

THE ROLE OF CORRELATION IN CALCULATIONS ON 1,2-DIFLUOROETHYLENES. THE CIS-TRANS ENERGY DIFFERENCE

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Correlation-corrected ab initio calculations predict cis-1,2-difluoroethylene to be more stable than trans. With second-order Rayleigh-Schrödinger Møller-Plesset theory, the cis form is lower by 0.9–1.3 kcal/mol, depending on the basis set, in agreement with the experimental energy difference $\Delta E = 1.1$ kcal/mol. The positive ΔE is primarily due to greater intra-pair correlation energy in the cis form.

1. Introduction

According to simple electrostatic models of cis- and trans-1,2-difluoroethylene (**1** and **2**) the cis isomer **1** should be destabilized relative to **2** by unfavorable dipole-dipole interactions (see fig. 1). Thermodynamic studies, however, show that **1** is more stable than **2** ($\Delta E = E(\text{trans}) - E(\text{cis}) = 1.08$ kcal/mol [1], an observation which has also been made on other 1,2-dihaloethylenes [1]. This apparent contradiction to the general finding that molecular systems prefer a form with lower "steric" or electrostatic repulsion has intrigued theoreticians.

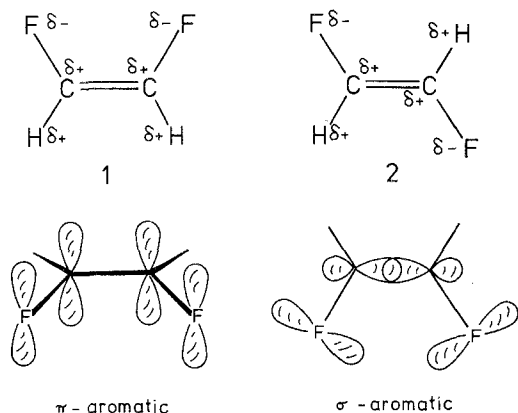


Fig. 1. Qualitative description of charge distributions in **1** and **2** (above). Possible orbital interactions involving the fluorine atoms of **1** (below).

Based on earlier work by Hoffmann and Olofson [2], the concept of steric attraction between the fluorine atoms of the cis form was developed [3]. Steric attraction may be described as resulting from homoaromatic conjugation involving the CC double bond and the F atoms. The F and C $2p_\pi$ orbitals constitute a set of four MOs occupied by 6 electrons. The HOMO of these π -type MOs is stabilized in **1** by 1,4 bonding. Similarly, the σ -type lone-pair orbitals of the F atoms can be combined with the carbon sp^2 hybrid orbitals leading to a four-orbital system again occupied by 6 electrons. Thus the unusual stability of **1** can be attributed to its homoaromatic 6π and 6σ electron ensembles. This description has been useful in rationalizing conformational features of miscellaneous compounds [4].

Epiotis et al. [5] analyzed σ - σ^* and π - π^* orbital interactions in **1** and **2**. They demonstrated that the cis isomer is stabilized relative to **2** by favorable two-electron two-orbital interactions involving the anti-symmetric combination of the n_σ and n_π orbitals of F and the σ^* and π^* MO of the C=C bond. In **1** a preferential charge transfer out of the n_σ - n'_σ and n_π - n'_π combinations to the σ^* and π^* MOs takes place, thus leading to some stabilizing F...F bonding which is absent in **2** [5].

Although these qualitative descriptions of the stabilizing attractive F...F interactions in **1** are plausible [6], quantitative confirmation of the effect by reproducing the experimentally observed energy dif-

ference ΔE was lacking. All ab initio calculations published so far [7–9] severely underestimate the stability of **1**, mostly predicting the trans form to be more stable than the cis form. This is rather annoying in view of the fact that both the qualitative and quantitative attempts to rationalize the positive ΔE value are based on MO theory.

Binkley and Pople [9] attributed the failure to calculate the correct ΔE value to basis-set deficiencies. An insufficient description of the “outer tails” of the F valence functions which must play an important role in the steric attraction model should lead to an underestimation of F...F overlap and, hence, an underestimation of attractive F...F interactions. Restricted Hartree–Fock (RHF) calculations with an augmented basis set of triple-zeta (TZ) quality in the valence shell carried out by Binkley and Pople (BP) [9] gave support to this argument. Using standard geometry models of **1** and **2**, the correct order of stabilities, i.e. $\Delta E > 0$, was calculated.

