO φ_i with an empty MO φ_j , q the electron transfer resulting from such interaction, H_{ij} the interaction matrix element between φ_i and φ_j , and $\delta\epsilon_{ij}$ their energy separation.

$$\text{SE} = 2H_{ij}^2/\delta\epsilon_{ij} \quad (1)$$

$$q = (H_{ij}/\delta\epsilon_{ij})^2 \quad (2)$$

Estimates of the matrix elements H_{ij} and the energy differences $\delta\epsilon_{ij}$ showed that the H_{ij} term favors greater stabilization and greater π donation by the first-row heteroatom, while $\delta\epsilon_{ij}$ works in the opposite direction. These facts lead one to anticipate the following situations:

(a) When the LUMO of the substrate lies high in energy, the variation of H_{ij} will dominate that of $\delta\epsilon_{ij}$ and the first-row heteroatom will be a better π donor than the corresponding second-row heteroatom.

(b) When the LUMO of the central fragment lies low in energy, the variation of the energy gap will dominate, and, thus, the second-row heteroatom will be the better donor.

Since these ideas may have wide applicability to chemical problems, it is important to test them in a rigorous manner. Recently we have investigated three different procedures that provide quantitative information about the energy effects associated with orbital interactions.³ One of these procedures is based on the procedure suggested by Wolfe et al.,⁴ while the other two are derived from those suggested by Baird⁵ and Schweig et al.⁶ We have found that in all cases investigated so far, which include also the problems investigated in the present paper, these procedures provide very similar results. Here we shall report only the results obtained with the procedure based on that suggested by Wolfe et al., since this is the procedure that we have chosen to use in our analyses of π -orbital interactions. This choice follows from the fact that this procedure requires less computational effort.

In this paper we shall report the results obtained in a comparative analysis of the effects of OH vs. F and of SH vs. Cl (a comparison along a row of the periodic table) and those obtained in a comparative analysis of the effects of OH vs. SH and of F vs. Cl (a comparison along a column of the periodic table) with respect to various substrates.

Ab Initio Results

The purpose of the present paper is to examine the response of the substituents OH, SH, F, and Cl toward various substrates and, in particular, the effects associated with the π interactions occurring between the heteroatom lone pair and the π systems of the various substrates. The molecular species considered in this investigation are $^+\text{CH}_2\text{-X}$, $\text{BH}_2\text{-X}$, and $\text{CH}_2=\text{CH-X}$ with $\text{X} = \text{OH}, \text{SH}, \text{F}$, and Cl . The π interactions occurring between X and the adjacent substrates are illustrated in Figure 1. The three systems are representative of situations where the LUMO of the π system of the substrates has different energies. In particular, the LUMO of $^+\text{CH}_2\text{-}$ lies very low in energy, while those of $\text{BH}_2\text{-}$ and $\text{CH}_2=\text{CH-}$ lie high in energy.

In order to obtain the data required for a quantitative discussion of the effects associated with the various π interactions, we have carried out the following two sets of calculations:

(a) An SCF-MO calculation⁷ was performed for the various molecular species under examination. These computations have been carried out at two computational levels, minimal STO-3G⁸ and split valence 4-31G.⁹ For the $^+\text{CH}_2\text{-X}$ species, we have used the corresponding optimized geometries and for the remaining species, the STO-3G optimized geometries. The computed geometrical parameters of $^+\text{CH}_2\text{-X}$ and $\text{CH}_2=\text{CH-X}$ have been reported in a previous work.² For $\text{BH}_2\text{-X}$ the STO-3G computed geometrical parameters are given in Chart I.

