(2) (a) C. W. De Kock and D. A. Van Leirsburg, *J. Am. Chem. Soc.*, **94**, 3235 (1972); (b) D. A. Van Leirsburg and C. W. De Kock, *J. Phys. Chem.*, **78**, 134 (1974).
(3) J. W. Hastie, R. H. Hauge, and J. L. Margrave, *High Temp. Sci.*, **3**, 257 (1971).
(4) G. E. Leroi, G. E. Ewing, and G. Pimentel, *J. Chem. Phys.*, **40**, 2298 (1964).
(5) J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966).
(6) (a) H. M. Gladney and A. Veillard, *Phys. Rev.*, **180**, 385 (1969); (b) B. Roos, A. Veillard, and G. Vinot, *Theor. Chim. Acta*, **20**, 1 (1971).
(7) H. Basch, C. J. Hornback, and J. W. Moskowitz, *J. Chem. Phys.*, **51**, 1311 (1969).
(8) J. D. Petke, J. L. Whitten, and A. W. Douglas, *J. Chem. Phys.*, **51**, 256

(1969).
(9) J. L. Whitten and M. Hackmeyer, *J. Chem. Phys.*, **51**, 5584 (1969).
(10) B. D. Neumann and J. W. Moskowitz, *J. Chem. Phys.*, **50**, 2216 (1969).
(11) R. C. Sahni and B. C. Sawhney, *Trans. Faraday Soc.*, **2**, 64 (1968).
(12) The NiF distance corresponds to values in the perovskite structure (2.007 Å) and the rutile structure, 1.98 and 2.01 Å; 2.007 Å = 3.79 au.
(13) L. Brewer, G. R. Somayajulu, and E. Brackett, *Chem. Rev.*, 111 (1963).
(14) N. S. Hush and M. L. Williams, *J. Mol. Spectrosc.*, **50**, 349 (1974).
(15) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, N.Y., 1955.
(16) S. Besnainou and P. Labarbe, *J. Mol. Struct.*, **2**, 499 (1968).
(17) C. L. Angell and P. C. Schaffer, *J. Phys. Chem.*, **70**, 1413 (1966).
(18) G. Blyholder, *J. Phys. Chem.*, **68**, 35 (1964).

Molecular Orbitals from Group Orbitals. 6. Quantitative Evaluation and Nature of the Stabilizing and Destabilizing Orbital Interactions in Difluoroethylenes and Fluoropropenes

Myung-Hwan Whangbo, David J. Mitchell, and Saul Wolfe*

Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6. Received August 22, 1977

Abstract: Ab initio SCF–MO calculations, with extensive geometry optimization at the STO-3G level, have been performed on the three isomeric difluoroethylenes and on the 1- and 2-fluoropropenes. For the fluoropropenes, this basis set reproduces the principal experimental differences between the isomers, viz., (1) the relative stabilities are 2- > *cis*-1 > *trans*-1; (2) the F–C–CH$_3$ angle in 2-fluoropropene is significantly smaller than 120°; (3) eclipsed conformations (methyl CH eclipsed to C=C) are more stable than staggered conformations; (4) the methyl rotational barrier is lower in *cis*-1-fluoropropene than in *trans*-1-fluoropropene. For the difluoroethylenes, the STO-3G basis set incorrectly predicts the trans isomer to be more stable than the cis; however, the preferred stability of the 1,1 isomer and the small FCF angle in this compound are reproduced correctly. The results have been analyzed in terms of a recently described perturbational molecular orbital procedure which calculates orbital interactions between molecular fragments quantitatively using fragments and fragment orbitals derived from the ab initio wave functions. Two fragmentation modes have been examined: method a, in which XFC$_2$H$_2$ is dissected into XF and C$_2$H$_2$; and method b, in which XFC$_2$H$_2$ is dissected into X and FC$_2$H$_2$. Method a predicts incorrectly that the 1,1-disubstituted alkenes are much less stable than the 1,2 isomers. On the other hand, use of the FC$_2$H$_2$ fragment orbitals of method b leads to an internally consistent description of the stereochemical behavior of all six molecules. Only the π-type fragment orbitals are needed to achieve agreement with the various trends in the total energies. The reason for this is that only these orbitals contribute to the highest occupied molecular orbitals (HOMOs) of the various molecules and, in all cases, the stereochemical behavior of the HOMO parallels that of the total energy. The quantitative results are supplemented by a detailed qualitative description of the nature and origin of the fragment orbitals, the relative magnitudes of the different orbital interactions, and the importance of overlap effects. This discussion includes a set of simple rules, based on second-order perturbation theory, for obtaining the orbitals, and the relative magnitudes of the atomic coefficients in these orbitals, in a general fragment C=C–X.

One of the most useful concepts in stereochemistry is that the geometries of molecules can be rationalized in terms of a minimization of repulsive forces between bonds, between nuclei, and between lone pairs. The valence shell electron pair repulsion model (VSEPR)[1] is a well-known example of the successful application of this concept to geminal effects, i.e., effects associated with bonds, nuclei, and lone pairs grouped about a central atom. Extensions of such thinking, from geminal effects to vicinal effects, can be found in textbooks of organic chemistry and conformational analysis. Thus, the gauche conformation of *n*-butane is said to be less stable than the anti conformation because of "steric repulsion between the methyl groups";[2] alternatively, ". . . the instability of the gauche form of butane may be ascribed entirely to the Me‑·Me interaction".[3]

Empirical force field calculations[4] treat "steric repulsion" explicitly in terms of explicit relations for nonbonded repulsive interaction energies of the van der Waals type. However, to achieve quantitative agreement with experiment, it is also necessary to include, inter alia, London attractive forces in the

description of nonbonded interactions, as can be seen upon inspection of the well-known Hill,[5] Lennard–Jones,[6] and Buckingham potentials[7] which are employed in force field methods.

Thus, the notion that intramolecular *attractive* forces play a significant role in conformational analysis is as firmly established as is the concept of minimization of repulsive forces. Nevertheless, the discovery[8] of conformational effects, associated especially with the presence of lone electron pairs and/or polar bonds, which seem to be at variance with the concept of minimization of repulsive forces, came as a surprise, and this "surprise" has triggered extensive discussion in recent years into the nature and the magnitude of intramolecular attraction. Unfortunately, the force field method cannot yet be applied reliably to this problem, because of a lack of suitable potential functions for nonhydrocarbon molecules,[9] with the result that progress in the *qualitative* understanding of attractive effects has been achieved principally by the application of molecular orbital and, especially, perturbational molecular orbital (PMO)[10] methods.

A result of this work has been the development of important new concepts such as "steric attraction",[11] "overlap repulsion",[12] "lone pair attraction",[13] and "aromaticity"[14] and "antiaromaticity" of acyclic systems. These can be derived by qualitative application of the PMO method, which contains in it a methodology for the description of a specific orbital interaction as "stabilizing" or "destabilizing".

However, there is an arbitrariness associated with qualitative PMO arguments, because it is often possible to rationalize a conformational observation by focusing *either* on those interactions that lead to a maximization of stabilization *or* on those interactions that lead to a minimization of destabilization. Some of the controversy that has become associated with these novel concepts[15] is the result of an insistence by different workers that one or the other type of interaction dominates.