However, the TZ results still underestimated the experimental ΔE value by 0.6 kcal/mol. This was attributed to the correlation error of the RHF approach [9]. If electron correlation is greater in the cis than the trans form, a correlation-corrected method may lead to a correct description of the stability of **1**. First attempts to test this hypothesis were only partially successful. Calculations with second-order Rayleigh–Schrodinger Møller–Plesset (RSMP2) perturbation theory lead to an increase in the ΔE value by 0.3–0.4 kcal/mol but the basis sets used were too small to describe the right order of stabilities [9]. Thus it was not clear to what extent the perturbation theory approach compensated some of the basis-set deficiencies.

The main purpose of this paper is to present an accurate account of the relative energies of **1** and **2**. In order to fulfil this objective the influence of correlation corrections on the difference ΔE is analyzed in detail.

2. Numerical details

Standard RHF theory [10] has been used to obtain the zeroth-order wavefunction and molecular energy in the RSMP approach. In second-order RSMP theory [11] the correlation correction comprises all

pair correlation energies which can be split into intra- and inter-pair contributions.

In order to have a means of comparing RSMP results with those of BP [9], we use Pople's 6-31G* [12] and 6-311G* [13] basis sets in this study. Since these basis sets are only heavy-atom augmented, a third basis set, namely the 6-31G** set, is employed, which has also p-type polarization functions in the hydrogen set [12]. In all calculations six rather than five second-order gaussians have been employed. They are equivalent to five 3d and a single 3s gaussian-type function (GTF).

3. Results and discussions

In table 1 total molecular energies for **1** and **2** obtained with the RHF and RSMP2 method are summarized. Computed correlation corrections and their intra- and inter-pair contributions are also listed.

The first set of calculations has been carried out using standard geometries for **1** and **2** [14] as suggested by BP [9]. Although the right order of stabilities is calculated, the ΔE (RSMP2) value of 0.5 kcal/mol is still too small. It is 0.1 kcal/mol lower than the estimate given by BP [9] who assumed a constant RSMP2 contribution to ΔE of 0.4 kcal/mol. Obviously, the improvement of ΔE obtained with small basis sets at the RSMP2 level partially results from compensation of basis-set deficiencies.

If one compares the standard geometries of **1** and **2** with the experimentally observed structures [15], it becomes obvious that a trigonal carbon with bond angles of 120° leads to an underestimation of the CCF angle in **1** (123.7° [15]) and the CCH angle in **2** (129.3° [15]). Thus at standard geometry the F...F distance is underestimated and, correspondingly, F...F repulsion overestimated for **1**. For the trans isomer **2**, vicinal H...F attraction is overestimated since the corresponding distances come out too small at standard geometry. Both effects lead to an artificial destabilization of **1** relative to **2**.

In order to eliminate these effects, a second set of calculations has been carried out using experimental geometries of **1** and **2** [15]. The total molecular energies thus obtained are lower than those computed for standard geometries, as can be seen by comparing the corresponding 6-311G* results. Again, RHF energies

Table 1
RHF, second-order correlation, and RSMP energies (hartree) of cis- and trans-1,2-difluoroethylene ^{a)}

Basis	Energy	cis-C ₂ F ₂ H ₂	trans-C ₂ F ₂ H ₂	ΔE ^{b)} (kcal/mol)
(A) standard geometry				
6-311G*	RHF	-275.78867	-275.78822	0.28
	CORR	-0.68281	-0.68240	0.26
	intra	-0.10554	-0.10551	0.02
	inter	-0.57727	-0.57689	0.24
	RSMP2	-276.47148	-276.47062	0.54
(B) experimental geometry [15]				
6-31G*	RHF	-275.71933	-275.71960	-0.17
	CORR	-0.60469	-0.60303	1.04
	intra	-0.08972	-0.08810	1.02
	inter	-0.51497	-0.51493	0.02
	RSMP2	-275.32402	-276.32264	0.87
6-31G**	RHF	-275.72340	-275.72357	-0.11
	CORR	-0.61693	-0.61505	1.18
	intra	-0.09162	-0.08989	1.09
	inter	-0.52531	-0.52516	0.09
	RSMP2	-276.34033	-276.33862	1.07
6-311G*	RHF	-275.79083	-275.79046	0.23
	CORR	-0.68307	-0.68141	1.04
	intra	-0.10620	-0.10452	1.05
	inter	-0.57687	-0.57689	-0.01
	RSMP2	-276.47390	-276.47187	1.27

^{a)} Abbreviations intra and inter stand for intrapair and interpair correlation contributions.

