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On the Fragmentation Modes in PMO Analyses

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The molecular species 1,1- and 1,2-disubstituted alkenes have been used as model systems for a comparative discussion of the results obtained with quantitative orbital analyses using different fragmentation modes. It is shown that when indices of the overall energy effects are used, the results of a quantitative orbital analysis are independent of the chosen fragmentation mode. On the other hand, the results of such analysis can depend on the fragmentation mode when indices of partial energy effects are used.

Key words: Perturbational MO analyses, fragmentation modes in ~ – Disubstituted alkenes

1. Introduction

Perturbational Molecular Orbital (PMO) analyses have proven to be a very useful tool for elucidating a variety of reactivity and structural problems [1]. Recently, procedures for carrying out such analyses in a quantitative way in the framework of *ab initio* SCF MO computations, have been suggested [2, 3].

In recent studies [4, 5], Wolfe *et al.* have compared the results of quantitative orbital analysis obtained with different fragmentation schemes and have proposed that one fragmentation mode can be better than another one. However this problem necessitates a more detailed discussion, because some aspects of it have not been completely analyzed. The purpose of this paper is to present a comparative discussion of the results obtained with quantitative orbital analyses using different fragmentation modes. The molecular species investigated in this paper are 1,1- and 1,2-disubstituted alkenes and the discussion is limited only to the effects associated with orbital interactions involving π MO's.

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2. Indices of π Interactions

Quantitative orbital analyses can be used to construct three different indices of the energy effects of the π interactions under examination. The correct use of such indices is very important for obtaining reliable information from such analyses. In the following the indices are defined and a brief discussion of the energy effect which they describe is provided.

The procedure used in the present paper for carrying out the orbital analyses is that described by Wolfe *et al.* [2]. Such a procedure provides the energies and eigenvectors of the π MO's of the fragments, as well as the matrix elements and overlap integrals between the interacting fragments. The energy effects associated with the various orbital interactions can then be estimated using the following second-order perturbation expressions [6]:

$$\Delta E_{ij}^{2} = 2(H_{ij} - S_{ij}\varepsilon_i)^2/(\varepsilon_i - \varepsilon_j) \tag{1}$$

$$\Delta E_{ij}^{4} = 4(\varepsilon_0 S_{ij}^{2} - H_{ij}S_{ij})/(1 - S_{ij}^{2}) \tag{2}$$

where ε_i and ε_j are the energies of the two unperturbed MO's φ_i and φ_j, S_{ij} their overlap integral, H_{ij} their matrix element and ε_0 the mean of the energies of the φ_i and φ_j MO's before mixing. The insertion of the computed values in expressions (1) and (2) makes it possible to obtain estimates of the various two-electron π stabilization energies ΔE_{ij}^{2} and four-electron π destabilization energies ΔE_{ij}^{4}.

We have recently suggested [3] the implementation of the procedure suggested by Wolfe *et al.* [2] with the computation of the total energy of the system in the absence of the π interactions, defined by the following expression:

$$E_T^0 = \mathrm{tr}\,[(h^0 + F^0)R^0] \tag{3}$$

Here the density matrix R^0 is formed from the doubly occupied σ MO's obtained in the SCF computation and the doubly occupied non-interacting π fragment MO's obtained with the procedure of Wolfe *et al.* [2], h^0 is the matrix of the one-electron Hamiltonian and F^0 the Fock matrix computed from R^0 with all non-diagonal matrix elements between atomic orbitals of π symmetry belonging to the different interacting fragments set equal to zero.

