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THE MANIFESTATION OF NON-BONDED ATTRACTION IN THE PHYSICAL PROPERTIES OF *cis* AND *trans* OLEFINS

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Abstract—Non-bonded attraction is suggested to account for a host of differences in the physical properties of *cis* and *trans* olefins of the type XHC=CHX. The main predictions are: (i) The *cis* isomer is more stable than the *trans* isomer; (ii) The C=C bond is longer and the C-X bonds are shorter for the *cis* isomer; (iii) The π MO's orbital energies of the two isomers differ such that the *trans* isomer is a better electron donor and electron acceptor than the *cis* isomer. *Ab initio* calculations at the STO-3G and the 4-31G levels in support of the model are presented. The photoelectron spectra of *cis* and *trans* difluoro, dichloro and dibromoethylene are discussed, and found to be in accord with our qualitative model.

Recently, we have argued that non-bonded attraction plays a key role in determining the relative stability of geometric isomers.[1] In order to further test the validity of this model, we have carried out SCF-MO *ab initio* calculations of the geometric isomers of 1,2-difluoroethylene, as model systems. Furthermore, we have sought to develop an understanding of how non-bonded attraction is manifested in the physical properties of *cis* and *trans* olefins by comparing the results of *ab initio* calculations with the existing chemical evidence.

Theory

In the course of our analysis, we shall make use of the following general results of One Electron MO (OEMO) theory.

(a) The interaction of a doubly occupied MO, ϕ_i, with a vacant MO ϕ_j, leads to two electron stabilization, which is inversely proportional to the energy separation of the two MO's, $E_i - E_j$, and directly proportional to the square of their overlap integral, S_{ij}. This is a well known result of perturbation theory[2] and the assumptions involved in its derivation are valid for the systems studied in this work.[3] The algebraic expression for the two electron stabilization is given below, where k is an energy constant.

$$\Delta E^2 = S_{ij}^2(k - E_i)^2/(E_i - E_j). \qquad (1)$$

(b) The interaction of two doubly occupied MO's, ϕ_i and ϕ_j, leads to four-electron destabilization which increases as the overlap integral of the two MO's, S_{ij}, and the mean of their energies, $(E_i + E_j)/2$, increase.[4] This result is obtained by application of the variational method to the case of a two orbital four electron interaction and involves no special assumptions other than the usual approximation of the interaction matrix element as a linear function of the overlap integral.[5] The four electron destabilization energy is given by eqn (2) where E_0 is the mean of the energies of the unperturbed MO's, ϕ_i and ϕ_j.

$$\Delta E^4 = 4S_{ij}^2(E_0 - k)/(1 - S_{ij}^2). \qquad (2)$$

In summarizing the results of our previous work, we now proceed to outline briefly the pi non-bonded attraction concept by reference to *cis* and *trans* 1,2-difluoroethylene as the model systems.

Theoretically, 1,2-difluoroethylene can be viewed as the result of the union of a central -CH=CH- fragment (fragment A) with two vicinal F atoms, F_1 and F_2 (fragment B). We first proceed to construct the π MO's of fragment B from the $2p_z$ AO's of the F atoms. This is depicted in Fig. 1, which illustrates the interaction between $2p_z$ AO's of the two F atoms. In the case of the *cis* isomer, the $2p_z$ AO of F_1 can overlap with that of F_2,

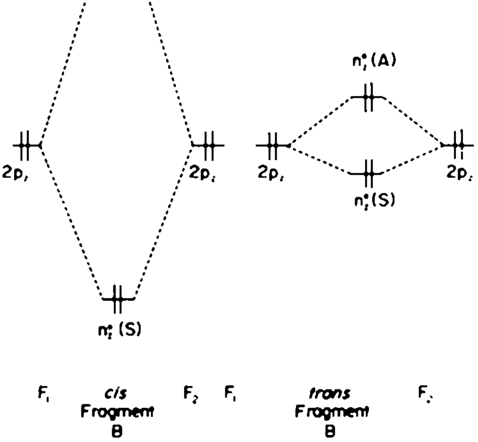

Fig. 1. Interaction diagram for *cis* and *trans* difluoroethylene describing the group MO's for fragment $B(F_1 + F_2)$. Symmetry designations are with respect to the plane bisecting the C=C bond (*cis* olefin) and with respect to the two-fold axis perpendicular to the plane of the molecule (*trans* olefin).

