On the Origin of *cis*-Effect in 1,2-Difluoroethene

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(Received June 18, 1997; CL-970463)

The origin of *cis*-effect in 1,2-difluoroethene has been identified by quantitative analysis of electron delocalization using natural bond orbital analysis at the HF/6-311++G(3df, 3pd) level. It was concluded that both the delocalization of halogen lone-pair electrons (LP effect) and the antiperiplanar effects (AP effect) between vicinal antiperiplanar bonds are most likely to be the major sources of *cis*-effect with the latter effect being the more predominant.

"*cis*-Effect", which refers to the remarkable phenomenon that in 1,2-disubstituted ethenes the *cis* form is often thermodynamically more stable than the *trans* form, has been a long-standing puzzle in basic organic chemistry. A number of controversial explanations employing 1,2-difluoroethene as a model compound have appeared to date. Major historical explanations include the two-electron stabilizing interaction between the π_{CC} and the lone pair electrons,[1] π-electron delocalization,[2,3] and nonbonded attraction[4] including van der Waals attractive force between two halogen atoms.[5] Among these the last one is the most widely accepted explanation that frequently appears in common organic chemistry textbooks.[5b] Recently two new explanations, one of which is based on the "bent C=C bond concept",[6a,b] have been proposed.[6] Described herein is a novel theoretical interpretation for the origin of "*cis*-effect" using natural bond orbital (NBO) analysis.[7]

Figure 1 shows the structures of 1,2-difluoroethene (**1**) obtained by geometry optimization at the B3LYP/6-311++(3df,3pd) level.[8] A comparison between the calculated structural parameters and the experimental data[9] indicated in parenthesis immediately reveals the reliability of the computational method employed. Indeed a single point calculation of the electronic energy difference at the MP4(SDTQ)/6-311++G(3df,3pd) level using the B3LYP-optimized geometries almost precisely reproduced the gas phase electronic energy differences for **1**. Calculated (observed[10]) electronic energy difference is 1.13 (1.080 ± 0.120) kcal mol^{-1}. Further inspection of the structural parameters indicates that the C=C bond length and the ∠CCF angle are greater in the *cis* isomer than in the *trans* isomer, whereas the C–F bond length is longer in the *trans* isomer than in the *cis* isomer. The wider angle ∠CCF of the *cis* isomer suggests that some repulsive force may be operative between the two halogens in the *cis* isomer rather than attractive force. It was presumed that such distinct structural trends might have some clues to the origin of *cis*-effect.

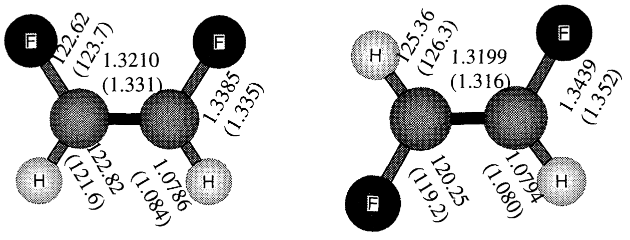

Figure 1. Selected bond lengths (Å) and bond angles (°) for 1,2-difluoroethenes optimized at the B3LYP/6-311++G(3df, 3pd) level. Experimental data are indicated in parenthesis.[9]

An energy analysis of electron delocalization based on the 2nd order perturbation theory[11] applied to NBO analysis[7] was selected as the most effective tool for quantitative identification of the element(s) of *cis*-effect. The Hartree-Fock method was chosen with the same basis set as employed above. The results are collected in Table 1. It is seen that two major delocalization effects operate in both the *cis* and *trans* isomers, namely the antiperiplanar effect between the vicinal antiperiplanar C–F (or C–H) and the C–H (or C–F) bonds (AP effect) and the delocalization of the lone pair electrons of a halogen into the C=C bond system (LP effect). It is suspected that the magnitude of these electron delocalization effects should be responsible for relative thermodynamic stability of the *cis* isomer of **1**. Several notable features are seen from Table 1.