In part 3 of this series,[16] a method was developed for the quantitative PMO analysis of ab initio SCF–MO wave functions. This method permits a quantitative assessment of the contributions of stabilizing and destabilizing π-type orbital interactions to the total energy behavior of a molecule. The purpose of the present paper is to reexamine some currently controversal problems using this quantitative procedure. The systems that have been investigated are the three difluoroethylenes **1, 2,** and **3** and the three fluoropropenes **4, 5,** and **6.** We wish to know (1) whether the quantitative interaction
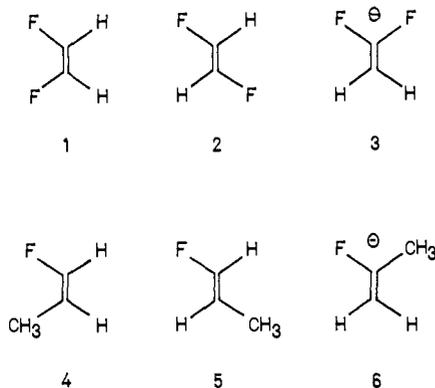
analysis successfully reproduces the observations that the 1,1 isomers are more stable than the 1,2 isomers, that the cis isomers are more stable than the trans isomers, that the valence angle θ in the 1,1 isomers is significantly less than 120°, that eclipsed conformations of **4, 5,** and **6** are more stable than staggered conformations, and that the rotational barrier in the cis isomer **4** is lower than the barrier in the trans isomer **5;**[12] (2) the relative contributions of stabilizing and destabilizing effects to each of these observations; and (3) whether the quantitative results can be conveyed in terms of a simple and uniformly applicable qualitative procedure.

All computations were performed using a locally modified version of Gaussian 70, written for the Burroughs B6700 computer of Queen's University, and the STO-3G basis set. The program for the computation of orbital interactions is implemented by specification of a particular fragmentation mode following the SCF calculation at a particular geometry of interest; the fragment orbitals, and all of the properties of these orbitals required for the computation of orbital interactions, are then provided by the program. The two-orbital two-electron and two-orbital four-electron interaction energies are calculated using eq 1 and 2, respectively, where e_i^0 and e_j^0 are the energies of the fragment orbitals ϕ_i^0 and ϕ_j^0, and $\tilde{S}_{ij}$ and Δ_{ij} are the overlap integral and the interaction matrix element between the fragment orbitals, respectively.[16]

$$\Delta e_{ij} = 2(\Delta_{ij} - e_i^0 \tilde{S}_{ij})^2/(e_i^0 - e_j^0) \qquad (1)$$

$$\Delta e_{ij} = 2\tilde{S}_{ij}\{-2\Delta_{ij} + (e_i^0 + e_j^0)\tilde{S}_{ij}\}/(1 - \tilde{S}_{ij}^2) \qquad (2)$$

Table I. Calculated Total Energies and Geometries of the Difluoroethylenes and Fluoropropenes

Molecule	Geometry	Total energy, au	Rel energy, kcal/mol
1	r_{CC} 1.320 Å; r_{CF} 1.355 Å; ∠CCF 124.17°; ∠CCH 120.58°	-271.985 50	9.58
2	r_{CC} 1.320 Å; r_{CF} 1.354 Å; ∠CCF 123.03°; ∠CCH 121.85°	-271.985 91	9.33
3	r_{CC} 1.316 Å; r_{CF} 1.349 Å; ∠HCH 118.60°; ∠FCF 111.29°	-272.000 77	0.0
4	∠H$_1$CF 114.21°; ∠H$_1$CC 121.59°; ∠FCC 124.20°; ∠H$_2$C$_2$C$_1$ 118.47°; ∠C$_1$C$_2$C 123.54°; ∠H$_2$C$_2$C 117.99°	-213.116 65	1.94
5	∠H$_1$CF 114.22; ∠H$_1$C$_1$C$_2$ 121.52°; ∠FC$_1$C$_2$ 124.26°; ∠H$_2$C$_2$C$_1$ 119.45°; ∠C$_1$C$_2$C 123.41°; ∠H$_2$C$_2$C 117.14°	-213.116 46	2.06
6	∠FC$_1$C$_2$ 121.42°; ∠CC$_1$C$_2$ 124.26°; ∠FC$_1$C 114.32°	-213.119 74	0.0

Results and Discussion

A. Ab Initio SCF–MO Calculations. In part 5 of this series,[17] it was observed that the relative stabilities of isomeric olefins are predicted correctly by the quantitative PMO procedure when the analysis is based upon the optimized or experimental geometries of these isomers. Therefore, in the present work, extensive geometry optimization of the six molecules was performed prior to the initiation of the PMO analyses.

For the difluoroethylenes, the C–H bond lengths were maintained at 1.08 Å, and the C–F and C=C bond lengths and all valence angles were optimized. For the more stable eclipsed conformations of the fluoropropenes, valence angles were optimized using the following additional parameters: C–H (vinyl) = 1.08 Å; C–H (methyl) = 1.09 Å; C=C = 1.34 Å; C–C = 1.52 Å; C–F = 1.33 Å; tetrahedral angles at the methyl group. The methyl rotational barriers in the fluoropropenes were calculated by rigid rotation of the methyl group, using standard geometrical parameters[18] for both the eclipsed minima (methyl CH and C=C eclipsed) and the staggered transition states (methyl CH and C=C staggered). The results of these calculations on **1–3** and on the stable conformations of **4–6** are collected in Table I. The data for the computation of the methyl rotational barriers are shown in Table II.

The optimized FCF valence angle of **3** is 111.3°, in reasonable agreement with the experimental value of 109.3°,[19] and with the 111° value calculated by Kollman.[15a] The optimized FC(CH$_3$) valence angle of **6** is 114.3°, compared to an experimental value of 115.8°.[20]

In each of the fluoropropenes, the eclipsed (E) conformation is more stable than the staggered (S) conformation. The methyl rotational barriers of the cis and trans isomers are calculated

Table II. Calculated Rotational Barriers in the Fluoropropenes[a]

Molecule	Conformation	Total energy, au	Rotational barrier, kcal/mol
4	Staggered	−213.112 55	1.12
	Eclipsed	−213.114 35	
5	Staggered	−213.111 88	1.56
	Eclipsed	−213.114 37	
6[b]	Staggered	−213.116 12	0.87
	Eclipsed	−213.117 50	
6[c]	Staggered	−213.117 75	1.05
	Eclipsed	−213.119 42	
6[d]	Staggered	−213.116 49	1.29
	Eclipsed	−213.118 55	

[a] The following geometrical parameters were employed: $r_{C=C}$ = 1.34 Å; r_{C-C} = 1.52 Å; r_{C-H} = 1.09 Å for the methyl group and 1.08 Å elsewhere; r_{C-F} = 1.33 Å. Except where indicated, valence angles associated with the double bond are 120° and those associated with the methyl group are tetrahedral. [b] θ = 120°. [c] θ = 115°. [d] θ = 110°.

Table III. Orbital Energies (e_i^0) and Gross Populations (Q_i) of the π-Type Fragment Orbitals in 1,1-Difluoroethylene (Method a)

	$\theta = 110°$		$\theta = 120°$	
ϕ_i^0	e_i^0, au	Q_i	e_i^0, au	Q_i
n_+	−0.5155	1.841	−0.5182	1.848
n_-	−0.5110	2.000	−0.5171	2.000
π_{CC}	−0.3992	1.978	−0.3966	1.979
π_{CC}^*	0.2058	0.181	0.2110	0.174

to be 1.12 and 1.56 kcal/mol, respectively. The corresponding experimental barriers are 1.06[21] and 2.20[22] kcal/mol, respectively. Thus the present calculations reproduce the experimental observation that the methyl rotational barrier is lower in the cis isomer than in the trans isomer, as do the previous calculations of Allen[23a] and of Palke.[23b] For the methyl rotational barrier of **6**, the present calculations give 1.05 kcal/mol at θ = 115°, in poor agreement with the experimental value of 2.44 kcal/mol[20] and the barrier calculated by English and Palke[23b] (2.01 kcal/mol).