From the results obtained with such a procedure we can construct the three following indices of the energy effects associated with the π interactions under examination:

$$I_A = E_T - E_T^0 \tag{4}$$

where E_T is the total energy of the system obtained in the SCF computation. This value represents an estimate of the overall energy effect associated with the π orbital interactions of interest;

$$I_B = \sum_{i}^{\mathrm{occ}} 2\eta_i - \sum_{i}^{\mathrm{occ}} 2\varepsilon_i \tag{5}$$

where η_i denotes the orbital energy of a π MO of the composite system computed in the SCF computation and ε_i the orbital energy of a π MO of an interacting fragment computed with the procedure described by Wolfe *et al.* [2]. This value represents an estimate of the delocalization energy associated with the π orbital interactions under examination;

$$I_C = \sum \Delta E_{ij}^4 + \sum \Delta E_{ij}^2. \tag{6}$$

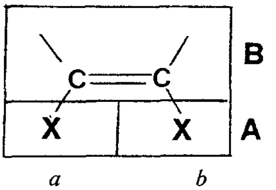
This value represents the second-order contribution to the delocalization energy I_B.

3. Fragmentation Modes

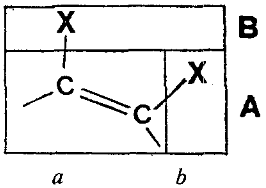
A general assumption of a PMO analysis is that the result of the analysis is independent of the fragmentation mode. As already pointed out, Wolfe *et al.* have recently suggested that the results of a quantitative PMO analysis depend on the fragmentation mode [4, 5]. In this paper we re-examine this problem, studying the same molecules discussed by Wolfe *et al.*, i.e. 1,1- and 1,2-difluoroethylenes, isobutene and 1,2-butenes. The computations have been carried out at the same computational level used by Wolfe *et al.*, i.e. STO-3G level [7]. The geometries used for the difluoroethylenes have been reported recently [3] (they differ only slightly from those used by Wolfe *et al.*).

For the butenes, we have considered the lowest energy conformer of each isomer: for 1,2-butene we have used the geometries previously optimized [8] (the same geometries have also been used by Wolfe *et al.*), while for isobutene we have used a fully STO-3G optimized geometry [9].

For each molecule we have considered the two fragmentation modes illustrated here for a *cis* 1,2-disubstituted alkene:



mode 1



mode 2

In their analyses, Wolfe *et al.* have considered only the dissection of the molecule into the fragments A and B, and have neglected the dissection of the fragment A into the sub-fragments A_a and A_b. However this second dissection is essential for comparing the results of the two fragmentation modes, since the comparison has meaning only if we start from the same basic fragments and all stages of the interactions are properly taken into account. If this is done, both fragmentation modes lead to the same three basic interacting fragments.

The key orbital interactions occurring between the π MO's of the various fragments in the various stages of the two processes are shown in Figs. 1 and 2 for isobutene and 1,2-butene and in Figs. 3 and 4 for 1,1- and 1,2-difluoroethylenes.

In order to assess quantitatively the energy effects associated with the π-orbital interactions occurring in the various phases of the two modes of union, we have carried out the complete quantitative orbital analysis for a situation where the π interactions between the fragments A_a, A_b and B are decoupled (complete decoupling) and for a situation where only the π interactions between the fragments A and B, but not those between the fragments A_a and A_b, are decoupled (partial decoupling). We denote with E_T^0 the total energy computed in the absence of the π interactions in the case of the complete decoupling and $E_T^{0\prime}$ the corresponding value in the case of the partial decoupling. We denote also with ε_i the orbital energy of a fragment π MO in the case of the complete decoupling and with ε_i' the corresponding value in the case of the partial decoupling. From the results of such quantitative analyses we have computed the values of the various indices of the energy effects associated with the π interactions in the various phases of the process of union. Such values are listed in Table 1 for the butenes and in Table 2 for the difluoroethylenes. As it follows from the previous definitions, $I_A = E_T - E_T^0$ represents the overall energy effect associated with the π interactions, $I_A' = E_T^{0\prime} - E_T^0$ the energy effect associated just with the π interactions of the subfragments A_a and A_b, and $I_A'' = E_T - E_T^{0\prime}$ the energy effect associated with the π interactions of the fragments A and B. Similar definitions hold for the other indices.