(b) Computation, for the various species, of the π -fragment MO's and related orbital energies, matrix elements, and overlap integrals with the procedure suggested by Wolfe et al. was carried out. These calculations are then followed by the computation of the corresponding total energy values in the absence of the π interactions according to the expression³

$$E_{\text{T}}^0 = \text{tr } \mathbf{R}^0(\mathbf{h}^0 + \mathbf{F}^0) \quad (3)$$

Here the density matrix \mathbf{R}^0 is formed with the doubly occupied σ MO's obtained in the SCF computation and with the doubly occupied noninteracting π -fragment MO's obtained with the procedure suggested by Wolfe et al. The matrices \mathbf{h}^0 and \mathbf{F}^0 are the matrix of the one-electron Hamiltonian and the Fock matrix computed from \mathbf{R}^0 , with all nondiagonal matrix ele-

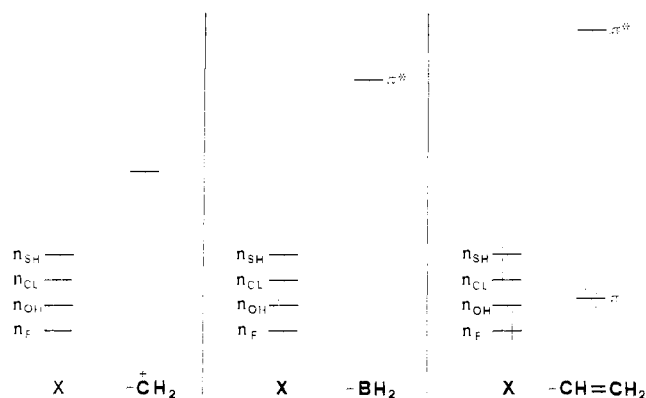


Figure 1. π interactions occurring in ${}^+\text{CH}_2\text{-X}$, $\text{BH}_2\text{-X}$, and $\text{CH}_2=\text{CH-X}$ ($\text{X} = \text{OH, SH, F, Cl}$).

ments between atomic orbitals of π symmetry belonging to the different interacting fragments set equal to zero.

The total energy values obtained for the various species in the two sets of computations are listed in Table I, where E_T denotes the total energy computed in the complete SCF procedure and E_T^0 denotes the total energy computed in the absence of π interactions (π decoupling), as described in (b). Therefore the value $E_T - E_T^0$ represents an estimate of the overall energy effect associated with the π interactions under examination. On the other hand, the insertion in a perturbation formalism of the orbital energies of the π -fragment MO's and related matrix elements and overlap integrals, computed as described in (b), allows us to obtain estimates of the energy effects associated with the interaction of two isolated π MO's. The explicit expressions used to estimate these energy effects are the usual OEMO equations¹⁰ including overlap (see eq 4 and 5). ΔE_{ij}^2 denotes the stabilization energy arising from the interaction of a doubly occupied MO, φ_i , with a vacant MO, φ_j , and ΔE_{ij}^4 denotes the destabilization energy arising from the interaction of two doubly occupied MO's, φ_i and φ_j . In these expressions ϵ_i and ϵ_j are the energies of the two unperturbed MO's, S_{ij} is their overlap integral, H_{ij} is their matrix element, and ϵ_0 is the mean of the energies of the φ_i and φ_j MO's.

$$\Delta E_{ij}^2 = 2(H_{ij} - S_{ij}\epsilon_i)^2/(\epsilon_i - \epsilon_j) \quad (4)$$

$$\Delta E_{ij}^4 = 4(\epsilon_0 S_{ij}^2 - H_{ij} S_{ij})/(1 - S_{ij}^2) \quad (5)$$

Discussion

From the analysis of the energy values listed in Table I, it follows that at both computational levels the overall effect associated with the π interactions occurring between the

Chart I

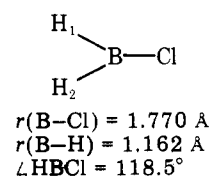
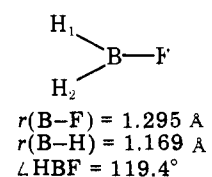
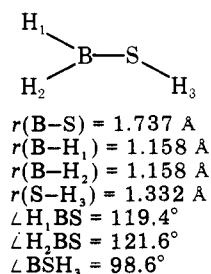
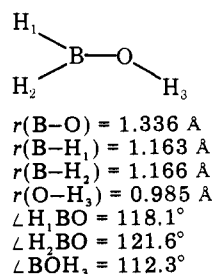


