Quantitative Nonempirical Estimates of the Effects of Orbital Interactions. Applications to Difluoroethylenes

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Abstract: The role of π nonbonded interactions in determining the relative stability of *cis*- and *trans*-1,2-difluoroethylene and the FCF angle in 1,1-difluoroethylene is investigated using a procedure that provides, in the framework of the ab initio SCF–MO computations, quantitative estimates of the effects associated with π orbital interactions. The quantitative results provide support for the qualitative conclusions reached on the basis of simple interaction diagrams.

Introduction

In recent years, the importance of energy effects associated with nonbonded interactions of atoms or groups in problems of molecular structure has been emphasized, in particular, by Hoffmann[2] and Epiotis.[3] The original theoretical treatments made use of one electron MO (OEMO) theory and the key arguments were illuminated with the aide of MO interaction diagrams. Subsequently, the original qualitative arguments were checked by explicit one determinental ab initio SCF–MO computations[4] and it was demonstrated that the combined use of quantitative calculations and qualitative MO interaction analyses can be very fruitful in elucidating interesting structural trends.[5] Indices of nonbonded interactions such as overlap populations, charge transfers, etc., predicted at the qualitative OEMO level were found to be in close agreement with the results of the ab initio computations.

The OEMO analysis used in our previous investigations involves the following steps:[5] (a) sequential dissection of the molecule under consideration into component fragments; (b) construction of the group MO's of each fragment; (c) examination of the key group orbital interactions which obtain in the course of the union of the component fragments to yield the composite system in a specified geometry. These interactions are either second order in energy for nondegenerate and first order in energy for degenerate levels.

In the course of such analysis, we have made use of the following results of OEMO theory. (a) The interaction of a doubly occupied MO, Φ_i, with a vacant MO, Φ_j, leads to a two-electron stabilization given by the following expression:[5]

$$\Delta E_{ij}{}^2 = 2(H_{ij} - S_{ij}\epsilon_i)^2/(\epsilon_i - \epsilon_j) \qquad (1)$$

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, and H_{ij} their matrix element. (b) The interaction of two doubly occupied MO's, Φ_i and Φ_j, leads to four-electron destabilization given by the following expression:

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

where ϵ_0 is the mean of the energies of the Φ_i and Φ_j MO's before mixing.

Very often these equations have been used only in a qualitative way to rationalize certain SCF results or experimental trends.[3a] In other cases, estimates of $\Delta E_{ij}{}^2$ and $\Delta E_{ij}{}^4$ have been computed using values for the matrix elements, overlap integrals, and orbital energies taken from different sources, for instance, orbital energies estimated from experimental ionization potentials or calculated orbital energies and matrix elements from various approximate expressions using overlap

integrals computed from standard packages.[3b] Attempts to estimate quantitatively the effect associated with a certain orbital interaction within the framework of an SCF computation have been made recently at the semiempirical level by Baird[6] and Schweig[7] and at the nonempirical level by Wolfe et al.[8] and by Payne.[9]

In the present paper, we examine various computational procedures which are able to provide quantitative expressions for orbital energies, matrix elements, overlap integrals, and the total energy of the system in the absence of the π orbital interactions under examination. The difference between the total energies computed with and without π interactions provides an estimate of the overall energy effect associated with these interactions. The insertion of computed values in expressions 1 and 2 allows us to obtain estimates of the related two-electron π stabilization, $\Delta E_{ij}{}^2$, and four-electron π destabilization, $\Delta E_{ij}{}^4$, energies.

For illustrative purposes, we treat two problems which have already been the object of qualitative OEMO investigations, i.e., the role of π nonbonded interactions in determining the relative stabilities of *cis*- and *trans*-CHF=CHF and the value of the FCF angle in $CF_2{=}CH_2$.