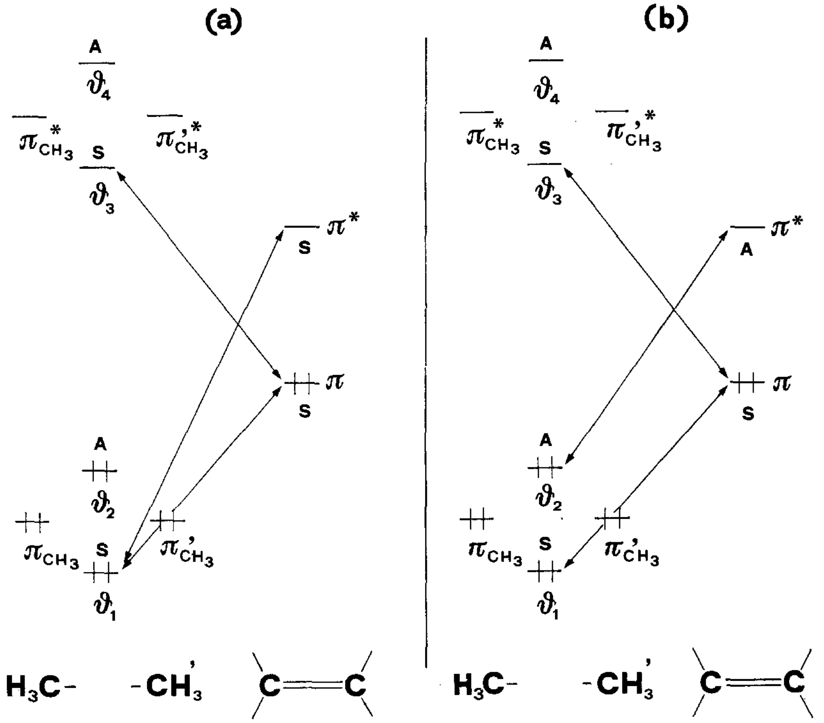


Fig. 1. Key orbital interactions occurring between the π MO's of the various fragments in isobutene (a) and 1,2-butene (b) using the fragmentation mode 1

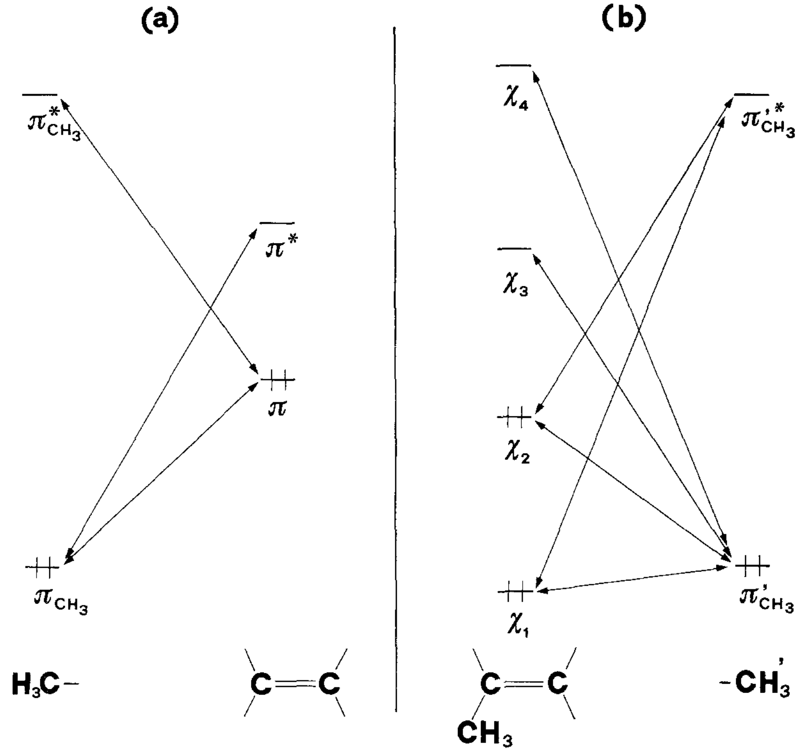


Fig. 2. Key orbital interactions occurring between the π MO's of the various fragments in isobutene and 1,2-butene using the fragmentation mode 2