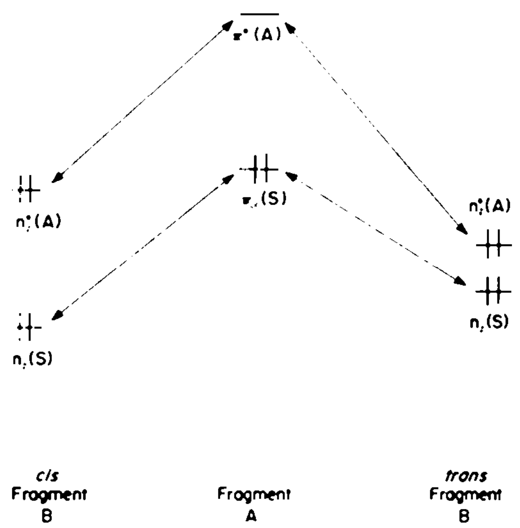

Fig. 2. Interaction diagram for *cis* and *trans* difluoroethylene describing the A + B union. Symmetry designations as in Fig. 1.

while in the *trans* isomer this type of overlap is substantially reduced. Hence, the splitting between the $n_z(S)$ and $n_z^*(A)$ pi MO's of the composite fragment (B) is greater in the case of the *cis* isomer and 4-electron destabilization favors the *trans* over the *cis* isomer.

Next, we construct the composite system of 1,2-difluoroethylene from fragments A and B. The orbital interactions which obtain in this union are depicted in Fig. 2. Two types of interaction should be considered:

(a) A 4-electron destabilizing interaction between the $n_z(S)$ MO of the B fragment and the $\pi_{CC}(S)$ MO of the -CH=CH- group. In this case, the two variables in eqn (2) favor the *cis* over the *trans* isomer. Specifically, the overlap integral between these MO's is larger in the case of the *trans* isomer because the normalization constant for the $n_z(S)$ MO has the form $(2 + 2S_{FF})^{1/2}$ and will be smaller in the case of the *cis* isomer since $S_{FF}(cis) > S_{FF}(trans)$. Similarly, E_0, the mean energy of the $\pi_{CC}(S)$ and the $n_z(S)$ MO's is more negative and, hence, leads to a smaller $(E_0 - k)$ value for the *cis* isomer. Therefore, on the basis of eqn (2), we conclude that this 4-electron destabilizing interaction will be smaller for the *cis* isomer.

(b) A 2-electron stabilizing interaction between $n_z^*(A)$ and $\pi_{CC}^*(A)$. In this case, the following trends can be noted: (i) the energy difference $E_{n_z^*} - E_{\pi^*}$ is smaller in the *cis* isomer; (ii) the quantity $(k - E_{n_z^*})$ is greater for the *cis* isomer; (iii) the overlap integral $S_{n_z^*\pi^*}$ is larger for the *cis* isomer because the normalization factor of the $n_z^*(A)$MO, given by the expression $(2 - 2S_{FF})^{1/2}$, is greater for the *cis* isomer. We conclude, therefore, that the 2-electron stabilization will favor the *cis* over the *trans* isomer.

The question now arises as to whether the destabilizing interaction involved in the $F_1 + F_2$ union or the interactions involved in the A + B union will dominate the relative stability of the two isomers. Clearly, the interactions in the second union are much larger than that in the first union due to a much larger overlap between fragments A and B than between F_1 and F_2.[3] Hence, although the $F_1 + F_2$ union favors the *trans* isomer, the A + B union exerts a predominant effect in the opposite direction.