Computational Results

We have examined three computational procedures:

(i) A procedure described by Wolfe et al. was supplemented by the computation of the total energy of the system in the absence of π interactions. The procedure of Wolfe et al. provides the energies and eigenvectors of the π MO's of the fragments. From these, one can compute the magnitude of the two-electron stabilization and four-electron destablization resulting from the π orbital interactions under focus. In addition, the value of the total energy of the system in the absence of the π interactions can be computed on the basis of the following expression:

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

Here, the density matrix $\mathbf{R}^0$ is defined as $\mathbf{R}^0 = \mathbf{TT}^+$, where $\mathbf{T}$ is the matrix formed with the doubly occupied σ MO's obtained in the SCF computation and with the doubly occupied noninteracting π fragments MO's obtained with the procedure of Wolfe et al. $\mathbf{h}^0$ is the matrix of the one-electron Hamiltonian and $\mathbf{F}^0$ the Fock matrix computed from $\mathbf{R}^0$ with all nondiagonal matrix elements between atomic orbitals of π symmetry belonging to the different interacting fragments set equal to zero. We denote this computational procedure as the Whangbo–Schlegel–Wolfe (WSW) procedure.

(ii) A procedure very similar, in principle, to that suggested by Baird and Schweig was appropriately modified in order to be used in the framework of ab-initio computations. It consists

Table I. Total Energies in the Absence of π Interactions and Related ΔE_{ij}^2 and ΔE_{ij}^4. Values Computed at the STO-3G Level with the Three Procedures Described in the Text

	∠FCF	120°	115°	111°	108°
			WSW Procedure		
E_T^0, au		-272.01673	-272.01795	-272.01705	-272.01521
$E_T - E_T^0$, kcal/mol		13.26	11.56	10.29	9.39
$\Delta E_{ns-\pi}^4$, kcal/mol		47.65	47.06	46.61	46.28
$\Delta E_{ns-\pi^*}^2$, kcal/mol		-40.81	-42.02	-42.93	-43.57
			BS Procedure		
E_T^0, au		-272.02142	-272.02280	-272.02203	-272.02028
$E_T - E_T^0$, kcal/mol		16.21	14.61	13.42	12.58
$\Delta E_{ns-\pi}^4$, kcal/mol		48.56	47.92	47.43	47.07
$\Delta E_{ns-\pi^*}^2$, kcal/mol		-41.44	-42.68	-43.61	-44.25
			Modified BS Procedure		
E_T^0, au		-272.01717	-272.01841	-272.01753	-272.01570
$E_T - E_T^0$, kcal/mol		13.55	11.85	10.59	9.70
$\Delta E_{ns-\pi}^4$, kcal/mol		46.00	45.35	44.85	44.49
$\Delta E_{ns-\pi^*}^2$, kcal/mol		-45.11	-46.59	-47.71	-51.12

of an additional SCF computation where in each iteration all nondiagonal matrix elements and overlap integrals between atomic orbitals of π symmetry belonging to different interacting fragments are set equal to zero. The quantities of interest derived from the additional SCF computation are the total energy of the system in the absence of the π interactions under examination and the energies and eigenvectors of the π MO's of the fragments. The availability of quantitative expressions for the fragments MO's allows us to obtain estimates in the framework of the SCF computation of the matrix elements and overlap integrals between the interacting MO's using a computational scheme similar to that described by Wolfe et al. We shall denote this procedure as the Baird–Schweig (BS) procedure.

(iii) The third procedure consists again of an additional SCF computation where in each iteration all nondiagonal matrix elements and overlap integrals between atomic orbitals of π symmetry belonging to the different interacting fragments are set equal to zero and the MO's of σ symmetry are kept fixed in the form obtained in the full SCF computation. This procedure differs from that described in (ii) only insofar as the σ MO's are not allowed to change during the additional SCF computation. This constraint has been introduced in order to keep all σ interactions of the same order of magnitude as in the full SCF computation. We shall denote this procedure as the modified BS procedure.

All three computational procedures provide a value of the total energy of the system in the absence of the π interactions under examination, denoted by E_T^0. This value is very informative, since the difference, $E_T - E_T^0$, where E_T is the total energy of the system, represents an estimate of the overall energy effect associated with the π orbital interactions of interest. On the other hand, the ΔE_{ij}^2 and ΔE_{ij}^4 values, computed on the basis of expressions 1 and 2 with the values of the orbital energies, matrix elements, and overlap integrals obtained with the corresponding computational procedure as previously described, represent estimates of the energy effects associated with the interactions of two isolated π MO's. Therefore, the value $E_T - E_T^0$ can differ significantly from the summation of the related ΔE_{ij}^2 and ΔE_{ij}^4 values. However, if eq 1 and 2 describe properly the energy effects associated with the π orbital interactions under examination, the trend of the values of the summation of the various ΔE_{ij}^2 and ΔE_{ij}^4 quantities will parallel that of the $E_T - E_T^0$ values. In any case, the combination of these two sets of values is very informative since the $E_T - E_T^0$ values provide information about the trend and magnitude of the overall energy effect associated with the π interactions under examination while