First the total LP effects for each isomer (66.36, 63.56 kcal mol^{-1} for *cis* and *trans* isomers, respectively) are much greater than the total AP effects (19.38, 15.16 kcal mol^{-1}). This is due to the considerably larger magnitude of conjugation of one of the lone pairs, which lies out of the molecular plane (LP_{π}) within the

Table 1. Second-order perturbation analysis with natural bond orbital (NBO) method[7,12] on the geometrical isomers of 1,2-difluoroethene.[a]

	AP Effects (kcal mol^{-1})			LP Effects (kcal mol^{-1})		
cis	$\sigma_{CH}\rightarrow\sigma_{CX}^*$	$\sigma_{CX}\rightarrow\sigma_{CH}^*$	Total[b]	$n_{\sigma}\rightarrow\sigma_{CC}^*$	$n_{\pi}\rightarrow\pi_{CC}^*$	Total[b]
	8.07	1.62	19.38	8.74	24.44	66.36
trans	$\sigma_{CX}\rightarrow\sigma_{CX}^*$	$\sigma_{CH}\rightarrow\sigma_{CH}^*$	Total[b]	$n_{\sigma}\rightarrow\sigma_{CC}^*$	$n_{\pi}\rightarrow\pi_{CC}^*$	Total[b]
	2.86	4.72	15.16	8.01	23.77	63.56
		Δ_{AP}[c]	4.22		Δ_{LP}[c]	2.80

[a] HF/6-311++G(3df,3pd). [b] Total values of AP effects or LP effects for each isomer. [c] Δ_{AP} and Δ_{LP} denote *cis-trans* difference in the total value of AP effects and LP effects, respectively.

π-electron network (24.44, 23.77 kcal mol^{-1}) compared to the delocalization of the in-plane σ-lone pair (LP$_\sigma$) which lies roughly antiperiplanar to the C=C bond (8.74, 8.01 kcal mol^{-1}). It should be noted that both lone pair delocalization mechanisms prefer the *cis* isomer and that the LP$_\pi$ mechanism is by far important compared to the LP$_\sigma$ mechanism.

Secondly as seen in the Δ value which denotes the difference in the overall AP or LP effects between the *cis* and the *trans* isomer (Δ_{AP} and Δ_{LP}), the magnitude of both the total AP effect and the total LP effect is larger in the *cis* than in the *trans* form. The combined effect amounts to 7.02 kcal mol^{-1}, which implies overwhelming thermodynamic preponderance of the *cis* isomer owing to the dual mechanism (AP and LP effects) of intramolecular electron delocalization. It is interesting to note that since Δ_{AP} is greater than Δ_{LP}, it can be concluded that the *cis* isomer of **1** should be stabilized chiefly *via* the antiperiplanar conjugation mechanism. Furthermore it is apparent from the Table that the difference in the magnitude of the lone pair π-electron delocalization mechanism (LP$_\pi$ mechanism) between the two isomers, which was previously proposed by Epiotis to be the major origin of the *cis* effect in **1**,[1] is found to be only marginal (0.67 kcal mol^{-1}). It should be noted here that while Epiotis suggested the importance of the energy difference between the π_{CC}* and the antibonding molecular orbital of the two out-of-plane lone pair combination,[1] it seems the Fock matrix elements that should contribute more significantly to the LP$_\pi$ mechanism.[12]

The above results are consistent with the structural difference between the isomers of **1**. The reduction in the C–X distance and the increment in the C=C distance can be rationalized by predominance of the LP effects over the AP effects. The widening of the ∠CCF angle (122.6°) due to the repulsive lone pair (four-electron) interaction between two closely located halogens in the *cis* isomer may cause distortion of the in-plane lone pairs toward the direction antiparallel to the vicinal σ_{CC} in addition to slight spatial approach, both of which should contribute to further enhancement of the stabilizing antiperiplanar interactions between σ_{CC}* and the vicinal antiperiplanar lone pairs in the *cis* isomer.

We thank the Computer Center of the Institute for Molecular Science for considerably generous offer of CPU time. Thanks are also due to the Ministry of Education, Science, Sports and Culture of Japan for Grant-in Aid for Scientific Research (Project Nos.(year): 09440215 (1997) and 09239207 (1997), 07454161 (1996)).

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11 The second order perturbation energy is expressed as the following formula,

$$E_2 = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i}$$

where q_i is the electron population of the *i*th donor orbital, ε_i and ε_j is the energy level of the *i*th and *j*th orbital, and $F(i, j)$ is the (i, j) element of the Fock matrix.[7] Application of the theory to organic molecules has been described in; A. E. Reed and F. Weinhold, *Israel J. Chem.*, **31**, 227 (1991) and P. v. R. Schleyer, M. Kaupp, F. Hampel, M. Bremer, and K. Mislow, *J. Am. Chem. Soc.*, **114**, 6791 (1992).

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