A simplifying reduction of the preceeding analysis of stabilizing and destabilizing interactions can be accomplished by recourse to the concept of aromaticity. Specifically, we expect that 1,2-difluoroethylene, a 6π-electron system, will be "aromatic" in the *cis* form and "non-aromatic" in the *trans*. These ideas can also be extended to analyze sigma non-bonded interactions.

We shall now enumerate some of the physical manifestations of non-bonded attraction and we shall compare our predictions with the results of *ab initio* calculations and with the body of chemical evidence.

I. *Relative stability of* cis *and* trans *olefins*

As we have already stated, the *cis* olefin is predicted to be more stable than the *trans*. This trend will be upset in cases where severe steric repulsions are present.

II. *Bond strength and bond length*

The difference in the strength of MO interactions in the *cis* and *trans* isomers is expected to be responsible for differences in bond strengths and lengths. Specifically, since the interactions of the second union (A + B) dominate those of the first union ($F_1 + F_2$), the following results are expected:

(a) Greater charge transfer[1c] from $n_z^*(A)$ to $\pi_{CC}^*(A)$ in the *cis* isomer leads to a weaker C=C bond and induces a partial bond between the two F atoms in the *cis* isomer.

(b) The more favorable interactions (stabilizing and destabilizing) between fragments A and B in the case of the *cis* isomer will lead to stronger and shorter C–F bonds in this isomer.

III. *Ionization potentials*

According to Koopmans' Theorem,[6] the ionization potential equals the negative energy of the MO from which an electron has been ejected. Accordingly, the validity of our model can be scrutinized by inspecting the ionization potentials of the π MO's. The relative energies of the occupied MO's of *cis* and *trans* difluoroethylene, as developed by means of the interaction diagram in Fig. 2, are depicted in Fig. 3. The following trends can be noted:

(a) $E(\phi_1^c) > E(\phi_1^t)$. This results from the larger interaction between the $\pi_{CC}(S)$ MO and the $n_z(S)$ MO in the case of the *trans* isomer. This is true even though the result of the initial union places the *cis* $n_z(S)$ MO lower in energy than that of the *trans* since the interactions obtained in the second union will predominate.

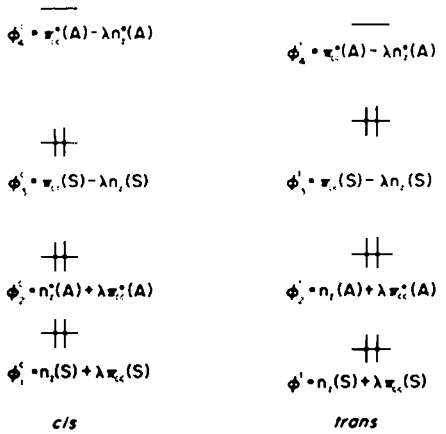

Fig. 3. The π-MO relative energies for *cis* and *trans* difluoroethylene as predicted by the non-bonded attraction model.

(b) $E(\phi_2^c) \gtrsim E(\phi_2^t)$. The *cis* $n_z^*(A)$ MO is destabilized with respect to the *trans* $n_z^*(A)$ MO in the initial union ($F_1 + F_2$). However, the former is lowered in energy with respect to the latter MO due to the interaction between the $n_z^*(A)$ MO and the $\pi^*_{CC}(A)$ MO in the second union (A + B). The $\pi^*_{CC}(A)$–$n_z^*(A)$ interactions are weak due to a large energy gap separating the two interacting orbitals. Consequently, it cannot be predicted qualitatively whether the interactions of the A + B union will dominate those of the $F_1 + F_2$ union.