Table I. Total Energies Computed with the Full SCF Procedure (E_T) and Computed in the Absence of π Interactions (E_T^0)

	E_T , au	E_T^0 , au	$E_T - E_T^0$, kcal/mol
STO/3G			
${}^+\text{CH}_2\text{-OH}$	-112.707 02	-112.533 86	-108.66
${}^+\text{CH}_2\text{-SH}$	-432.056 31	-431.903 59	-95.83
${}^+\text{CH}_2\text{-F}$	-136.272 79	-136.149 69	-77.24
${}^+\text{CH}_2\text{-Cl}$	-492.783 44	-492.715 43	-42.68
$\text{BH}_2\text{-OH}$	-99.986 15	-99.894 97	-57.22
$\text{BH}_2\text{-SH}$	-419.302 33	-419.245 34	-35.76
$\text{BH}_2\text{-F}$	-123.603 60	-123.516 81	-54.46
$\text{BH}_2\text{-Cl}$	-480.130 43	-480.101 57	-18.11
$\text{CH}_2=\text{CH-OH}$	-150.915 67	-150.924 24	5.38
$\text{CH}_2=\text{CH-SH}$	-470.256 18	-470.266 38	6.40
$\text{CH}_2=\text{CH-F}$	-174.532 46	-174.540 02	4.74
$\text{CH}_2=\text{CH-Cl}$	-531.077 85	-531.092 47	9.17
4/31G			
${}^+\text{CH}_2\text{-OH}$	-113.979 05	-113.880 93	-61.57
${}^+\text{CH}_2\text{-SH}$	-436.274 48	-436.168 44	-66.54
${}^+\text{CH}_2\text{-F}$	-137.895 49	-137.835 16	-37.86
${}^+\text{CH}_2\text{-Cl}$	-497.577 32	-497.512 11	-40.92
$\text{BH}_2\text{-OH}$	-101.172 34	-101.134 46	-23.77
$\text{BH}_2\text{-SH}$	-423.448 67	-423.414 77	-21.27
$\text{BH}_2\text{-F}$	-125.157 48	-125.126 36	-19.53
$\text{BH}_2\text{-Cl}$	-484.815 04	-484.793 08	-13.78
$\text{CH}_2=\text{CH-OH}$	-152.666 48	-152.712 18	28.68
$\text{CH}_2=\text{CH-SH}$	-474.967 58	-475.008 55	25.71
$\text{CH}_2=\text{CH-F}$	-176.649 79	-176.690 30	25.42
$\text{CH}_2=\text{CH-Cl}$	-536.352 48	-536.358 83	20.93

substituent X ($\text{X} = \text{OH, SH, F, Cl}$) and the adjacent substrate is stabilizing in ${}^+\text{CH}_2\text{-X}$ and in $\text{BH}_2\text{-X}$ (negative value of $E_T - E_T^0$) and destabilizing in $\text{CH}_2=\text{CH-X}$ (positive value of $E_T - E_T^0$). Furthermore, at both computational levels the stabilization is larger in ${}^+\text{CH}_2\text{-X}$ than in $\text{BH}_2\text{-X}$.

The energy values of Table I reveal the following: (a) In the comparative analysis of the effects of OH and F, at both computational levels the stabilization in ${}^+\text{CH}_2\text{-X}$ and $\text{BH}_2\text{-X}$ is significantly larger when $\text{X} = \text{OH}$ (i.e., when the less electronegative heteroatom is involved) and the destabilization in $\text{CH}_2=\text{CH-X}$ is slightly smaller when $\text{X} = \text{F}$ (i.e., when the more electronegative heteroatom is involved). In the comparative analysis of the effects of SH and Cl the same trend is observed at the 4-31G level where it is found that the stabilization in ${}^+\text{CH}_2\text{-X}$ and $\text{BH}_2\text{-X}$ is larger when the less electronegative heteroatom is involved (i.e., $\text{X} = \text{SH}$) and the destabilization in $\text{CH}_2=\text{CH-X}$ is smaller when the more electronegative heteroatom is involved (i.e., $\text{X} = \text{Cl}$). On the other hand, at the STO-3G level, the trend of the stabilization caused by SH and Cl in ${}^+\text{CH}_2\text{-X}$ and $\text{BH}_2\text{-X}$ remains the same as that observed at the 4-31G level, while that of the destabilization in $\text{CH}_2=\text{CH-X}$ is the opposite.