We discuss first the results obtained for the butenes. Obviously, the values of I_A and I_B, that represent energy effects associated with all the π interactions occurring between the three basic interacting fragments, are the same in the two fragmentation modes. Furthermore the sign and the trend of the I_A and I_B values are the same, and also their order of magnitude is very similar, indicating that the delocalization energy not only dictates the trend of the overall energy effect, but also represents its largest contribution. These results indicate that the overall energy effect associated with the π interactions is destabilizing and that such destabilization follows the trend:

cis > *iso* > *trans*.

It is important to point out that the trend of the destabilization energy changes when we consider the indices I_A'' and I_B'', representing the energy effects associated with the interactions between the fragments A and B. As it can be seen from the values of I_A' and I_B', the energy effects associated with the interactions between the subfragments A_a and A_b are crucial for obtaining the correct trend in the comparison between the 1,1 and 1,2 isomers, while they are not so important in the comparison between *cis* and *trans* 1,2-isomers. In the fragmentation mode 1, I_A' and I_B' represent the energy effects associated with the interactions of the π MO's of the two methyl

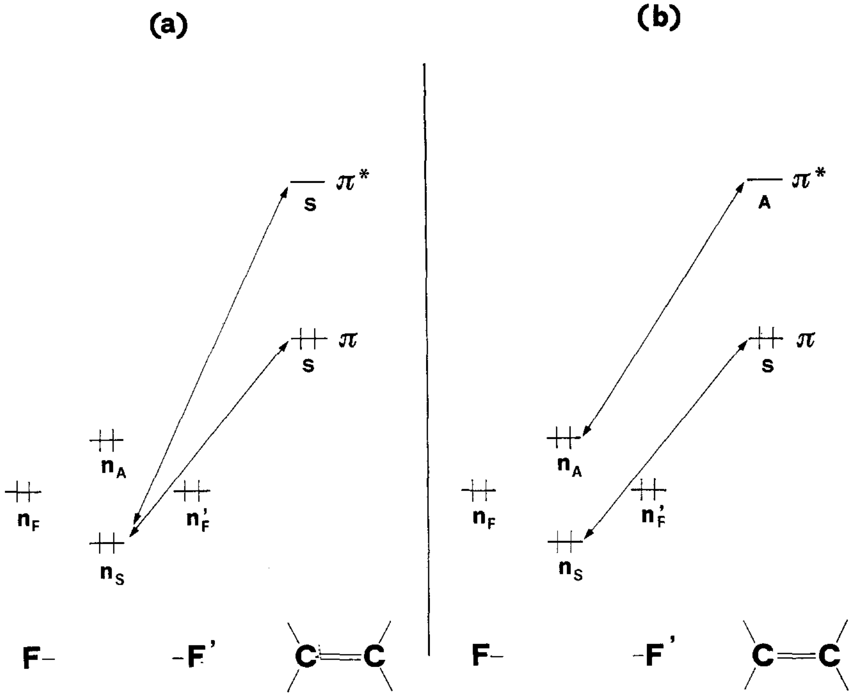


Fig. 3. Key orbital interactions occurring between the π MO's of the various fragments in 1,1- (a) and 1,2-difluoroethylene (b) using the fragmentation mode 1