The 1,1-disubstituted ethylenes are more stable than the 1,2-disubstituted ethylenes, in agreement with experimental findings on such isomers.[24] The cis isomer of 1,2-difluoroethylene is calculated to be 0.25 kcal/mol less stable than the trans isomer, in disagreement with the experimental result (cis more stable by 1.08 kcal/mol[25]), and with a recent very detailed calculation at the 6-311G* level,[26] in which the cis isomer is 0.26 kcal/mol more stable. In the case of the fluoropropenes, the cis isomer is calculated to be 0.12 kcal/mol more stable than the trans; the experimental value is 0.8 kcal/mol in favor of the cis isomer.[27]

B. PMO Analysis. Difluoroethylenes. Two fragmentation modes, illustrated below for **3**, seem appropriate for the difluoroethylenes: method a, in which the fragmentation is F·· ·C=C···F, the procedure employed by Epiotis,[12] and method b, in which the fragmentation is F···C=C-F.
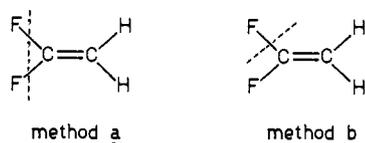
method a   method b

Analysis by Method a. (a) The π-Type Orbital Interactions in 1,1-Difluoroethylene. Tables III and IV summarize the results of the PMO analysis of **3** at θ = 120 and 110°, using method a. The orbital energies e_i^0 and gross populations Q_i of the π-type fragment orbitals[28] are listed in Table III. These

Table IV. Matrix Elements, Interaction Energies, and Overlap Populations between the π-Type Fragment Orbitals in 1,1-Difluoroethylene (Method a)

θ	Interaction $(\phi_i^0-\phi_j^0)$	$\tilde{S}_{ij}$	Δ_{ij}, au	Δe_{ij}, kcal/mol
110°	$(n_+-\pi_{CC})$	0.1360	−0.2135	52.64
	$(n_+-\pi_{CC}^*)$	0.1308	−0.2318	−47.02
120°	$(n_+-\pi_{CC})$	0.1380	−0.2157	53.88
	$(n_+-\pi_{CC}^*)$	0.1283	−0.2273	−44.52
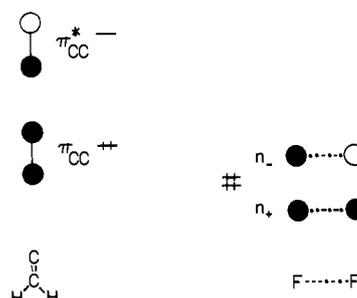
Figure 1. The π-type fragment orbitals of 1,1-difluoroethylene for fragmentation method a. Note: in this and other figures, only projected views of π-type orbitals are displayed.

$n_+-\pi_{CC}$ $n_--\pi_{CC}^*$
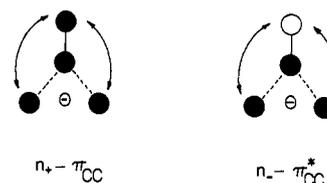
Figure 2. The phase relationships in the $(n_+-\pi_{CC})$ and $(n_+-\pi_{CC}^*)$ interactions of 1,1-difluoroethylene. Primary overlap is shown by a dotted line; secondary overlap is shown by double headed arrows.

are the only fragment orbitals that contribute to the HOMO of the molecule, and they are shown schematically in Figure 1.

Computation of the orbital interaction energies Δe_{ij} was performed using eq 1 and 2. The results are presented in Table IV. As the FCF valence angle θ decreases from 120 to 110°, the four-electron destabilizing (repulsive) interaction $(n_+-\pi_{CC})$ *decreases*, by 1.24 kcal/mol, and the two-electron stabilizing (attractive) interaction $(n_+-\pi_{CC}^*)$ increases, by 2.50 kcal/mol. In terms of these interactions, the 110° structure is more stable by a total of 3.74 kcal/mol, because it both maximizes the stabilizing interactions and minimizes the destabilizing interactions. The corresponding difference in the total energies of the two structures is 2.89 kcal/mol.

The fact that the destabilizing $(n_+-\pi_{CC})$ interaction is *smaller* at the smaller FCF angle is, perhaps, surprising. However, a qualitative rationalization of this finding can be offered, in terms of the phase relationships between the fragment orbitals, as shown in Figure 2. In the $(n_+-\pi_{CC})$ interaction, the (secondary) overlap and, therefore, the destabilizing interaction between n_+ and π_{CC} *decrease* as θ decreases. In the $(n_+-\pi_{CC}^*)$ interaction, the (secondary) overlap and, therefore, the stabilizing interaction between n_+ and π_{CC}^* *increase* as θ decreases. A possible conceptual problem arises at this point, since one might reasonably ask why a repulsive F···F interaction, greater at 110° than at 120°, can be ignored. The reason for this is that method a treats F···F as a unit (group), and only interactions *between* the F···F and vinyl groups are meaningful in the PMO analysis. Furthermore, although both n_+ and n_- are destabilized slightly as θ is decreased, π_{CC} and π_{CC}^* are both

Table V. Orbital Energies (e_i^0) and Gross Populations (Q_i^0) of the Fragment Orbitals of 1,1-Difluoroethylene That Exhibit σ-Type Interactions (Method a; $\theta = 110°$)

ϕ_i^0	e_i^0, au	Q_i	ϕ_i^0	e_i^0, au	Q_i
n_π	−0.5461	1.871	σ	−0.5728	1.703
n_π^*	−0.5090	1.932	σ*	0.8876	0.022
n_σ	−0.4815	1.384	π_1	−0.6217	1.664
n_σ^*	−0.4040	1.488	π_2	−0.4179	1.031
			π_3	0.7851	0.001

Table VI. Orbital Energies (e_i^0) and Gross Populations (Q_i) of the π-Type Fragment Orbitals (ϕ_i^0) of the *cis-* and *trans-*Difluoroethylenes (Method a)[a]

ϕ_i^0	Cis		Trans	
	e_i^0, au	Q_i	e_i^0, au	Q_i
n_+	−0.4952	2.000	−0.4984	2.000
n_-	−0.4874	1.865	−0.4934	1.868
π	−0.3998	2.000	−0.3994	2.000
π^*	0.2185	0.135	0.2197	0.132

[a] Optimized geometries.

Table VII. Orbital Interactions (Δe_{ij}) between the π-Type Fragment Orbitals of the *cis-* and *trans-*Difluoroethylenes (Method a)[a]

Interaction	Δe_{ij}, kcal/mol	
	Cis	Trans
$n_+-\pi$	38.46	38.82
$n_--\pi^*$	−47.41	−46.48

[a] Optimized geometries.

Figure 3. The fragment orbitals of 1,1-difluoroethylene which engage in σ-type interactions, when fragmentation method a is employed.

Figure 4. The π-type fragment orbitals of the *cis-* and *trans-*1,2-difluoroethylenes for fragmentation method a: (a) cis; (b) trans.

stabilized (see Table III). Finally, calculations on F_2 at bond lengths corresponding to the F···F distances in the 120 (2.304 Å) and 110° (2.179 Å) structures of 1,1-difluoroethylene indicate negligible repulsion between the π-type atomic orbitals in both cases.

(b) The σ-Type Orbital Interactions in 1,1-Difluoroethylene. As stated above, σ-type orbital interactions make no contribution to the HOMO of the molecule. Table V lists the orbital energies e_i^0 and the gross populations Q_i of the fragment orbitals that engage in such interactions. These orbitals are shown schematically in Figure 3. The computations reveal that each of the F···F lone pair orbitals is the result of an appropriate combination of fluorine $2p_x$ and $2p_z$ atomic orbitals.