^{b)} $\Delta E = E(\text{trans}) - E(\text{cis})$.

tend to underestimate the stability of **1**. With an improvement of the basis this tendency becomes less severe. The inclusion of p-type polarization functions in the H basis turns out to be less important for an improvement of ΔE than the augmentation of the F basis by diffuse s and p GTFs. This is in accord with the observations made by BP [9].

A significant improvement of ΔE , however, is achieved at the RSMP2 level of theory. With all three basis sets a ΔE value is computed which is in good agreement with the experimental energy difference of 1.08 ± 0.12 kcal/mol [1]. The 6-31G* value underestimates ΔE by 0.2 kcal/mol while the 6-311G* result is 0.2 kcal/mol too high. With the fully augmented 6-31G** basis, $\Delta E = 1.07$ kcal/mol is found.

The results of table 1 clearly illustrate that consideration of correlation corrections is important in an

investigation of the relative stabilities of **1** and **2**. The correlation contributions to ΔE are slightly higher than 1 kcal/mol for the three basis sets considered. It is interesting to note that this relatively high contribution is solely due to the difference of the intrapair energies. The interpair contribution to ΔE adopts small positive or negative values, as shown in table 1.

This is contrary to what is found when standard geometries are used. Then, the interpair rather than the intrapair correlation energies lead to an improvement of ΔE . This seems to be a result of an artificial enhancement of F...F interactions in the cis form caused by standard CCF angles of 120°. At least, this is suggested by the Mulliken F...F overlap populations ρ [16] listed in table 2. Both the σ and the π part of the total overlap population are slightly more F...F bonding for **1** than for **2**, lending some support to the

Table 2
Fluorine-fluorine overlap populations $\rho \times 10^4$

Basis		Standard geometry		Experimental geometry	
		1	2	1	2
6-31G*	σ	3	6	-1	1
	π	10	<1	6	3
	total	13	6	5	3
6-311G* ^{a)}	σ	23	16	28	18
	π	30	2	19	2
	total	53	18	47	20

a) Overlap populations at standard geometry deviate from those published in ref. [9] since 6 rather than 5 d GTFs have been used in this work.

steric attraction hypothesis. On the other hand, π bonding is significantly reduced when using experimental geometries. This reduction is only partially compensated by a simultaneous increase of σ bonding. We conclude that for the cis isomer F...F interactions and, accordingly, the interpair correlation energy is actually smaller than computed with the standard geometry model.

In order to understand the role of the intrapair correlation energy contribution to ΔE , it has to be stressed that the relative stability of **1** is very sensitive to charge-repulsion effects. Comparison of the RHF electron populations of **1** and **2** reveals that diffuse outer density, associated with the F tails, decreases markedly from the trans to the cis form. In order to keep Coulomb repulsion between the negatively charged F atoms low, electron density is more confined to the inner valence shell region in **1** than in **2**. As a consequence, the MOs of **1** are more constrained to the area of the nuclear framework, thus leading to enhanced intrapair correlation. This is similar to the observation made in RSMP calculations on cis and trans-H₂O₂ [7].

From the known correlation energies of CH₄ (-0.293 [13]), CH₃F (-0.629 [18]), and C₂H₄ (-0.503 hartree [19]), the total correlation energy $E(\text{CORR})$ of 1,2-difluoroethylene can be estimated to be ≈ 1.18 hartree. With RSMP2/6-311G* calculations just 58% of $E(\text{CORR})$ is covered. Improvement of the basis can increase this to 70–80% [17]. The rest is due to many-electron correlations, especially

pair-pair correlations, which are neglected by RSMP2 theory. Thus, it may be questioned whether a consistent description of cis, trans isomers is possible at the RSMP2 level. If, for example, pair-pair correlations would contribute to ΔE , RSMP2 calculations of geometrical isomers could lead to erroneous results, meaning that in the case of 1,2-difluoroethylene the observed agreement between the experimental and the RSMP2 values of ΔE is fortuitous.

In order to examine the reliability of the RSMP2 results on **1** and **2**, parallel investigations have been carried out on the isomers of 2-butene, CH₃CH=CHCH₃ [20], and difluorodiazene, FN=NF [18]. In both cases the RSMP2 energy differences ΔE have been found to be in good agreement with the corresponding experimental values.

Further evidence for the reliability of RSMP2 theory has been given by Pople et al. [21], who compared RSMP energies with those obtained by the coupled pair many-electron (CPME) theory of Čížek [22]. They demonstrated that for diazene, HN=NH the cis-trans energy differences ΔE , computed at the second-, third-, and fourth-order RSMP level, coincide with the corresponding CPME value within 0.1 kcal/mol. This suggests that a reliable account of the relative stabilities of **1** and **2** is provided by RSMP2 theory.