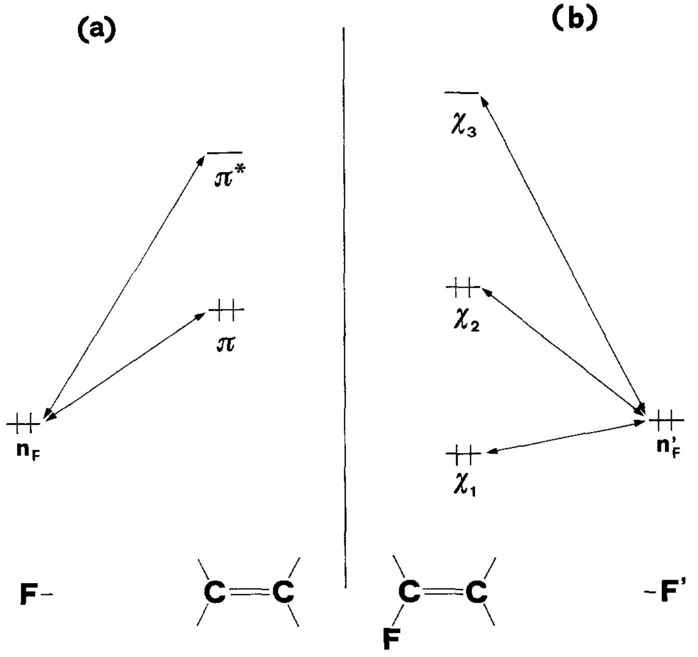
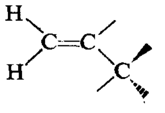
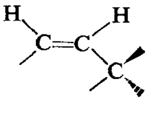


Fig. 4. Key orbital interactions occurring between the π MO's of the various fragments in 1,1- and 1,2-difluoroethylene using the fragmentation mode 2

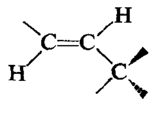
groups; such energy effect is destabilizing and the destabilization is larger in the 1,1- than in the 1,2-isomer, because of the larger interaction. In the fragmentation mode 2, I_A' and I_B' represent the energy effects associated with the π interactions occurring in the following fragments:



1 (*iso*)



2 (*cis*)



3 (*trans*)

It could be expected that the energy effects under study should be almost the same for these three fragments because at the level of Hückel theory the π MO's are the same. However, at the more sophisticated computational level used here, the energy effects for the three fragments differ significantly. Such differences arise from the different geometries of the three fragments (since the computations are carried out at the optimized geometries of the corresponding composite molecules) and from the differences in the σ skeletons.

Table 1. Indices[a] (kcal/mol) of the energy effects associated with the π orbital interactions occurring in isobutene and *cis* and *trans* 2-butenes computed at the STO-3G level

	Fragmentation mode 1			Fragmentation mode 2		
Indices	*iso*	*cis*	*trans*	*iso*	*cis*	*trans*
$I_A\ (\equiv E_T - E_T^0)$	24.72	24.94	24.45	24.72	24.94	24.45
$I_{A'}\ (\equiv E_T^{0\prime} - E_T^0)$	1.16	0.01	0.01	12.46	12.07	11.82
$I_{A''}\ (\equiv E_T - E_T^{0\prime})$	23.56	24.93	24.44	12.26	12.87	12.63
$I_B\ (\equiv 2\sum\eta_i - 2\sum\varepsilon_i)$	18.68	18.75	18.32	18.68	18.75	18.32
$I_{B'}\ (\equiv 2\sum\varepsilon_i' - 2\sum\varepsilon_i)$	0.97	0.06	−0.01	9.45	8.99	8.75
$I_{B''}\ (\equiv 2\sum\eta_i - 2\sum\varepsilon_i')$	17.71	18.69	18.33	9.23	9.76	9.57
I_C[b]	20.39	19.05	18.68	19.43	19.72	19.27
$I_{C'}$[c]	0.87	0.01	0.00	9.90	9.45	9.23
$I_{C''}$[d]	19.52	19.04	18.68	9.53	10.27	10.04

[a] For definition of the various symbols, see text.

[b] $I_C = I_{C'} + I_{C''}$.