(b) In the comparative analysis of the effects of OH and SH and of F and Cl, the stabilization in ${}^+\text{CH}_2\text{-X}$ is larger when $\text{X} = \text{OH}$ and $\text{X} = \text{F}$ at the STO-3G level and when $\text{X} = \text{SH}$ and $\text{X} = \text{Cl}$ at the 4-31G level, the stabilization in $\text{BH}_2\text{-X}$ is larger when $\text{X} = \text{OH}$ and $\text{X} = \text{F}$ at both computational levels, and the destabilization in $\text{CH}_2=\text{CH-X}$ is smaller when $\text{X} = \text{OH}$ and $\text{X} = \text{F}$ at the STO-3G level and when $\text{X} = \text{SH}$ and $\text{X} = \text{Cl}$ at the 4-31G level. We have already pointed out in the analysis of the π -donating ability of heteroatoms² that in the ${}^+\text{CH}_2\text{-X}$ species the STO-3G results, obtained with a more rigid basis set optimized for the neutral atoms, seem less reliable than the 4-31G results obtained with a larger, more flexible basis set. Therefore, it seems plausible to conclude that in the ${}^+\text{CH}_2\text{-X}$ species, a second-row heteroatom (SH, Cl) introduces a larger π stabilization than the corresponding first-row heteroatom (OH, F). Also the trend of the destabi-

Table II. Matrix Elements^a (H_{ij}), Overlap Integrals (S_{ij}), and Orbital Energies^a (ϵ_i) for Various Systems, Consistent with SCF-MO Computations at the STO/3G and 4/31G Levels

	ϵ_{π}	ϵ_{π^*}	ϵ_{n_x}	$H_{n_x-\pi}$	$H_{n_x-\pi^*}$	$S_{n_x-\pi}$	$S_{n_x-\pi^*}$
STO/3G							
+CH ₂ -OH		-0.3782	-0.7318		-0.4039		0.1864
+CH ₂ -SH		-0.3286	-0.5560		-0.3055		0.1666
+CH ₂ -F		-0.3888	-0.8698		-0.3779		0.1528
+CH ₂ -Cl		-0.3411	-0.7196		-0.2681		0.1462
BH ₂ -OH		0.1394	-0.3791		-0.2835		0.1873
BH ₂ -SH		0.1567	-0.2695		-0.1976		0.1676
BH ₂ -F		0.1257	-0.4637		-0.2922		0.1633
BH ₂ -Cl		0.1301	-0.4036		-0.1768		0.1514
CH ₂ =CH-OH	-0.3581	0.2755	-0.4075	-0.1328	-0.1612	0.0999	0.1064
CH ₂ =CH-SH	-0.3475	0.2957	-0.2855	-0.0962	-0.1090	0.0926	0.0939
CH ₂ =CH-F	-0.3672	0.2713	-0.4841	-0.1323	-0.1591	0.0869	0.0913
CH ₂ =CH-Cl	-0.3868	0.2633	-0.4065	-0.0947	-0.0968	0.0879	0.0845
4/31G							
+CH ₂ -OH		-0.4323	-0.8243		-0.4500		0.3196
+CH ₂ -SH		-0.4203	-0.6247		-0.3479		0.2907
+CH ₂ -F		-0.4352	-0.9865		-0.4105		0.2477
+CH ₂ -Cl		-0.4186	-0.7354		-0.3321		0.2526
BH ₂ -OH		-0.0068	-0.5132		-0.2816		0.3215
BH ₂ -SH		-0.0277	-0.3813		-0.2248		0.3239
BH ₂ -F		-0.0091	-0.6494		-0.2904		0.2662
BH ₂ -Cl		-0.0020	-0.4608		-0.2135		0.2709
CH ₂ =CH-OH	-0.4134	0.1184	-0.5252	-0.1652	-0.1883	0.1696	0.2210
CH ₂ =CH-SH	-0.4120	0.1211	-0.3875	-0.1327	-0.1367	0.1701	0.2110
CH ₂ =CH-F	-0.4276	0.1166	-0.6482	-0.1642	-0.1895	0.1437	0.1832
CH ₂ =CH-Cl	-0.4276	0.1184	-0.4624	-0.1240	-0.1317	0.1440	0.1789