The results of the present work can be summarized as follows: (1) If realistic geometries and sufficiently flexible basis sets are used, an accurate account of the relative stabilities of **1** and **2** is provided by correlation corrected ab initio calculations. The cis isomer is found to be more stable than the trans by 0.9–1.3 kcal/mol which is in good agreement with experiment [1]. (2) More than 80% of the theoretical ΔE value is due to correlation corrections, especially to the difference of the intrapair correlation energies. (3) Overlap populations indicate that a small part of the stabilization of **1** stems from steric attraction involving both the σ - and π -type lone pairs of the fluorine atoms.

While this work demonstrates the importance of correlation-corrected methods in calculations on **1** and **2**, it shows at the same time that steric attraction between the F atoms in **1** has been overestimated in recent work on 1,2-difluoroethylene [3,5,7,8]. We shall reconsider the steric attraction hypothesis in a forthcoming investigation. The effects of geometry optimization and rescaling of the basis functions at the RSMP2 level will also be investigated [18].

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References

- [1] H.G. Viehe, *Chem. Ber.* 93 (1960) 1697;
N.C. Craig and E.A. Entemann, *J. Am. Chem. Soc.* 83 (1961) 3047;
N.C. Craig and J. Overend, *J. Chem. Phys.* 51 (1969) 1127.
- [2] R. Hoffmann and R.A. Olofson, *J. Am. Chem. Soc.* 88 (1966) 943.
- [3] N.D. Epiotis, *J. Am. Chem. Soc.* 95 (1973) 3007;
N.D. Epiotis and R.L. Yates, *J. Am. Chem. Soc.* 98 (1976) 461;
N.D. Epiotis, W.W. Cherry, S. Shaik, R. Yates and F. Bernardi, *Topics Current Chem.* 70 (1977) 1.
- [4] D. Cremer, J.S. Binkley, J.A. Pople and W.J. Hehre, *J. Am. Chem. Soc.* 96 (1974) 6900.
- [5] N.D. Epiotis, R.L. Yates, J.R. Larson, C.R. Kirmaier and F. Bernardi, *J. Am. Chem. Soc.* 99 (1977) 8379.
- [6] P. Kollman, *J. Am. Chem. Soc.* 96 (1974) 4363;
R.C. Bingham, *J. Am. Chem. Soc.* 98 (1976) 535.
- [7] A. Skancke and J.E. Boggs, *J. Am. Chem. Soc.* 101 (1979) 4063.
- [8] M.H. Whangbo, D.J. Mitchell and S. Wolfe, *J. Am. Chem. Soc.* 100 (1978) 3698.
- [9] J.S. Binkley and J.A. Pople, *Chem. Phys. Letters* 45 (1977) 197.
- [10] C.C.J. Roothaan, *Rev. Mod. Phys.* 23 (1951) 69;
G.G. Hall, *Proc. Roy. Soc. A*205 (1951) 541.
- [11] C. Møller and M.S. Plesset, *Phys. Rev.* 46 (1934) 618;
J.A. Pople, S. Binkley and R. Seeger, *Intern. J. Quantum Chem.* 10S (1976) 1.
- [12] P.C. Hariharan and J.A. Pople, *Theoret. Chim. Acta* 28 (1973) 213.
- [13] J.A. Pople and J.S. Binkley, *Mol. Phys.* 29 (1975) 599.
- [14] J.A. Pople and M.S. Gordon, *J. Am. Chem. Soc.* 89 (1967) 4253.
- [15] J.L. Carlos Jr., R.R. Karl and S.H. Bauer, *Faraday Trans. II* 70 (1974) 177.
- [16] R.S. Mulliken, *J. Chem. Phys.* 23 (1955) 1833.
- [17] D. Cremer, *J. Chem. Phys.* 69 (1978) 4440.
- [18] D. Cremer, to be published.
- [19] A.C. Hurley, *Advan. Quantum Chem.* 7 (1973) 315.
- [20] D. Cremer, *J. Am. Chem. Soc.*, to be published.
- [21] J.A. Pople, R. Krishnan, H.B. Schlegel and J.S. Binkley, *Intern. J. Quantum Chem.* 14 (1978) 545.
- [22] J. Čížek, *J. Chem. Phys.* 45 (1966) 4256;
J. Paldus, J. Čížek and I. Shavitt, *Phys. Rev. A*5 (1972) 50.