[c] $I_{C'} = \Delta E^4_{\pi\mathrm{CH_3}\pi'\mathrm{CH_3}} + \Delta E^2_{\pi\mathrm{CH_3}\pi'\overset{*}{\mathrm{C}}\mathrm{H_3}} + \Delta E^{2'}_{\pi\mathrm{CH_3}\pi\overset{*}{\mathrm{C}}\mathrm{H_3}}$ (Mode 1), $\Delta E^4_{\pi\mathrm{CH_3}\pi} + \Delta E^2_{\pi\mathrm{CH_3}\pi^*} + \Delta E^2_{\pi\pi\overset{*}{\mathrm{C}}\mathrm{H_3}}$ (Mode 2).

[d] $I_{C''} = \Delta E^4_{\theta 1\pi} + \Delta E^2_{\theta\pi *} + \Delta E^2_{\pi\theta 3}$ (Mode 1), $\Delta E^{4'}_{\pi\mathrm{CH_3}\chi 1} + \Delta E^{4'}_{\pi\mathrm{CH_3}\chi 2} + \Delta E^{2'}_{\pi\mathrm{CH_3}\chi 3} + \Delta E^{2'}_{\pi\mathrm{CH_3}\chi 4} + \Delta E^2_{\chi 1\pi\overset{\prime *}{\mathrm{C}}\mathrm{H_3}} + \Delta E^2_{\chi 2\pi\overset{\prime *}{\mathrm{C}}\mathrm{H_3}}$ (Mode 2).

The results listed in Table 1 show also that in these molecules the Eqs. (1) and (2) provide energy effects of the correct order of magnitude (compare the I_C values with the corresponding I_B values). In terms of the I_C values, the trend between *cis* and *trans* isomers is always correct, while that between the 1,1- and the 1,2-isomers depends on the fragmentation mode chosen. Therefore the results are independent on the fragmentation mode only when the indices used involve overall energy effects. When the indices involve only partial energy effects, as it is the case of the index I_C based on the second-order contributions described by Eqs. (1) and (2), the results can critically depend on the fragmentation mode. For instance, when the energy effects associated with the orbital interactions are described in terms of the Eqs. (1) and (2), second-order mixing between orbitals of the same fragment via an orbital of another fragment is neglected in the fragmentation mode 1, but somewhat included in the fragmentation mode 2. It can be expected that the energy effects associated with the higher order mixing are similar in *cis* and *trans* 1,2-butenes, but somewhat different in the 1,1-isomer. Therefore, when the energy effects are discussed in terms of Eqs. (1) and (2), a fragmentation mode can be better than another. In the case of the butenes the results show, in agreement with our discussion, that only fragmentation mode 2 provides the correct trend of the I_C values for the comparison between 1,1- and 1,2-isomers, while both fragmentation modes provide the correct result for the comparison between the *cis* and *trans* isomers.

Table 2. Indices[a] (kcal/mol) of the energy effects associated with the π orbital interactions occurring in 1,1-*cis* 1,2- and *trans* 1,2-difluoroethylenes computed at the STO-3G level

	Fragmentation mode 1			Fragmentation mode 2		
Indices	1,1	*cis* 1,2	*trans* 1,2	1,1	*cis* 1,2	*trans* 1,2
$I_A\ (\equiv E_T - E_T^0)$	10.29	9.56	10.52	10.29	9.56	10.52
$I_{A'}\ (\equiv E_T^{0\prime} - E_T^0)$	0.05	0.00	0.00	5.25	2.28	2.79
$I_{A''}\ (\equiv E_T - E_T^{0\prime})$	10.24	9.56	10.52	5.04	7.28	7.73
$I_B\ (\equiv 2\sum \eta_i - 2\sum \varepsilon_i)$	−1.74	−4.57	−3.61	−1.84	−4.56	−3.61
$I_{B'}\ (\equiv 2\sum \varepsilon_i' - 2\sum \varepsilon_i)$	0.00	0.00	0.00	+0.09	−5.37	−4.95
$I_{B''}\ (\equiv 2\sum \eta_i - 2\sum \varepsilon_i')$	−1.74	−4.57	−3.61	−1.93	+0.82	+1.34
I_C[b]	3.69	−9.17	−8.05	0.73	−2.28	−1.27
$I_{C'}$[c]	0.01	0.00	0 .00	1.56	−4.41	−3.97
$I_{C''}$[d]	3.68	−9.17	−8.05	−0.83	2.13	2.70

[a] For definition of the various symbols, see text.