^a Energies expressed in au.**Table III.** Two-Electron Stabilization ($\Delta E_{n_x-\pi^*2}$) and Four-Electron Destabilization ($\Delta E_{n_x-\pi^*4}$) Energies^a Computed at the STO/3G and 4/31G Levels

	$\Delta E_{n_x-\pi^*2}$		$\Delta E_{n_x-\pi^*4}$	
	STO/3G	4/31G	STO/3G	4/31G
+CH ₂ -OH	-253.93	-111.38 ^b (-124.79) ^c		
+CH ₂ -SH	-250.06	-169.76 ^b (-175.08) ^c		
+CH ₂ -F	-156.65	-62.83 ^b (-68.08) ^c		
+CH ₂ -Cl	-88.02	-84.89 ^b (-87.74) ^c		
BH ₂ -OH	-109.30	-33.69 ^b (-40.30) ^c		
BH ₂ -SH	-68.39	-36.45 ^b (-40.00) ^c		
BH ₂ -F	-99.74	-27.07 ^b (-31.27) ^c		
BH ₂ -Cl	-31.47	-21.50 ^b (-23.23) ^c		
CH ₂ =CH-OH	-25.54	-10.16 ^b (-13.21) ^c	23.95	37.53
CH ₂ =CH-SH	-14.58	-7.46 ^b (-9.21) ^c	15.67	28.46
CH ₂ =CH-F	-21.93	-8.20 ^b (-9.44) ^c	20.95	32.01
CH ₂ =CH-Cl	-7.32	-5.19 ^b (-5.89) ^c	13.30	22.12

^a Energies expressed in kcal/mol. ^b Two-electron stabilization energy involving only the LUMO of the substrate. ^c Two-electron stabilization energy involving all empty MO's of π symmetry of the substrate.

lization in CH₂=CH-X is basis-set dependent, but in this case it is more difficult to say which basis set is more reliable. The detailed analysis of the orbital interactions presented below will better clarify this point.

Details about the substituent effects can be obtained from the data of Tables II and III. Using the OEMO expressions 4 and 5 and the matrix elements, overlap integrals, and orbital energies computed with the procedure previously described, we have obtained estimates of the energy effects associated with the various π -orbital interactions. The following trends are of interest:

(a) In the comparative analysis of the effects of substituents belonging to the same row of the periodic table, the results show that, in all molecular systems investigated and at both computational levels, the two-electron, two-orbital stabilization

$\Delta E_{n_x-\pi^*2}$ is always larger when the less electronegative heteroatom is involved, i.e., when X = OH in the comparison with X = F and when X = SH in the comparison with X = Cl. In all cases, the energy separation of the interacting levels favors a greater interaction of the lone pair of the less electronegative heteroatom with the LUMO of the substrate due to the higher orbital energy of the O 2p lone pair as compared with the F 2p lone pair and of the S 3p lone pair as compared with the Cl 3p lone pair. Since in all cases the matrix element between the heteroatom lone pair and the LUMO of the substrate remains almost unchanged in going from OH to F and from SH to Cl, the trend in the stabilization energy is controlled by the denominator of eq 4, i.e., by the energy separation of the interacting levels. Furthermore, the stabilization energy decreases (i.e., becomes more stabilizing) along the series

$\text{CH}_2=\text{CH}-\text{X}$, BH_2-X , $^+\text{CH}_2-\text{X}$ because along this series the matrix element increases in absolute magnitude and the energy gap decreases.