Inspection of the gross populations Q_i shown in Table V reveals that a quantitative treatment of the σ-type orbital interactions is not possible. Except for n_π^* and, to a lesser extent, n_π, none of the occupied orbitals has a population close to 2, so that computations of interaction energies using eq 1 and 2 would be inappropriate.[29] This is observed generally in the case of occupied σ-type fragment orbitals. Furthermore, if one were to assume double occupancies for n_σ, n_σ^*, n_π, and n_π^*, then, after counting n_+, n_- and the double occupancies of the 1s and 2s orbitals on each of the fluorines, F···F would be found to be an assembly of two *fluoride anions!* To achieve electroneutrality in the combined system, the C=CH₂ fragment would have to be regarded as a dication. This is unrealistic.

(c) The π-Type Orbital Interactions in *cis-* and *trans-*1,2-Difluoroethylene. Tables VI and VII summarize the results of the PMO analyses of 1 and 2 using method a. The π-type fragment orbitals appropriate to these molecules are shown schematically in Figures 4a and 4b, respectively. According to the quantitative data of Table VI, the gap between n_+ and n_- is larger in the cis isomer, as expected from the greater overlap in this isomer between the atomic orbitals that produce
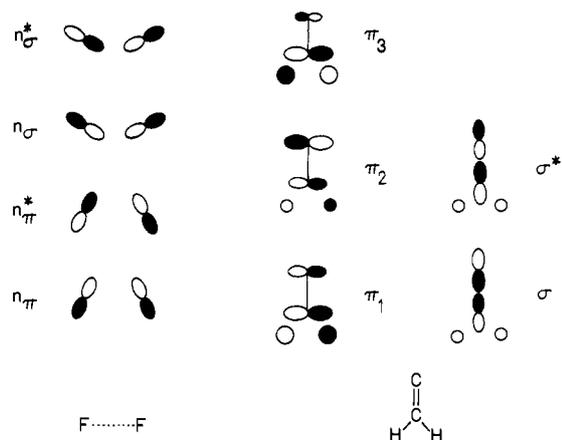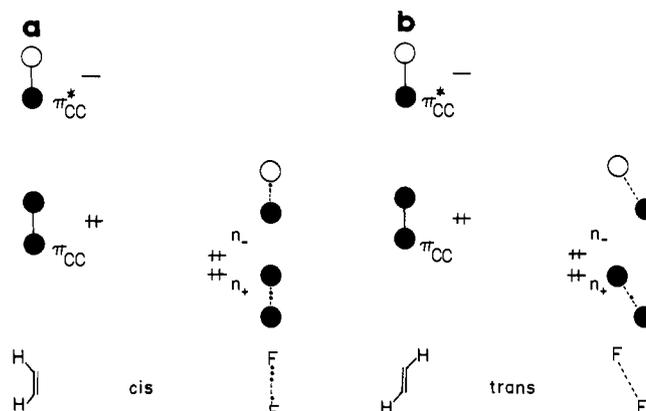
n_+ and n_-. In contrast to the 2-butenes,[17] where the use of optimized geometries leads to a significant difference in the energies of the π_{CC} orbitals of the vinyl fragments of the two isomers, in the present case the π and π^* levels are virtually the same in the two compounds.

The Δe_{ij} values presented in Table VII have been calculated with an assignment of electron occupancies of 2 for n_+, n_-, and π_{CC}, and 0 for π_{CC}^*. The sum of the π-type orbital interactions ($\Sigma \Delta e_{ij}$) is −8.95 and −7.65 kcal/mol in 1 and 2, respectively. Thus, in terms of the π-type interactions, the cis isomer is predicted to be 1.30 kcal/mol more stable than the trans. The corresponding total of the π-type orbital interactions in 1,1-difluoroethylene is +5.62 kcal/mole at $\theta = 110°$.

In terms of method a, the relative stabilities of the three difluoroethylenes should, therefore, be **1 > 2 ≫ 3**. *These predicted relative stabilities are completely incorrect,* because the relative stabilities associated with the calculated total energies are **3 > 2 > 1.** On the basis of these quantitative data, it must be concluded that method a is deficient. This fragmentation method is also cumbersome for qualitative discussion, because the 1,1 and 1,2 isomers have to be discussed separately. This difficulty is removed in fragmentation method b.

Analysis by Method b. (a) The Nature of the C=C-F Group Orbitals. Tables VIII and IX summarize the results of the quantitative analyses of the difluoroethylenes based on fragmentation method b. The π-type fragment orbitals appropriate to this mode of fragmentation are depicted in Figure 5. In each case, the different sizes (weights) of the orbitals reflect the different contributions of the atomic orbitals to the group orbitals. Since an understanding of the reason for the different

Table VIII. Orbital Energies (e_i^0) and Gross Populations (Q_i) of the π-Type Fragment Orbitals (ϕ_i^0) of the Difluoroethylenes (Method b)

ϕ_i^0	Cis[a]		Trans[a]		1,1[a]		1,1[b]	
	e_i^0, au	Q_i	e_i^0, au	Q_i	e_i^0, au	Q_i	e_i^0, au	Q_i
π_α	-0.5504	2.000	-0.5532	2.000	-0.5727	1.999	-0.5819	1.999
π_β	-0.3450	1.996	-0.3454	1.996	-0.3414	1.997	-0.3304	1.996
π_γ	0.2662	0.072	0.2666	0.071	0.2645	0.076	0.2577	0.081
n	-0.4911	1.932	-0.4947	1.933	-0.5095	1.928	-0.5176	1.924

[a] Optimized geometry. [b] Standard geometrical parameters at $\theta = 120°$.
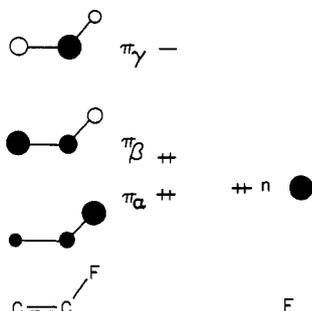
Figure 5. The π-type fragment orbitals of the difluoroethylenes.

magnitudes of the atomic orbital coefficients of each C=C-F π-type orbital is important to the qualitative discussion which follows later, we examine in some detail how these C=C-F orbitals originate from the π and π^* orbitals of the vinyl group and the p orbital of the fluorine atom.

The qualitative orderings of π, π^*, and p are shown in Figure 6; in this figure, the phases of the orbitals are drawn so as to give positive overlap between π and p, and between π^* and p. The first order mixing of p with π and π^* affords an in-phase combination π_+, an out-of-phase combination π_-, and an out-of-phase combination π_-^*. In this simple first-order treatment, the lowest lying C=C-F group orbital should be the same as π_+. It is the mixing-in of both π and π^* that leads to the greater weighting on C1 than on C2 in π_α. The C=C-F orbitals designated π_β and π_γ correspond respectively to π_- and π_-^*, in which C1 and C2 have the same weights. Thus the first order analysis leads to correct C1, C2, and F weightings in π_α but incorrect weightings on C1 and C2 in π_β and π_γ. The reason is that π and π^* actually mix into π_-^* and π_-, respectively, but cannot do this in first order because these orbitals are orthogonal. The mixing takes place via p, and *this is a second-order effect*. To derive the correct weightings on C1 and C2 in the C=C-F orbitals, it is therefore necessary to take these second-order effects into account.