ΔE_{ij}^2 and ΔE_{ij}^4 provide information about the trend and the magnitude of the energy effect associated with each orbital interaction.

We have applied these three computational procedures to the analysis of the π orbital interactions in various kinds of molecules and in all cases we have found that they provide very similar results. Typical data are shown in Table I for the molecule 1,1-difluoroethylene. The computational details are described in the next section together with the implications of these results. Here, we wish to point out that the trends and magnitudes of the overall effect $E_T - E_T^0$ and related ΔE_{ij}^2 and ΔE_{ij}^4 quantities computed with the three different procedures are very similar. In particular, it is found that the optimum value of the F_1CF_2 angle computed in the absence of the π interactions is about 115° with all three computational procedures (114.6, 114.8, and 115.3° with the procedures i, ii, and iii, respectively) and that in all cases angle shrinkage leads to a decrease of the four-electron destabilization energy $\Delta E_{ns-\pi}^4$ and to an increase of the two-electron stabilization energy $\Delta E_{ns-\pi^*}^2$.

Therefore, on the basis of these and other results, these procedures seem almost equivalent. Hence, we have chosen to use the one that requires the least computational effort. This is the procedure described in (i).

Quantitative Estimates of the Effects of π Nonbonded Interactions in Difluoroethylenes

We first consider how π nonbonded interactions influence bond angles in molecules. Our approach will be illustrated by reference to the model system 1,1-difluoroethylene. The detailed OEMO analysis of the π interactions occurring in this molecular species has been reported elsewhere.[5] Here we summarize briefly the basic approach and we discuss the quantitative results.

The analysis employs the following dissection:
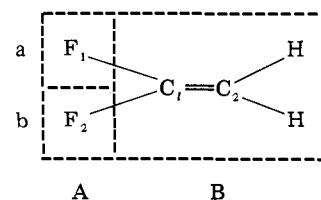
The appropriate interaction diagram for the π system only is shown in Figure 1. Only MO's of the same symmetry can interact; consequently, the only possible interactions are the four-electron destabilizing interaction $n_S-\pi$ and the two-electron stabilizing interaction $n_S-\pi^*$.

Table II. Total Energies Computed at the STO-3G Level for 1,1-Difluoroethylene at Various Values of the F_1CF_2 Angle in the Full SCF Computation (E_T) and with Partial ($E_T^{0'}$) and Complete (E_T^0) Decoupling of the π Interactions between the Various Fragments

∠F_1CF_2	120°	115°	111°	108°
E_T, au	−271.99559	−271.99952	−272.00065	−272.00023
$E_T^{0'}$, au	−272.01669	−272.01789	−272.01697	−272.01509
E_T^0, au	−272.01673	−272.01795	−272.01705	−272.01521
$E_T - E_T^0$, kcal/mol	13.26	11.56	10.29	9.39
$E_T - E_T^{0'}$ kcal/mol	13.24	11.53	10.24	9.32
$E_T^{0'} - E_T^0$, kcal/mol	0.02	0.03	0.05	0.07

Table III. Orbital Energies[a] (ϵ_i), Matrix Elements[a] (H_{ij}), and Overlap Integrals (S_{ij}) Computed at the STO-3G Level for 1,1-Difluoroethylene at Various Values of the F_1CF_2 Angle together with the Two Electrons Stabilization Energies[b] (ΔE_{ij}^2) and the Four-Electron Destabilization Energies[b])ΔE_{ij}^4)