As illustrated in Figure 1, the two-electron, two-orbital interaction in $^+\text{CH}_2-\text{X}$ and BH_2-X is the only π -orbital interaction to be considered, while in the $\text{CH}_2=\text{CH}-\text{X}$ systems there is also the additional destabilizing four-electron, two-orbital interaction. At both computational levels the related destabilization energy $\Delta E_{n-\pi^*}^4$ is larger (i.e., more destabilizing) when $\text{X} = \text{OH}$ as compared with $\text{X} = \text{F}$ and when $\text{X} = \text{SH}$ as compared with $\text{X} = \text{Cl}$ (see Table III). As can be seen from the values listed in Table II, the trend in $\Delta E_{n-\pi^*}^4$ is controlled by ϵ_0 , the mean of the energies of the two interacting MO's n and π , and by the overlap integral $S_{n-\pi}$, and both of these terms favor a smaller destabilization when $\text{X} = \text{F}$ as compared with $\text{X} = \text{OH}$ and when $\text{X} = \text{Cl}$ as compared with $\text{X} = \text{SH}$. The overall effect in $\text{CH}_2=\text{CH}-\text{X}$ will be stabilizing or destabilizing depending on the relative magnitudes of $\Delta E_{n-\pi^*}^2$ and $\Delta E_{n-\pi^*}^4$. From the values of Table III it follows that the overall effect is basis-set dependent; in particular, for first-row heteroatoms it is stabilizing at the STO-3G level and destabilizing at the 4-31G level, while for second-row heteroatoms it is destabilizing at both computational levels. Furthermore, at the STO-3G level this overall effect is found to favor OH and SH, while at the 4-31G level is found to favor F and Cl.

(b) In the comparative analysis of the effects of substituents belonging to the same column of the periodic table, the two-electron, two-orbital stabilization energy $\Delta E_{n-\pi^*}^2$ favors in all systems under investigation OH as compared with SH and F as compared with Cl at the STO-3G level; while at the 4-31G level $\Delta E_{n-\pi^*}^2$ favors OH and F in BH_2-X and $\text{CH}_2=\text{CH}-\text{X}$ but SH and Cl in $^+\text{CH}_2-\text{X}$. It is important to point out that at the 4-31G level there are various empty orbitals of π symmetry and we have to consider the interaction of the heteroatom lone pair with all these empty orbitals. The corresponding values of the stabilization energies are reported in parentheses in Table III. The comparison with the values involving only the interaction lone pair-LUMO shows that the latter interaction provides in all cases the largest contribution and determines the trend of the stabilization energy in $^+\text{CH}_2-\text{X}$ and $\text{CH}_2=\text{CH}-\text{X}$ but not in BH_2-X , where the additional contribution arising from the other empty MO's becomes of critical importance.

As can be seen from the values listed in Table II, the matrix element favors in all cases greater interaction of OH and F with the adjacent LUMO, while the energy gap of the interacting levels favor the opposite trend because the orbital energy of the O 2p lone pair is lower than that of the S 3p lone pair and that of the F 2p lone pair is lower than that of the Cl 3p lone pair. Consequently the two-electron, two-orbital stabilization energy $\Delta E_{n-\pi^*}^2$ is energy-gap controlled in the $^+\text{CH}_2-\text{X}$ species at the 4-31G level and matrix-element controlled in all other cases.