[b] $I_C = I_{C'} + I_{C''}$.

[c] $I_{C'} = \Delta E^4_{n_F n_F'}$ (Mode 1), $\Delta E^4_{n_F\pi} + \Delta E^2_{n_F\pi^*}$ (Mode 2).

[d] $I_{C''} = \Delta E^4_{n_S\pi} + \Delta E^2_{n\pi^*}$ (Mode 1), $\Delta E^{4\prime}_{n_F\chi_1} + \Delta E^{4\prime}_{n_F\chi_2} + \Delta E^{2\prime}_{n_F\chi_3}$ (Mode 2).

The results for the difluoroethylenes (see Table 2) parallel in various aspects those for the butenes. The main difference between the results of Table 1 and Table 2 is that in the difluoroethylenes the order of magnitude of the I_A, I_B and I_C values differ significantly. The origin of these differences resides in the high electronegativity of the fluorine substituents that makes the other energy effects, in particular those associated with the energy variations of the σ MO's caused by the replacement of the delocalized π MO's with the non-interacting fragment MO's, very large.

In these cases the results of the quantitative analyses have to be used with caution and only the conclusions that emerge very clearly should be drawn. In the present case the point that can be safely deduced is that the π interactions favor *cis* 1,2 over the other two isomers, i.e. *trans* 1,2- and 1,1-difluoroethylene. On the other hand it is not possible to assess with confidence the trend of the π energy effect in the comparison 1,1- versus *trans* 1,2-difluoroethylene since the I_B and I_C indices favor the *trans* isomer, while the index of overall π energy effect I_A favors slightly the 1,1 isomer (in these cases the indication provided by the index of the delocalization energy I_B seems preferable). However this problem can be solved using other information provided by the quantitative analysis. In fact, a comparative inspection of the total energies computed with complete decoupling shows that also in the absence of the π interactions the 1,1-isomer remains more stable than the two 1,2-isomers of similar amounts. Therefore, we can assess with confidence that the greater stability of the 1,1-isomer is not caused by the energy effects associated with the π interactions.

The results of the quantitative analyses obtained so far suggest that this computational procedure can be a very useful instrument for understanding the effects of orbital interactions. However, these analyses have to be used in a correct way. The results listed in Tables 1 and 2 show that it is important to use an index that describes an overall energy effect, and not a partial energy effect. For instance, Wolfe *et al.* have recently compared the effects of the π orbital interactions in butenes [4] and difluoroethylenes [5] in terms of the I_C'' index and have found trends of such energy effects that differ from those they would have found in terms of indices describing overall energy effects such as I_A and I_B. Furthermore these analyses have to be used at the present time also in a critical way because the limitations of this computational procedure are not well established yet. We are presently examining a variety of situations to clarify this point.

4. Conclusions

The point of interest of the present work can be summarized as follows:

1) when indices of overall energy effects are used, the results of quantitative orbital analyses are independent of the chosen fragmentation mode;
2) the results of orbital analyses can depend on the fragmentation mode when indices of partial energy effects are used or when the index used is the summation of the various orbital interaction energies computed according to Eqs. (1) and (2).

Consequently, we suggest to use indices such as I_A and I_B for assessing the overall energy effect and the delocalization energy associated with the π interactions under examination, and to use the orbital interaction energies to understand the trends of the various contributing effects.

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