∠F_1CF_2	120°	115°	111°	108°
ϵ_{n_F}	−0.5131	−0.5110	−0.5092	−0.5078
ϵ_{n_S}	−0.5135	−0.5120	−0.5109	−0.5101
ϵ_{n_A}	−0.5128	−0.5100	−0.5075	−0.5054
ϵ_π	−0.4016	−0.4030	−0.4041	−0.4048
$\epsilon_{\pi*}$	0.2230	0.2203	0.2183	0.2170
$H_{n_{F1}n_{F2}}$	−0.0012	−0.0021	−0.0030	−0.0039
$S_{n_{F1}n_{F2}}$	0.0015	0.0020	0.0025	0.0030
$H_{n_S-\pi}$	−0.2028	−0.2017	−0.2009	−0.2002
$S_{n_S-\pi}$	0.1304	0.1293	0.1286	0.1280
$H_{n_S-\pi*}$	−0.2184	−0.2207	−0.2224	−0.2235
$S_{n_S-\pi*}$	0.1238	0.1251	0.1261	0.1267
$\Delta E_{n_{F1}-n_{F2}}^4$	0.00	0.01	0.01	0.02
$\Delta E_{n_S} - \pi^4$	47.65	47.06	46.61	46.28
$\Delta E_{n_S-\pi*}^2$	−40.81	−42.02	−42.93	−43.57
$Q^{b,c}$	6.84	5.05	3.69	2.73

[a] Values in au. [b] Values in kcal/mol. [c] Defined as the sum of the three interactions energies. A plus sign implies that the interaction energy is destabilizing.
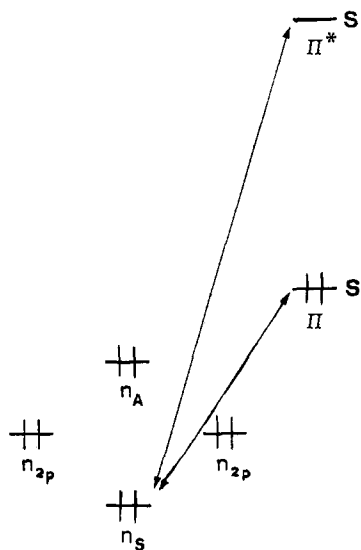
Figure 1. Dominant π orbital interactions in 1,1-difluoroethylene. The symmetry labels are assigned with respect to a mirror plane.

In order to obtain the various quantitative information required to assess the effects caused by these two interactions, we have carried out the following types of calculations:[11]

(a) Standard SCF–MO computations were performed with the STO-3G basis set at the following values of the FCF angle: 120, 115, 111, and 108°. In all such computations the remaining geometrical parameters have been kept fixed at the following values: r(C–C) = 1.3185 Å; r(C–R) = 1.3507 Å; r(C–H) = 1.07 Å, and ∠HCC = 120°. The values of r(C–C) and r(C–F) are the corresponding optimized values while those of r(C–H) and ∠HCC are standard values.

(b) Computations were performed at the various values of the FCF angle, with the procedure suggested by Wolfe et al., of the π fragments MO's and related orbital energies, matrix elements, and overlap integrals for a dissection of the molecule such that the π interactions between the fragments A_a, A_b, and B are decoupled (complete decoupling). Such calculations are then followed by the computation of the corresponding E_T^0 values according to expression 3.

(c) Computations of the type described in (b), but where only the π interactions between the fragments A and B are decoupled (partial decoupling) were also performed.

The relevant data are listed in Tables II and III. The first interesting information provided by the results of Table II is illustrated in Figure 2, where the total energies E_T and E_T^0 are plotted as a function of the FCF angle. It follows that the optimum value of the FCF angle computed in terms of the E_T values, i.e., in terms of energy values that include all the effects associated with the π interactions, is found to be 111°[15] (this value agrees well with the experimental value of 109.3°). *This value becomes 114.6° when it is computed in the absence of the π interactions between the various fragments.* This result is a clear indication of the importance of the energy effects associated with the π nonbonded interactions occurring between the fragments A_a, A_b, and B in determining the optimum FCF angle.

The total energy values of Table II show also that the overall effect associated with the π interactions under investigation is destabilizing and that the overall destabilization decreases with a decrease of the F_1CF_2 angle. It is also shown that the destabilization associated with the interaction between the two fluorine lone pairs, which tends to increase with a decrease of the F_1CF_2 angle, remains always almost negligible.