As we have already pointed out, in the $\text{CH}_2=\text{CH}-\text{X}$ systems there is also the $n-\pi$ four-electron, two-orbital interaction to be considered. The related destabilization energy $\Delta E_{n-\pi}^4$ is, at both computational levels, larger when $\text{X} = \text{OH}$ as compared with $\text{X} = \text{SH}$ and when $\text{X} = \text{F}$ as compared with $\text{X} = \text{Cl}$. The analysis of the values listed in Table II shows that the variation of the destabilization energy $\Delta E_{n-\pi}^4$ is controlled by the variation of the related matrix element, that is, in absolute magnitude, larger for OH as compared with SH and for F as compared with Cl. The overall effect associated with the π interactions in the $\text{CH}_2=\text{CH}-\text{X}$ systems will be again stabilizing or destabilizing depending on the relative magnitudes of $\Delta E_{n-\pi^*}^2$ and $\Delta E_{n-\pi}^4$. In particular, it is found to be slightly stabilizing for $\text{X} = \text{OH}$ and $\text{X} = \text{F}$ and destabilizing for $\text{X} = \text{SH}$ and $\text{X} = \text{Cl}$ at the STO-3G level and significantly destabilizing with all substituents at the 4-31G level. Fur-

thermore, the overall effect favors OH and F at the STO-3G level but SH and Cl at the 4-31G level.

The values of the energy effects associated with the π interactions under examination computed through eq 4 and 5 differ significantly from the corresponding values obtained in terms of the total energies (see Table I). The discrepancies are particularly large in the case of the $^+\text{CH}_2-\text{X}$ and BH_2-X systems. It is important to point out that the $E_T - E_T^0$ values, in addition to the effects described by eq 4 and 5, which refer to the energy effects associated with the interactions of two isolated π MO's, involve also other effects, in particular, those associated with variations of the σ MO's caused by the replacement of the delocalized π MO's with the noninteracting fragment MO's, those associated with higher order mixing, and those associated with explicit two-electron effects. However, although the actual values of the two estimates of these energy effects differ significantly, the related trends are very consistent. In particular, it can be seen that the trends in terms of the second-order effects $\Delta E_{n-\pi^*}^2$ parallel those obtained in terms of the $E_T - E_T^0$ values in all $^+\text{CH}_2-\text{X}$ and BH_2-X systems where the $n-\pi^*$ interaction is the only interaction occurring. In the $\text{CH}_2=\text{CH}-\text{X}$ systems, the comparison of the two sets of data is satisfactory at the 4-31G level where the overall effect is found to be in both cases destabilizing and of the same order of magnitude. At the STO-3G level the comparison is less satisfactory, particularly for first-row heteroatoms where the overall effect is found to be slightly destabilizing in terms of the $E_T - E_T^0$ values but slightly stabilizing in terms of the ΔE^2 and ΔE^4 values. It can be seen, from the values listed in Table III, that at the STO-3G level the stabilization energies $\Delta E_{n-\pi^*}^2$ are of the same order of magnitude as the corresponding destabilization energies $\Delta E_{n-\pi}^4$, while at the 4-31G level, the destabilization energies dominate.

These results show that the conclusions reached in terms of eq 4 and 5 are reliable only when one type of interaction (either stabilizing or destabilizing) occurs or dominates in the problem under investigation. In all cases where the energy effects associated with the stabilizing interactions are of the same order of magnitude as those associated with the destabilizing interactions, the conclusions about the overall effect reached in terms of eq 4 and 5 have to be considered in a critical way. In these cases, the $E_T - E_T^0$ values may be a more reliable index of the overall effects, and the ΔE^2 and the ΔE^4 values provide only information about the trends of the second-order and of the overlap-repulsion effects.

The previous results show also that on going from the STO-3G to the 4-31G level, the stabilization energies ΔE^2 are significantly reduced and the destabilization energies increased. The latter observation can be of a certain utility to understand the change observed in various quantities computed at the two levels.

Conclusions

In this work we have investigated the changes in the effects associated with the π interactions occurring between the substituent and the adjacent substrate when the substituent is changed along a column or a row of the periodic table. The results obtained here provide quantitative evidence for the following:

(i) As the substituent is changed from OH to F or from SH to Cl (a case where the heteroatom is changed from one column to another), the π -orbital interaction between the heteroatom lone pair and the LUMO of the adjacent substrate is controlled by the variation in the energy gap. Thus OH and SH will introduce a larger two-electron stabilization as well as will be better π donors.