This problem has been recognized previously by Libit and Hoffmann,[30] and the discussion which now follows is largely derived from the one given by these workers, but in terms of the SCF–MO formalism of part 3 of this series. From our analysis, the ratio $K = \Delta_{ij}/S_{ij}$ is found to be nearly constant for all of the π-type orbital interactions of **1**, **2**, and **3**. In the present case, $K \simeq -1.6$ au.[31] When the overlap integral S_{ij} between the two orbitals i and j is chosen to be positive,

$$(\Delta_{ij} - e_i^0 S_{ij}) \simeq (K - e_i^0)S_{ij} < 0 \tag{3}$$

because the magnitudes of the orbital energies e_i^0 under consideration are smaller than $|K|$.[32]

After interaction with p and π^*, π is modified to

$$\pi_\beta \simeq \pi + \lambda p + \gamma \pi^* \tag{4}$$

By using eq 3 and the orbital energy sequence of Figure 6, the sign of the first-order mixing coefficient λ is given by

$$\lambda = \frac{(\Delta_{\pi p} - e_\pi^0 S_{\pi p})}{(e_n^0 - e_p^0)} = \frac{(-)}{(+)} < 0$$

Table IX. Orbital Interactions between the π-Type Fragment Orbitals of the Difluoroethylenes (Method b)

Interaction	Δe_{ij}, kcal/mol			
	Cis[a]	Trans[a]	1,1[a]	1,1[b]
n–π_α	1.86	1.73	7.52	7.70
n–π_β	20.58	20.96	13.94	16.48
n–π_γ	-20.09	-19.78	-22.07	-23.18

[a] Optimized geometry. [b] Standard geometrical parameters at $\theta = 120°$.

The sign of the second-order mixing coefficient γ is

$$\gamma = \frac{(\Delta_{\pi^* p} - e_\pi^0 S_{\pi^* p})(\Delta_{p\pi} - e_\pi^0 S_{p\pi})}{(e_\pi^0 - e_{\pi^*}^0)(e_\pi^0 - e_p^0)} = \frac{(-)(-)}{(-)(+)} < 0$$

Therefore eq 4 may be graphically represented as follows
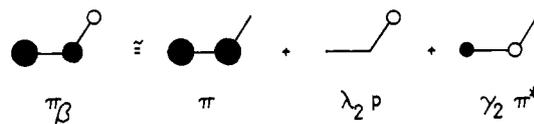
After interaction with p and π, π^* is modified to

$$\pi_\gamma \simeq \pi^* + \lambda' p + \gamma' \pi \tag{5}$$

where

$$\lambda' = \frac{(\Delta_{\pi^* p} - e_{\pi^*}^0 S_{\pi^* p})}{(e_{\pi^*}^0 - e_p^0)} = \frac{(-)}{(+)} < 0$$

and

$$\gamma' = \frac{(\Delta_{\pi p} - e_{\pi^*}^0 S_{\pi p})(\Delta_{p\pi^*} - e_{\pi^*}^0 S_{p\pi^*})}{(e_{\pi^*}^0 - e_\pi^0)(e_{\pi^*}^0 - e_p^0)} = \frac{(-)(-)}{(+)(+)} > 0$$

Thus eq 5 can be represented as follows
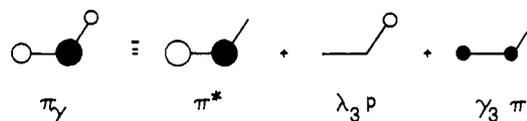
The second-order mixing discussed above refers to the interaction which can occur between orbitals of the same fragment via an orbital of another fragment. For the general case of a molecular system A–B, in which fragment A has two orbitals, ϕ_u^A and ϕ_l^A, where the subscripts u and l mean upper and lower, respectively, and fragment B has only one orbital, ϕ^B, three kinds of situations can be envisaged. These are depicted in Figure 7 as case A, case B, and case C. Case A is the one already discussed in detail. Analogous arguments can be employed to deduce the signs of the second-order mixing effects in cases B and C; these are summarized in Table X. To obtain these results, it is necessary to choose the phases of ϕ_u^A, ϕ_l^A, and ϕ^B in such a way as to create positive overlap between ϕ_u^A and ϕ^B, and between ϕ_l^A and ϕ^B.

(b) Details of the Analysis. The gross orbital populations listed in Table VIII reveal that, in each molecule, π_α, π_β, and n are doubly occupied, and π_γ is unoccupied prior to orbital interaction. The orbital interaction energies e_i^0 of Table VIII
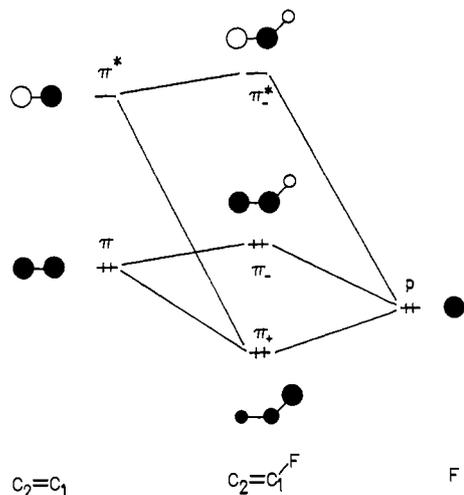
Figure 6. The qualitative orderings of π_{CC}, π_{CC}^*, and p_F of a C=C-F fragment, and the result of the first-order interaction of p with π and π^*, leading to the three C=C-F fragment orbitals π_+, π_-, and π_-^*.

Table X. Manner in Which the Upper and Lower Orbitals ϕ_u^A and ϕ_l^A Mix into Each Other for the General System A-B, in Which Fragment A Has Two Orbitals and Fragment B Has One Orbital

Mixing	Case A	Case B	Case C
ϕ_u^A into ϕ_l^A	−	+	+
ϕ_l^A into ϕ_u^A	+	+	−

indicate the degree of transferability of these fragment orbitals from molecule to molecule.

Summation ($\Sigma\Delta e_{ij}$) of the various orbital interaction energies collected in Table IX shows that the 110° geometry of **3** is 1.61 kcal/mol more stable than the 120° geometry. The corresponding difference in the total energies is 2.89 kcal/mol. The comparison of **1**, **2**, and **3** ($\theta = 110°$) in terms of $\Sigma\Delta e_{ij}$ indicates that the relative stabilities are **3** (−0.61) ≫ **1** (2.35) > **2** (2.92 kcal/mol). These are now in agreement with the SCF-MO result that 1,1-difluoroethylene is significantly more stable than either 1,2 isomer. The PMO procedure predicts that **1** is more stable than **2** by 0.57 kcal/mol, vs. a total energy difference of 0.55 in the opposite direction.

These quantitative findings can be expressed qualitatively in terms of overlap effects (Figure 8). The destabilizing (n-π_α) interaction is greater in **1** than in **2**, because the secondary overlap between the fluorines is larger in **1**. Further, since the primary overlap in **1** and **2** is less than that in **3** (because C2 has a smaller weight than C1 in π_α), the destabilization caused by the (n-π_α) interaction will be less in **1** and **2**.

In the destabilizing (n-π_β) interaction, both the primary and the secondary overlap is smallest in **3** and, in this latter molecule, the secondary overlap between n and π_β is smaller at 110° than at 120°. The qualitative stability relationship that results is **3** (110°) > **3** (120°) > **1** > **2**.

In the stabilizing (n-π_γ) interaction, both the primary and the secondary overlap are largest in **3**, and are larger at $\theta = 110°$ than at $\theta = 120°$. The qualitative stability relationship that results is **3** (110°) > **3** (120°) > **1** > **2**.