Details about the effects associated with the three interactions n_{F_1}–n_{F_2}, n_S–π, and n_S–$\pi*$ can be obtained from the values listed in Table III. Using the OEMO expressions (1) and (2) and the values of the matrix elements, overlap integrals, and

Table IV. Total Energies Computed at the STO-3G and 4-31G Levels for *cis*- and *trans*-1,2-Difluoroethylene in the Full SCF Computation (E_T) and with Partial ($E_T^{0'}$) and Complete (E_T^0) Decoupling of the π Interactions between the Various Fragments
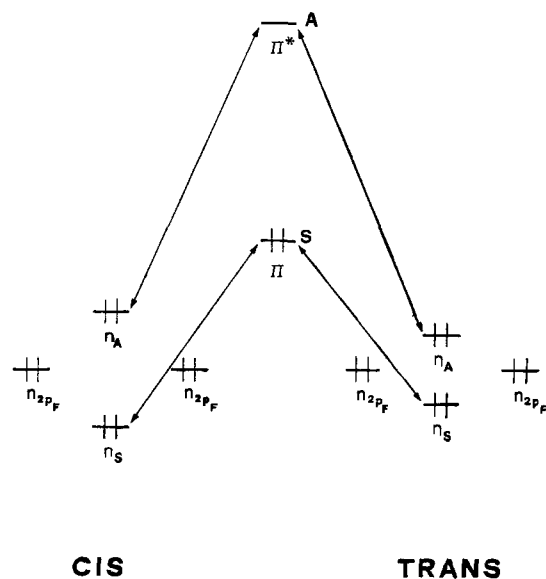
	STO-3G		4-31G	
	cis[a]	trans[b]	cis[c]	trans[d]
E_T, au	−271.98492	−271.98531	−275.36715	−275.36919
$E_T^{0'}$, au	−272.00016	−272.00207	−275.44034	−275.44676
E_T^0, au	−272.00016	−272.00207	−275.44037	−275.44679
$E_T − E_T^0$, kcal/mol	9.56	10.52	45.95	48.69
$E_T − E_T^{0'}$, kcal/mol	9.56	10.52	45.93	48.68
$E_T^{0'} − E_T^0$, kcal/mol	0.00	0.00	0.02	0.01

[a] Computations carried out at the STO-3G optimized geometry: r(C–C) = 1.3264 Å; r(C–F) = 1.3581 Å; ∠FCC = 124.2°; ∠HCC = 120.5°; r(C–H) = 1.07 Å (not optimized). [b] Computations carried out at the STO-3G optimized geometry: r(C–C) = 1.3256 Å; r(C–F) = 1.3572 Å; ∠FCC = 122.9°; ∠HCC = 121.9°; r(C–H) = 1.07 Å (not optimized). [c] Computations carried out at the 4-31G optimized geometry: r(C–C) = 1.3042 Å; r(C–F) = 1.3595 Å; ∠FCC = 124.1°; ∠HCC = 122.6°; r(C–H) = 1.07 Å (not optimized). [d] Computations carried out at the 4-31G optimized geometry: r(C–C) = 1.3025 Å; r(C–F) = 1.3601 Å; ∠FCC = 121.1°; ∠HCC = 125.3°; r(C–H) = 1.07 Å (not optimized).
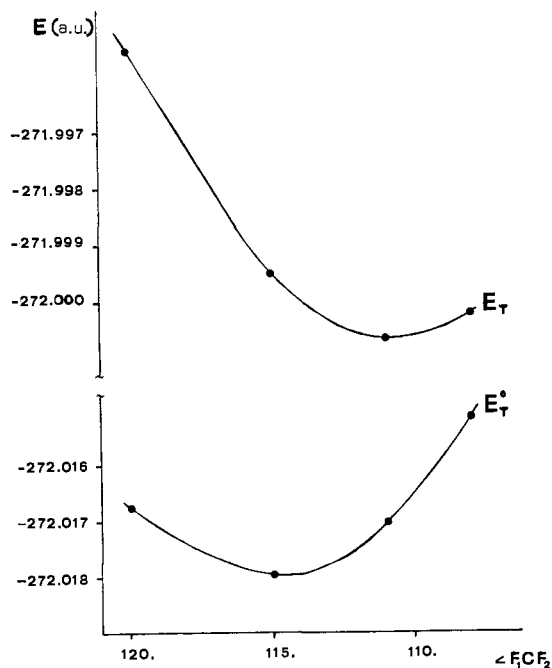
Figure 2. Total energies computed at the STO-3G level for 1,1-difluoroethylene with the full SCF computation (E_T) and with the SCF computation with complete decoupling (E_T^0) as a function of the F_1CF_2 angle.