(ii) As the substituent is changed from OH to SH or from F to Cl (a case where the heteroatom is changed from one row to another), the π -orbital interaction between the heteroatom

lone pair and the LUMO of the adjacent substrate is controlled by the variation of the matrix element when the LUMO of the substrate lies high in energy but will tend to become energy-gap controlled when the LUMO of the adjacent π system lies low in energy.

(iii) The destabilization energy associated with the four-electron interaction between the heteroatom lone pair and the HOMO of the adjacent π system increases in going from a more electronegative heteroatom to a less electronegative heteroatom when the heteroatom is changed from one column to another, i.e., in going from F to OH and from Cl to SH, but decreases in going from a more electronegative heteroatom to a less electronegative heteroatom when the heteroatom is changed from one row to another, i.e., in going from OH to SH and from F to Cl.

(iv) The overall π effect of the substituents OH, SH, F, and Cl, i.e., the energy effect associated with the π interactions occurring between the lone pair of these substituents and the π system of the substrate, is stabilizing in the $^+\text{CH}_2\text{—X}$ and $\text{BH}_2\text{—X}$ systems, where the only interaction occurring is the stabilizing $n\text{—}\pi^*$ interaction, and destabilizing in the $\text{CH}_2\text{=CH—X}$ systems, where also the destabilizing interaction $n\text{—}\pi$ occurs since the substrate has vacant and doubly occupied π MO's. It is important to point out that the overall π effect of a substituent depends critically on the adjacent substrate. As we have already seen, the π overall effect of a substituent, except in the simple cases of the $^+\text{CH}_2\text{—X}$ and $\text{BH}_2\text{—X}$ systems, is the result of the combination of two effects of opposite sign. In neutral systems, the destabilizing effects seem to dominate, while in other species such as charged species or transition states, the stabilizing effects may dominate.

(v) The overall π effect in the $\text{CH}_2\text{=CH—X}$ systems has been found to be more destabilizing for OH than for F and basis-set dependent in the comparison OH vs. SH, F vs. Cl, and SH vs. Cl. Therefore, while the trend of the two-electron stabilization and of the four-electron destabilization is the same at the two computational levels, the result of the combination of the two effects varies in the majority of cases going from a minimal to an extended basis set. It can be expected that the results obtained at the 4-31G level are more reliable, but this point requires further investigation.

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Comment on a Symmetry Criterion for the Necessity of Including Atomic d Orbitals in Computational Basis Sets

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Abstract: A recently proposed symmetry criterion for characterizing a qualitative as opposed to a quantitative need for including higher angular momentum functions in computational basis sets is examined. In typical numerical examples "symmetry required" d orbitals are not found to be of qualitatively different importance to other d orbitals.

I. Introduction

Recently Ratner and Sabin^{1,2} have discussed a criterion based on symmetry considerations for characterizing the need for higher angular momentum functions (d orbitals on first- and second-row atoms, p orbitals on hydrogen) in atomic orbital basis sets for molecular LCAO SCF calculations. According to this criterion,¹ for each occupied molecular orbital there should be at least one basis orbital per atomic center of a symmetry appropriate to contribute to the molecular orbital. Put another way, orbital population on a particular center should not be precluded in a molecular orbital because of the absence of basis functions spanning the irreducible representation of the molecular point group carried by the molecular orbital. If a nonpolarized atomic basis set is deficient in this respect, then there is a symmetry requirement for the inclusion

of higher angular momentum basis functions on the center concerned. This requirement is seen¹ to be "of fundamental importance in the *qualitative* bonding picture", and is distinguished from the *quantitative* effect resulting from the addition of higher angular momentum functions when they are not required by the symmetry criterion. The latter effect is regarded as "primarily numerical in nature".

While it seems reasonable that the proposed symmetry criterion should be taken into account in assessing the requirement for higher angular momentum functions in a particular application, the distinction drawn between the *qualitative* effect of symmetry-required functions and the *quantitative* effect of those not so required appears to require computational justification. It is argued here that this has not been provided by the previous¹ illustrative computations, and some alternative calculations bearing on the issue are presented.