(c) $E(\phi_3^c) < E(\phi_3^t)$. Here, a stronger $\pi_{CC}(S) - n_z(S)$ interaction in the case of the *trans* isomer will result in a higher energy MO than the corresponding MO for the *cis* isomer.

IV. *Electron affinities*

The electron affinity and reduction potential of a molecule are related to the energy of the Lowest Occupied MO (LUMO). Figure 3 shows that $E(\phi_4^c) > E(\phi_4^t)$. This is the result of the interaction between the $n_z^*(A)$ MO and the $\pi^*_{CC}(A)$ MO obtained in the final combination which is stronger for the *cis* isomer.

Ab initio *computations*

In order to gauge the importance of pi non-bonded attraction in determining the relative stability and the differences in the physical properties of the *cis* and *trans* isomers of 1,2-difluoroethylene, these systems were investigated with the STO-3G[7] and 4-31G[8] basis sets. All computations were carried out using a Gaussian 70 series of programs.[9] In these computations, the C–H bond lengths were kept fixed at 1.07 A and all other parameters were optimized. The optimum geometrical parameters,[10] the total energies computed, and the pi orbital energies are listed in Tables 1 and 3.

RESULTS AND DISCUSSION

We are now ready to compare our qualitative predictions with the computational results and with the available chemical data. The results of the *ab initio* calculations pertaining to total energy and molecular geometry (Table 1) have been summarized in a previous paper[11] and are included in this work for completeness. However, a detailed analysis is now presented in order to highlight the correlation of certain computational trends with the qualitative predictions.

Relative stability of cis *and* trans *1,2-difluoroethylene.* All the computations of the model systems indicate that the *trans* isomer is more stable than the *cis* isomer. Furthermore, 3 × 3 CI seems to emphasize this preference.[12] Thus, the *ab initio* calculations fail to reproduce the experimental results. In a previous publication,[11] we have pointed out that the failure of the extended basis set (4-31G) to reproduce the right order of stability of *cis* and *trans* difluoroethylene is likely to be attributed to deficiencies of this basis set.[11]

Molecular geometries. Inspection of Table 1 shows that, whereas the minimal basis set (STO-3G) fails to reproduce the right order of the C–F bond lengths, the extended basis (4-31G) results are in agreement with our qualitative predictions and the experimental data (Table 2), namely, a longer C–F bonds for the *trans* isomer.

At this point, an examination of the various components of the total pi overlap population is informative. The pertinent data are shown in Table 5. The following trends are significant:

(a) The total pi overlap population is greater for the *cis* isomer as expected on the basis of the qualitative analysis. Furthermore, the F . . . F long range pi overlap population is positive, albeit small, as predicted.

(b) The *relative* C–C and C–F pi overlap populations are in agreement with the qualitative predictions.

(c) The negative C–F overlap population suggests that at this level of computation the 4-electron destabilizing $n_z(S) - \pi_{CC}(S)$ interaction dominates and favors the *cis* form.

Table 1. STO-3G and 4-31G optimized geometric parameters and total energies

Geometric parameter	*cis*	*trans*
I. STO-3G		
'C–C (Å)	1.3264	1.3256
'C–F (Å)	1.3581	1.3572
'C–H (Å)	1.07†	1.07†
< CCF	124.20°	122.97°
< CCH	120.52°	121.89°
Total energy (a.u.)	− 271.98492	− 271.98531
total energy‡ (a.u.)	− 272.01287	272.01342
II. 4-31G		
'C–C (Å)	1.3042	1.3025
'C–F (Å)	1.3595	1.3601
'C–H (Å)	1.07†	1.07†
<CCF	124.14°	121.13°
<CCH	122.60°	125.30°
Total energy (a.u.)	− 275.36715	275.36919

†Not optimized.

‡These values are obtained from a 3 × 3 CI treatment, encompassing, in addition to the ground state, the lowest single and doubly exicted configurations.