Figure 3. Dominant π orbital interactions in *cis*- and *trans*-1,2-difluoroethylene. The symmetry labels are assigned with respect to a mirror plane (cis) and a rotational axis (trans).

orbital energies computed with the procedure described in the previous section, we have obtained estimates of the energy effect associated with each interaction. The destabilization $\Delta E_{n_{F_1}-n_{F_2}}^4$ associated with the four-electron interaction involving the two fluorine lone pairs is negligible for all values of the F_1CF_2 angle. On the other hand, the destabilization $\Delta E_{n_S-\pi}^4$ associated with the four-electron interaction $n_S-\pi$ and the stabilization $\Delta E_{n_S-\pi}^2$ associated with the two-electron interaction $n_S-\pi^*$ are both significant; with the decrease of the F_1CF_2 angle, $\Delta E_{n_S-\pi}^4$ becomes less destabilizing and $\Delta E_{n_S-\pi^*}^2$ more stabilizing. Therefore, π nonbonded interactions favor unequivocally a shrinkage of the FCF angle. This is mainly due to the fact that the spatial overlap between the fluorine $2p_\pi$ AO and the $2p_\pi$ AO of the nonadjacent carbon decreases with decreasing F_1CF_2 angle. As a result, the $S_{n_S-\pi}$ overlap integral will tend to decrease and the $S_{n_S-\pi^*}$ overlap integral will tend to increase, as it can be seen from the values listed in Table III.

It can also be noticed that the overall energy effect associated with the π orbital interactions (i.e., the $E_T − E_T^0$ values listed in Table II) and the energy effect described by expressions 1 and 2 (i.e., the Q values of Table III) show the same

trend and also are both destabilizing and of similar order of magnitude. This satisfactory agreement is indicative of the fact that the second-order effects,[16] $\Delta E_{n_S-\pi}^4$ and $\Delta E_{n_S-\pi^*}^2$, are the dominant contribution of the overall energy effect.

The present findings complete the OEMO analysis previously reported.[5] In fact, they confirm the conclusions reached before, the most important being that angle shrinkage decreases the $n_S-\pi$ overlap repulsion and increases the stabilizing effect of the $n_S-\pi^*$ interaction.

As a second example, we examine the role played by π nonbonded interactions in determining the relative stability of geometric isomers. Our model systems are taken to be *cis*- and *trans*-1,2-difluoroethylene. Again, this problem has already been the object of previous OEMO investigations.[3,5] Consequently, we summarize very briefly the basic approach. The dissection employed in the analysis follows:
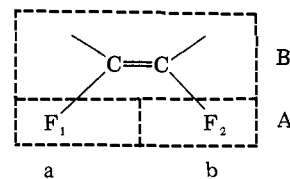
The π framework of *cis*- and *trans*-difluoroethylene can be constructed from the group MO's spanning the two $2p_\pi$ "lone

Table V. Orbital Energies[a] (ϵ_i), Matrix Elements[a] (H_{ij}), and Overlap Integrals (S_{ij}) Computed at the STO-3G and 4-31G Levels for *cis*- and *trans*-1,2-Difluoroethylene, together with the Two-Electron Stabilization Energies[b] (ΔE_{ij}^2) and the Four-Electron Destabilization Energies[b] (ΔE_{ij}^4)