The relative stabilities given by the three types of interactions of method b are summarized in Table XI. The frontier interactions (n-π_β) and (n-π_γ) correlate with the trend in the total π-type orbital interactions, $\Sigma\Delta e_{ij}$. The (n-π_α) interaction does not. Taking this interaction into account therefore reduces the energy difference between the 1,1 and 1,2 isomers and also the energy difference between the cis and trans isomers; in the latter case, the effect of (n-π_α) is not sufficient to cause the PMO analysis to reproduce the greater stability of the trans

(a) (b) (c)
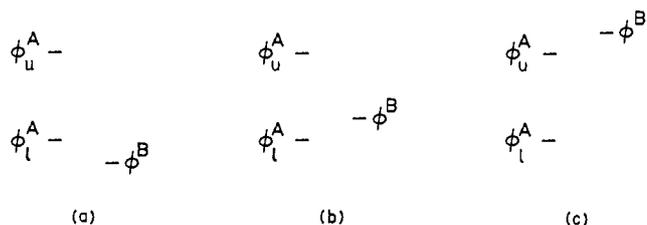
Figure 7. The relative positions of the upper and lower orbitals (ϕ_u^A and ϕ_l^A) of a fragment A and the orbital of a fragment B (ϕ^B). Case A, ϕ^B lies below ϕ_l^A; case B, ϕ^B lies between ϕ_l^A and ϕ_u^A; case C, ϕ^B lies above ϕ_u^A.

n − π_α

n − π_β

n − π_γ
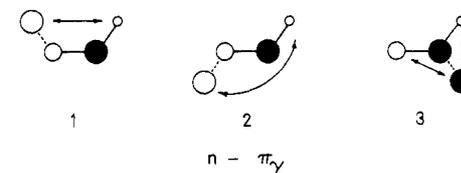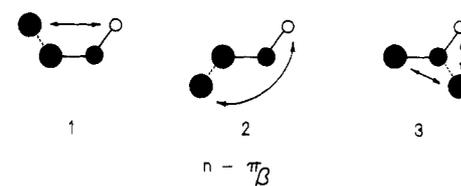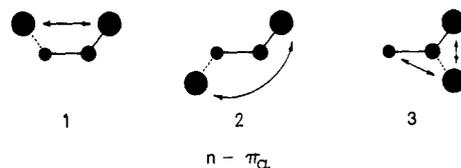
Figure 8. The phase relationships in the (n-π_α), (n-π_β), and (n-π_γ) interactions in the difluoroethylenes. Primary overlap is shown by dotted lines; secondary overlap is shown by double-headed arrows.

Table XI. Relative Stabilities of the Difluoroethylenes Associated With the n-π_α, n-π_β, and n-π_γ Orbital Interactions of Method b

Interaction	Rel stability
n-π_α	Trans > cis ≫ 1,1
n-π_β	1,1 > cis > trans
n-π_γ	1,1 > cis > trans

isomer found in the SCF-MO calculations (Table I).

The important points, however, are firstly, that the difluoroethylenes can be discussed qualitatively by focusing either on the destabilizing frontier interactions *or* on the stabilizing interactions; and, secondly, that the relative contributions of the two *cannot* be assessed by such qualitative arguments. The qualitative approach should therefore be quite useful to demonstrate that the 1,1 isomer is more stable than either 1,2 isomer, and that the cis compound should be more stable than the trans. This should be a sufficient and satisfying objective of the PMO method. Attempts to go beyond this can be dangerous, in the absence of quantitative data.

In his original discussion of the problem, Epiotis[13] emphasized two-orbital two-electron π-type and σ-type interactions associated with method a, and concluded that both kinds of interactions tend to stabilize *cis*-1,2-dihaloethylenes, but only the σ-type interactions are stabilizing in 1,1-dihaloethylenes.

Table XII. The Orbital Energies (e_i^0) and Gross Populations (Q_i) of the π-Type Fragment Orbitals of the Fluoropropenes

Conformation	Orbital	**4** e_{i}^{0}, au	**4** Q_i	**5** e_{i}^{0}, au	**5** Q_i	**6**[a] e_{i}^{0}, au	**6**[a] Q_i	**6**[b] e_{i}^{0}, au	**6**[b] Q_i
Eclipsed	π_α	−0.5446	2.000	−0.5441	2.000	−0.5484	1.999	−0.5464	1.999
	π_β	−0.3030	1.990	−0.3031	1.990	−0.2978	1.992	−0.2985	1.992
	π_γ	0.3043	0.017	0.3043	0.017	0.3063	0.017	0.3052	0.018
	π	−0.5295	1.983	−0.5329	1.984	−0.5426	1.983	−0.5423	1.983
	π^*	0.6957	0.010	0.6922	0.010	0.6826	0.009	0.6834	0.008
Staggered[c]	π_α	−0.5450	2.000	−0.5434	2.000	−0.5481	1.998	−0.5474	1.998
	π_β	−0.3009	1.991	−0.3010	1.991	−0.2976	1.995	−0.2988	1.995
	π_γ	0 3058	0.016	0.3060	0.015	0.3071	0.017	0.3061	0.017
	π	−0.5275	1.984	−0.5322	1.986	−0.5431	1.984	−0.5418	1.984
	π^*	0.6987	0.009	0.6943	0.008	0.6833	0.006	0.6844	0.006

[a] $\theta = 120°$. [b] Optimized geometry. [c] Standard geometrical parameters.

Table XIII. Interaction Energies between the π-Type Fragment Orbitals in theEclipsed and Staggered Conformations of the Fluoropropenes

Molecule	Interaction	Interaction energy, kcal/mol Eclipsed	Staggered	Eclipsed[a]	Staggered[a]
	$\pi-\pi_\alpha$	1.09	1.74		
	$\pi-\pi_\beta$	14.90	15.18		
4	$\pi-\pi_\gamma$	−2.86	−2.76		
	$\pi_\alpha-\pi^*$	−0.10	−0.02		
	$\pi_\beta-\pi^*$	−2.11	−2.00		
	$\Sigma\Delta e_{ij}$	10.92	12.14		
	$\pi-\pi_\alpha$	0.97	1.16		
	$\pi-\pi_\beta$	15.19	16.16		
5	$\pi-\pi_\gamma$	−2.76	−2.48		
	$\pi_\alpha-\pi^*$	−0.08	−0.06		
	$\pi_\beta-\pi^*$	−2.20	−1.80		
	$\Sigma\Delta e_{ij}$	11.11	12.98		
	$\pi-\pi_\alpha$	5.58	5.10	5.16	4.88
	$\pi-\pi_\beta$	9.37	10.70	10.10	11.26
6	$\pi-\pi_\gamma$	−2.99	−2.86	−2.94	−2.78
	$\pi_\alpha-\pi^*$	−0.21	−0.34	−0.20	−0.30
	$\pi_\beta-\pi^*$	−1.73	−1.04	−1.88	−1.12
	$\Sigma\Delta e_{ij}$	10.03	11.56	10.24	11.94

[a] Computed at $\theta = 120°$.

The contribution of σ-type stabilization has since been shown to be small;[15a] also, on the basis of the present work, these interactions cannot be assessed unambiguously.

More recently, Epiotis and Yates[12] have presented a more complete account of the *cis*- and *trans*-1,2-difluoroethylenes which properly emphasizes "a conspiracy of orbital interactions which maximize the stabilization and minimize the overlap destabilization of the cis relative to the trans isomer". This conclusion is more appropriate than the interpretation offered by Bingham,[15b] who focuses solely on the repulsive interactions in the two isomers.

Fluoropropenes. Three fragmentation methods can be considered for the PMO analysis of the fluoropropenes, as shown below for **6**. Methods c and d correspond to method b, and method e corresponds to method a. Since d is based upon the C=C-F group orbitals already discussed in detail, this method was used for all of the fluoropropenes **4**, **5**, and **6**.
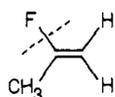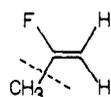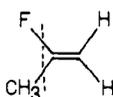
method c   method d   method e

The interactions to be considered are those between π_α, π_β, and π_γ of the C=C-F fragment, and the π and π^* methyl group orbitals shown in Figure 9. Tables XII and XIII sum-

marize the quantitative results. A comparison of the orbital energies of π_α, π_β, and π_γ listed in Tables VIII and XII reveals that these are higher lying in the fluoropropenes than in the difluoroethylenes.

The gross populations of Table XII show that, prior to orbital interaction, π_α, π_β, and π are doubly occupied, and π_γ and π^* are unoccupied. Computation of orbital interaction energies is, therefore, justified.