Table 2. Electron diffraction data for *cis* and *trans* isomers of difluoroethylene†

Geometric parameter	*cis*	*trans*
'C–C (Å)	1.331 ± 0.004	1.329 + 0.004
'C–F (Å)	1.335 ± 0.002	1.344 ± 0.001
'C–H (Å)	1.084 ± 0.007	1.080 ± 0.006
< CCF	123.72° ± 0.24	119.33° - 0.84
< CCH	121.56° + 0.90	129.25° + 1.2

†J. L. Carlos, R. R. Karl and S. H. Bauer, *Faraday II. J. Chem. Soc.* **70**, 177 (1974).

Table 3. π MO pattern for *cis* and *trans* difluoroethylene

		Orbital energies (eV)	
Molecular orbital	Geometry	STO-3G optimized geometry	4-31G optimized geometry
ϕ_4	*cis*	−8.331	+4.631
	trans	+8.333	+4.589
ϕ_3	*cis*	−8.010	10.992
	trans	8.019	− 10.980
ϕ_2	*cis*	−14.165	−18.335
	trans	−14.285	−18.546
ϕ_1	*cis*	−15.450	−19.092
	trans	−15.499	19.196

†The MO's are labelled according to Fig. 3.

Table 4. Photoelectron spectroscopic π MO patterns for *cis* and *trans* dichloroethylene and dibromoethylene†

Molecular orbital	Isomer	Orbital energies (eV) Dibromoethylene	Dichloroethylene
ϕ_3	*cis*	−9.63	−9.80
	trans	−9.55	−9.80
ϕ_2	*cis*	−11.55	−12.47
	trans	−11.57	−12.64
ϕ_1	*cis*	−12.86	−13.76
	trans	−12.90	−13.79

†See Ref. 15.

Table 5. 4-31G Pi overlap populations of *cis* and *trans* difluoroethylene

	Atom pair			
Isomer	C_1C_2	C_1F_1	F_1F_2	Total†
cis	0.2518	−0.0074	0.00025	0.2154
trans	0.2532	−0.0088	0.00001	0.2126
ΔP^{π}	−0.0014	+0.0014	+0.00024	+0.0028

†P^{π} Total is the sum of all π-overlap populations including $P^{\pi}_{C_1F_2}$ and $P^{\pi}_{C_2F_1}$ which were not included in this table.

Pi MO energies

(a) Ab initio *results*. The computed orbital energies are displayed in Table 3. It is evident that our predictions regarding the occupied orbitals, as summarized in Fig. 3, are reproduced at the 4-31G level and only partly at the STO-3G level. Specifically, at both levels the ϕ_1 lone pair MO is lower in energy in the case of the *trans* isomer, whereas the ϕ_3 pi type MO is lower in energy in the case of the *cis* isomer only at the 4-31G level. Finally, the extended basis set (4-31G) reproduces our predictions regarding the relative energy of the ϕ_4 vacant pi type MO.

(b) *Experimental evidence*. Basch *et al.*[14] have reported that the ionization potential corresponding to the π_{CC}(S) MO's of *cis* and *trans* difluoroethylene are 10.43 eV and 10.38 eV, respectively, in agreement with our qualitative model and the *ab initio* results. Unfortunately, the ionization potentials of the low energy orbitals of 1,2-difluoroethylene were not obtained. However, such data are available[15] for the isomers of 1,2-dichloroethylene and 1,2-dibromoethylene. The results are presented in Table 4. Here, the first ionization potentials of the isomers of 1,2-dichloroethylene were found to be identical at 9.80 eV. All other comparisons of the *cis* and *trans* isomers were found to be in agreement with the predictions of the non-bonded attraction model. Unfortunately, electron affinity data and/or reduction potentials of these systems have not been reported.

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[12] C.I. Treatment stabilizes the molecules by $-2K_{\pi\pi^*}$. This term can be viewed as a correlation effect which is expected to be larger in the case of the *trans* isomer. Further treatment of this interesting point is under active study.

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