	STO-3G		4-31G	
	cis	trans	cis	trans
ϵ_{n_F}	−0.4906	−0.4942	−0.6615	−0.6681
ϵ_{n_S}	−0.4945	−0.4966	−0.6648	−0.6691
ϵ_{n_A}	−0.4867	−0.4917	−0.6582	−0.6671
ϵ_{π}	−0.3979	−0.3981	−0.4819	−0.4818
ϵ_{π^*}	0.2163	0.2170	0.0502	0.0533
$H_{n_{F1}-n_{F2}}$	−0.0039	−0.0025	−0.0041	−0.0010
$S_{n_{F1}-n_{F2}}$	0.0001	0.0000	0.0013	0.0001
$H_{n_S-\pi}$	−0.1788	−0.1795	−0.2206	−0.2226
$S_{n_S-\pi}$	0.1182	0.1188	0.1891	0.1906
$H_{n_A-\pi^*}$	−0.2266	−0.2264	−0.2779	−0.2743
$S_{n_A-\pi^*}$	0.1319	0.1318	0.2656	0.2616
$\Delta E_{n_{F1}-n_{F2}}^4$	0.00	0.00	0.01	0.00
$\Delta E_{n_S-\pi}^4$	37.92	38.22	55.22	56.08
$\Delta E_{n_A-\pi^*}^2$	−47.09	−46.27	−18.84	−17.36
$Q^{b,c}$	−9.17	−8.05	36.39	38.72

[a] Values in au. [b] Values in kcal/mol. [c] Defined as the sum of the three interaction energies. A plus sign implies that the interaction energy in destabilizing.

pair" AO's of the fluorines and the ethylenic π MO's. Again, we distinguish three types of interactions (see Figure 3): (i) a four-electron destabilizing interaction between the fluorine lone pairs, $\Delta E_{n_{F1}-n_{F2}}^4$; (ii) a four-electron destabilizing interaction between n_S and π, $\Delta E_{n_S-\pi}^4$; (iii) a two electron interaction between n_A and π^*, $\Delta E_{n_A-\pi^*}^2$. In order to obtain quantitative information about the effects caused by these orbital interactions, we have carried out three types of calculations as described before in the case of 1,1-difluoroethylene. Here, the computational analysis has been carried out at the STO-3G and at the 4-31G levels. The relevant data are listed in Tables IV and V.

The total energy values (see Table IV) show that the overall effect associated with these interactions is destabilizing and it is less destabilizing in the cis than in the trans isomer. Again, the overlap repulsion, $\Delta E_{n_{F1}-n_{F2}}^4$, is negligible not only in the trans isomer, as it can be expected, but also in the cis. Details of the effects associated with these interactions can be obtained from the values listed in Table V. The explicit values of the orbital energies, matrix elements, and overlap integrals support completely the conclusions reached on the basis of the qualitative analysis.[5] In particular it can be seen that, at both computational levels, the four-electron interaction $\Delta E_{n_S-\pi}^4$ is less destabilizing in the cis isomer because $S_{n_S-\pi}$ is greater in the trans isomer and the term $(S_{ij}E_0 − H_{ij})$ smaller in the cis isomer and the two-electron interaction $\Delta E_{n_A-\pi^*}^2$ is more stabilizing in the cis isomer because the energy difference, $\epsilon_{n_A} − \epsilon_{\pi^*}$, is smaller for the cis isomer and the overlap integral, $S_{n_A-\pi^*}$, and matrix element, $H_{n_A-\pi^*}$, are both larger for the cis isomer. Therefore, the present quantitative analysis shows unequivocally that the π nonbonded interactions favor a greater stability of the cis isomer compared with trans. Interestingly, while the overall effect associated with the π interactions under examination is destabilizing at both computational levels, the effect described by expressions 1 and 2 (see the Q values in Table V) is stabilizing at the STO-3G level and destabilizing at the 4-31G level. The comparison of the $E_T − E_T^0$ values with the Q values suggest that in this case the ad-

ditional terms contributing to the overall energy effect are significant. However, the trend of the overall energy effect is controlled by the second-order effects.

Another interesting point concerns the role played by π nonbonded interactions in determining the greater stability of the 1,1 isomer vs. the 1,2 isomer. In most cases where experimental heats of formation are available, the 1,1 isomer is always more stable. This finding is also in agreement with the total energy values listed in Tables II and IV, where it is shown that 1,1-difluoroethylene is more stable than 1,2-difluoroethylene. The computational results also show that when the π interactions are partly removed, the 1,1 isomer remains more stable than the 1,2 isomers.

References and Notes

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