The total orbital interaction energies $\Sigma\Delta e_{ij}$ in the E conformations of **4**, **5**, and **6** ($\theta = 114.3°$) are +10.92, +11.11, and +10.03 kcal/mol, respectively. Thus, 2-fluoropropene is predicted to be more stable than either *cis*- or *trans*-1-fluoropropene, and the cis isomer is predicted to be more stable than the trans, in agreement with the SCF-MO computations.

The most appropriate qualitative representation of these results is shown in Figure 10, which emphasizes the frontier orbital interactions ($\pi-\pi_\beta$), ($\pi-\pi_\gamma$), and ($\pi_\beta-\pi^*$). In the destabilizing ($\pi-\pi_\beta$) interaction, both the primary and the secondary overlap between π and π_β are smallest in **6**. In the stabilizing ($\pi-\pi_\gamma$) interaction, the primary overlap between π and π_γ is largest in **6**, but secondary overlap is larger in **4** and **5**. In the ($\pi_\beta-\pi^*$) interaction, the primary overlap is greater in **4** and **5**, and the secondary overlap is greater in **6**.

As seen in Table XIII, the opposing primary and secondary overlap effects in ($\pi-\pi_\gamma$) and ($\pi_\beta-\pi^*$) cause the differences between these interactions in the different molecules to be
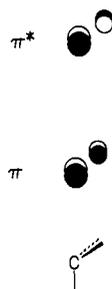
Figure 9. The π and π^* methyl group orbitals.

small, so that the destabilizing $(\pi-\pi_\beta)$ interaction is now the dominant factor that determines the relative stabilities of **4, 5,** and **6.** Bingham's generalizations[15b] would, therefore, be applicable to these molecules.

Turning to the methyl rotational barriers of **4, 5,** and **6,** the $\Sigma\Delta e_{ij}$ values of Table XIII predict the E conformations of **4, 5,** and **6** ($\theta = 114.3°$) to be more stable than the corresponding S conformations by 1.22, 1.87, and 1.53 kcal/mol, respectively. These numbers can be compared to the corresponding barriers obtained in the SCF–MO total energies, viz., 1.13, 1.56, and 1.06 kcal/mol. Thus, as found in part 3 of this series,[16] methyl rotational barriers are reproduced extremely well by the quantitative treatment of π-type orbital interactions.

Epiotis and Yates have argued[12] that the lower methyl rotational barrier in *cis*-1-fluoropropene as compared to *trans*-1-fluoropropene results mainly from a preferential stabilization of the transition state (the S conformation) in this molecule, and that this stabilization can be regarded as a consequence of Hückel "aromaticity". The present SCF–MO calculations indicate that the difference in the two rotational barriers is indeed caused by the difference in the energies of the two staggered conformations (see Table II). The lower energy E conformation of the cis isomer is more stable than that of the trans by 0.19 kcal/mol, and the higher energy S conformation of the cis isomer is more stable than that of the trans by 0.84 kcal/mol (leading to the 0.65 kcal/mol difference in the barriers); however, the stabilizing and destabilizing interactions contribute significantly to both differences.

It is important to note that the present quantitative PMO results lead to a fundamentally different interpretation from the one proposed by Epiotis and Yates. In their qualitative analysis, a consideration of the π-type interactions leads to the prediction that the S conformation of the cis isomer is more stable than the E conformation (because of the existence of π aromaticity in the former structure). They then argue that σ-type interactions favor the E conformation, and are dominant. The net conformational preference in favor of E is the result of this dominance of σ effects.

We believe that attempts to invoke σ effects introduce unnecessary ambiguity into the procedure, because, for this system, the π-type interactions already appear to contain the desired information. For example, in the present quantitative analysis, *a consideration of the π-type interactions is sufficient for the rationalization of the E conformational preference of cis-1-fluoropropene.* This result is not in agreement with the proposed concept of aromaticity. Such a concept may therefore be a useful heuristic device in some cases but, on the basis of the present data, no theoretical significance should be attached to it.

The conclusion just reached is based upon the quantitative analysis of the *cis-* and *trans-*1-fluoropropenes in terms of fragmentation method d. Since the work of Epiotis and Yates was based upon fragmentation method e, a quantitative computation of the π-type orbital interactions associated with method e was performed for the E and S conformations of *cis-*1-fluoropropene. In terms of the total π-type orbital in-
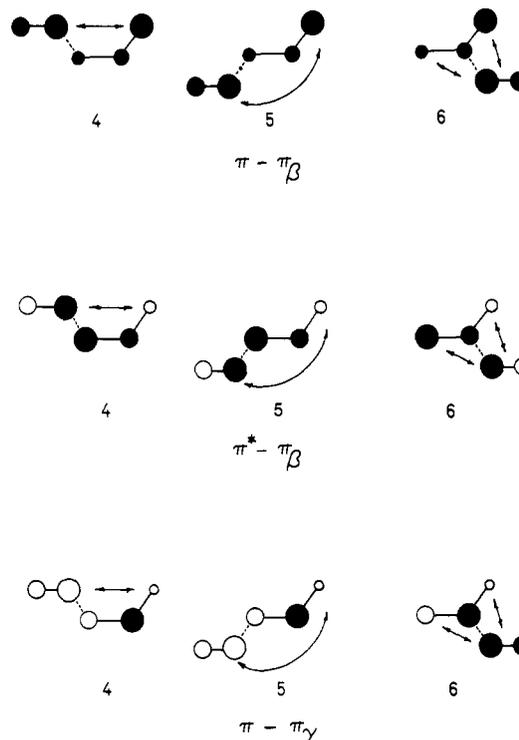
Figure 10. The phase relationships in the $(\pi-\pi_\beta)$, $(\pi-\pi_\gamma)$, and $(\pi_\beta-\pi^*)$ interactions in the fluoropropenes. Primary overlap is shown by dotted lines; secondary overlap is shown by double-headed arrows.

teraction energies, $\Sigma\Delta e_{ij}$, the "nonaromatic" E conformation was again found to be more stable, by 0.76 kcal/mol.

Concluding Remarks

The results of the present work can be summarized as follows: (1) a one-bond fragmentation of 1,1- and 1,2-disubstituted ethylenes into X and C=C-Y leads to a uniformly applicable qualitative PMO analysis, which can be supported by quantitative calculations of orbital interaction energies; (2) this qualitative analysis emphasizes primary and secondary overlap between X and C=C-Y; (3) the group orbitals of C=C-Y can be derived by simple qualitative arguments; (4) the various differences, between the 1,1- and 1,2-disubstituted molecules, between cis and trans isomers, and between eclipsed and staggered conformations are caused by a *combination* of stabilizing and destabilizing factors.

References and Notes

(1) R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963); **47**, 18 (1970).
(2) R. T. Morrison and R. N. Boyd, "Organic Chemistry", 3rd ed, Allyn and Bacon, Boston, Mass., 1973, p 78.
(3) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Interscience, New York, N.Y., 1965, p 13.
(4) For leading references, see J. E. Williams, P. J. Stang, and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.*, **19**, 531 (1968); C. Altona and D. H. Faber, *Top. Curr. Chem.*, **45**, 1 (1974); N. L. Allinger, *Adv. Phys. Org. Chem.*, **13**, 1 (1976).
(5) T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948).
(6) J. E. Lennard-Jones, *Proc. Phys. Soc., London*, **43**, 461 (1931).
(7) R. A. Buckingham, *Proc. R. Soc. London, Ser. A*, **168**, 264 (1938).
(8) S. Wolfe, *Acc. Chem. Res.*, **5**, 102 (1972).
(9) For recent progress in this area, and an indication of the problems involved, see N. L. Allinger and D. Y. Chung, *J. Am. Chem. Soc.*, **98**, 6798 (1976); A. Abe, *ibid.*, **98**, 6477 (1976).
(10) See, inter alia, W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals", Academic Press, New York, N.Y., 1973; R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971); B. M. Gimarc, *ibid.*, **7**, 384 (1974); S. David, O. Eisenstein, W. J. Hehre, L. Salem, and R. Hoffmann, *J. Am. Chem. Soc.*, **95**, 3806 (1973).
(11) R. Hoffmann, C. C. Levin, and R. A. Moss, *J. Am. Chem. Soc.*, **95**, 629

(1973).
(12) N. D. Epiotis and R. L. Yates, *J. Am. Chem. Soc.*, **98**, 461 (1976).
(13) N. D. Epiotis, *J. Am. Chem. Soc.*, **95**, 3087 (1973).
(14) D. Cremer, J. S. Binkley, and J. A. Pople, *J. Am. Chem. Soc.*, **96**, 6900 (1974).
(15) (a) P. A. Kollman, *J. Am. Chem. Soc.*, **96**, 4363 (1974); (b) R. C. Bingham, *ibid.*, **98**, 535 (1976).
(16) M.-H. Whangbo, H. B. Schlegel, and S. Wolfe, *J. Am. Chem. Soc.*, **99**, 1296 (1977).
(17) S. Wolfe, D. J. Mitchell, and M.-H. Whangbo, *J. Am. Chem. Soc.*, **100**, 1936 (1978).
(18) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).
(19) W. Edgell, P. A. Kinsey, and J. W. Amy, *J. Am. Chem. Soc.*, **79**, 269 (1957).
(20) L. Pierce and J. M. O'Reilly, *J. Mol. Struct.*, **3**, 536 (1959).
(21) R. A. Baudet and E. B. Wilson, Jr., *J. Chem. Phys.*, **37**, 1133 (1962).
(22) S. Siegel, *J. Chem. Phys.*, **27**, 989 (1957).
(23) (a) E. Scarzafava and L. C. Allen, *J. Am. Chem. Soc.*, **93**, 311 (1971); (b) A. D. English and W. E. Palke, *ibid.*, **95**, 8536 (1973).
(24) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970.
(25) N. C. Craig and J. Overend, *J. Chem. Phys.*, **51**, 1127 (1969).
(26) J. S. Binkley and J. A. Pople, *Chem. Phys. Lett.*, **45**, 197 (1977).
(27) Z. B. Alfassi, D. M. Golden, and S. W. Benson, *J. Chem. Thermodyn.*, **5**, 411 (1973).

(28) The gross populations shown in Table III indicate that, prior to orbital interaction, the π_{CC}, n_+, and n_- orbitals are doubly occupied, and the π^*_{CC} orbital is unoccupied. The calculation of orbital interaction energies with eq 1 and 2 is, therefore, meaningful.
(29) The n_π^* orbital interacts with π_1 and π_2; however, gross populations of these latter two orbitals deviate markedly from 2. On the other hand, a two-electron stabilizing interaction of the type (n_π–π^*) can be calculated, and is found to be −8.01 kcal/mol at θ = 120° and −7.05 kcal/mol at 110°. Since the magnitude of this attractive interaction is *smaller* at 110° than 120°, it cannot account for the observed relative stabilization of the 110° structure. The relative unimportance of a F···F attractive interaction also follows from the negative overlap populations between the two fluorine atoms (−0.0058 at 120° and −0.0104 at 110°) in the population analysis based upon atomic orbitals. This is consistent with the observations that the gross population of n_- is greater than that of n_+, that of n_σ^* is greater than that of n_σ, and that of n_π^* is greater than that of n_π.
(30) L. Libit and R. Hoffmann, *J. Am. Chem. Soc.*, **96**, 1370 (1974).
(31) Examination of quantitative PMO data on many systems reveals that Δ_{ij}/S_{ij} is always approximately constant for the various isomers of a given molecular system. The proportionality constant K varies with the system, but its magnitude is always greater than unity.
(32) There are some unusual bonding situations in which $(\Delta_{ij} - e_i^0 S_{ij}) > 0$, even when $S_{ij} > 0$. For details, see (a) M.-H. Whangbo and R. Hoffmann, *J. Chem. Phys.*, in press; (b) J. H. Ammeter, H.-B. Bürgi, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, submitted for publication.

Formation and Disappearance of Free Radicals, and the Micellar Equilibrium in the Detergent Sodium 4-(6'-Dodecyl)benzenesulfonate

A. Henglein* and Th. Proske

Contribution from the Hahn-Meitner-Institute für Kernforschung Berlin GmbH, Bereich Strahlenchemie, D-1000 Berlin 39, West Germany. Received October 3, 1977

Abstract: Aqueous N_2O-saturated solutions of sodium 4-(6'-dodecyl)benzenesulfonate were pulse irradiated with high-energy electrons and the formation and disappearance of radicals absorbing in the near-UV was observed. Most of the radicals were formed during the pulse by the addition of OH radicals from the radiolysis of water to the aromatic ring in the detergent molecules. A small fraction of the radicals was formed with a delay of some 200 μs. This effect is attributed to a slow reaction of alkyl radicals (formed by OH attack on the long aliphatic tail of the detergent molecules) with the aromatic ring. The radicals decay in a second-order process, the rate constant being $2k = 4.2 \times 10^8$ M^{-1} s^{-1} at an ionic strength of 0.1 M and at detergent concentrations below 2×10^{-3} M. Above this concentration, the rate constant becomes smaller. The dependence of the rate constant on the detergent concentration is understood in terms of the establishment of the micellar equilibrium $M\cdot_n \rightleftharpoons M_{n-1} + M\cdot$ for the radicals, followed by mutual deactivation of either two monomer radicals M· or a monomer radical with a radical in a micelle $M\cdot_n$. Deactivation between two radicals in micelles is too slow to contribute significantly to the disappearance of the radicals. Both the critical micelle concentration (2×10^{-3} M) and the rate constant (4×10^8 M^{-1} s^{-1}) of the back reaction in the micellar equilibrium (at an ionic strength of 0.1 M, maintained by added $NaClO_4$) were derived in the analysis of the kinetic data on the disappearance of the radicals.

Introduction

Micellar systems have often been used to solubilize complicated organic molecules in water and to study their reactions with free radicals (such as e_{aq}^-, OH, and H) produced by radiolysis of the solvent.[1] In most of these studies, the rate constant of reaction was determined using the method of pulse radiolysis, and in a few cases the fate of the radical that resulted from the attack of the solubilized molecule was also investigated.[1-5] However, the micelles themselves may be attacked by free radicals. OH radicals, for example, are reactive toward many detergents.[1] They generally react by abstracting a hydrogen atom from a C–H bond. The properties of the resulting radicals of the detergent have not yet been described.

In the present paper, the formation and especially the disappearance of radicals in aqueous solutions of sodium 4-(6'-dodecyl)benzenesulfonate (I) was investigated by using the method of pulse radiolysis. The solutions were irradiated under an N_2O atmosphere by a 50-ns pulse of high-energy electrons. Hydrated electrons from the radiolysis of water reacted

I
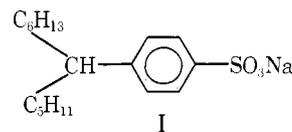
practically instantaneously according to $e_{aq}^- + N_2O + H_2O \rightarrow N_2 + OH^- + OH$, and the OH radicals attacked the detergent to form organic free radicals. These radicals were detected by their optical absorption in the near-UV. Their bimolecular disappearance was studied under various concentration conditions.

It soon became evident in these studies that the kinetics of reactions of detergent radicals are strongly linked to the kinetics of the micellar systems involved. Let M be a molecule of the detergent and n the mean aggregation number of a micelle. A dynamic equilibrium exists:

$$M_n \underset{k_+}{\overset{k_-}{\rightleftharpoons}} M_{n-1} + M \tag{1}$$