

(3 × 25 mL) and dried over anhydrous MgSO₄. Removal of solvent (rotary evaporator) gave 0.34 g of crude product. Distillation under reduced pressure afforded 0.18 g (36%) of a clear, colorless liquid: bp 68–69 °C (0.55 mmHg); PMR (CDCl₃) δ 2.01 (s, CH₃ + γ-H, 6 H), 1.86 (d, β-H, 6 H, J = 2.4 Hz), 1.70 (d, δ-H, 6 H, J = 2.4 Hz); IR (neat) 2910, 2860, 1655, 1450, 1345, 1300, 1045 cm⁻¹. Anal. Calcd for C₁₁H₁₈S: C, 72.46; H, 9.95. Found: C, 72.36; H, 10.06.

Kinetic Procedures. Each run was carried out by using nine sealed Kimble Neutraglas ampules. For runs with HFIP-containing solvents, each ampule contained 1 mL of solution, and for all other runs, each ampule contained 5 mL of solution. For runs in water, alcohols, and aqueous-organic mixtures, ampules were removed from the constant temperature bath at suitable time intervals, quenched in an ice bath, and the contents rinsed with acetone into 25 mL of acetone, containing Lacmoid (resorcinol blue) indicator, cooled within a solid CO₂-acetone slush bath. The acid produced was titrated against a standardized solution of sodium methoxide in methanol. The titration procedures for runs in acetic acid and formic acid and the calculation of the first-order

solvolytic rate coefficients were as previously described.²⁵

Product Studies. Ampules containing a ca. 0.01 M solution of 1-AdSMe₂⁺OTf⁻ in ethanol or the appropriate aqueous-ethanol solvent were allowed to react for at least ten half-lives at 70.6 or 100.1 °C. The products were directly analyzed by response-calibrated GLC, as previously described.³⁴ Only 1-adamantanol and 1-adamantyl ethyl ether were detected as products; in particular, no 1-adamantyl methyl sulfide was detected. The 1-adamantyl methyl sulfide was, however, detected after reaction in ethanol in the presence of a large excess of anhydrous⁶⁰ tetraethylammonium chloride.

Acknowledgment. This research was supported, in part, by the award of a Doctoral Research Fellowship to S.W.A. by the NIU Graduate School. D.N.K. thanks T. W. Bentley (University College of Swansea, University of Wales) and H. M. R. Hoffmann (Universität Hannover) for hospitality while this manuscript was being prepared.

Geometries and Energies of the Fluoroethylenes

David A. Dixon,* Tadamichi Fukunaga, and Bruce E. Smart

Contribution No. 3754, E. I. du Pont de Nemours & Co., Central Research & Development Department, Experimental Station, Wilmington, Delaware 19898. Received May 3, 1985. Revised Manuscript Received October 2, 1985

Abstract: The geometries of the fluorinated ethylenes have been gradient optimized at the SCF level with a double- ζ plus polarization function on carbon (DZ+D_C) basis set. The C=C and C—F bond lengths for C₂H₄, C₂H₃F, CH₂CF₂, *cis*-CHFCHF, *trans*-CHFCHF, and C₂F₄ have been optimized at the configuration-interaction level, including all single and double excitations (CI-SD). Good agreement with the original electron diffraction work was found. The values for $r(\text{C}=\text{C})$ and $r(\text{C}-\text{F})$ are found to decrease with increasing fluorine substitution. Correction factors to the SCF values are discussed and an estimated structure for C₂HF₃ is given. Isodesmic reaction enthalpies for the fluoroethylenes have been calculated with (DZ+D_C) and double- ζ plus polarization function (DZ+P) basis sets. Both basis sets gave comparable results in satisfactory agreement with experiment. The calculated heats of formation of *cis*- and *trans*-CHFCHF are -71.0 and -70.0 kcal/mol, respectively, which compare to the experimental values of -70.8 ± 3.1 and -69.4 ± 3.1 kcal/mol. Ionization potentials and dipole moments of the fluoroethylenes also have been calculated and are compared to experimental data.

Fluoroethylenes are very simple compounds and are extremely important monomers, but their structures are not unequivocally established.¹ In a systematic electron diffraction study, Bauer and co-workers² found that the C=C bond length decreases as fluorines are substituted for hydrogen in ethylene. The C=C bond length of 1.315 Å in CH₂CF₂ from a microwave study^{3a} agrees with an electron diffraction value of 1.316 Å.² The bond distances in C₂H₃F as determined by microwave^{3b} and electron diffraction were also in good agreement. Recently, however, the structures of the fluoroethylenes have been redetermined by using a combination of electron diffraction and microwave data,⁴⁻⁸ and the results did not show the expected general trend for a decrease in

the value of $r(\text{C}=\text{C})$ with increasing substitution of fluorine. In fact, the C=C bond lengths in CH₂CH₂, CH₂CF₂, and CHFCHF₂ were reported to be identical within experimental error.^{7,8} The similarity in values for $r(\text{C}=\text{C})$ and $r(\text{C}-\text{F})$ further complicated the analysis of the electron diffraction data.

As part of our general theoretical study of fluorocarbons, we have optimized the structures of the fluoroethylenes at the SCF level using a double- ζ (DZ) basis set augmented by polarization functions on carbon (DZ+D_C). To obtain accurate geometries and resolve the discrepancies among the experimental measurements, we subsequently optimized the C=C and C—F bonds for C₂H₄, C₂H₃F, the difluoroethylenes, and C₂F₄ with correlated wave functions starting from the optimum SCF structures. The results are compared with those from previous ab initio calculations.

To further test the reliability of the DZ+D_C basis set, the total energies of the fluoroethylenes were computed and used to calculate isodesmic reaction enthalpies, which are known experimentally. Ionization potentials and dipole moments also were calculated and compared to experiment.

Calculations. The calculations were performed with the HONDO program⁹ package on DEC VAX/11-780 and IBM 3083 computers. Geometries were optimized at the SCF level with the use of gradient techniques.¹⁰ The correlated wave

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functions were obtained at the level of a configuration interaction calculation including all single and double excitations (CI-SD) from the valence space to the virtual space. The C and F 1s core electrons were frozen in the calculation. The orbitals for the CI were obtained from a single-determinant Hartree-Fock calculation. The C=C and C-F bonds were optimized parabolically, starting from the SCF optimum geometries. The basis set for these calculations is of double- ζ quality in the valence space with exponents and coefficients from Dunning and Hay.¹¹ The basis set is augmented by a set of d polarization functions on each carbon¹¹ and has the form (9,5,1/9,5/4)/[3,2,1/3,2/2] in the order C, F, H. This basis set gives good structures at the SCF level and previous work¹² has shown that d orbitals on C are significantly more important than d orbitals on F at the SCF level. This basis set is also of tractable size for the CI calculations.

Results and Discussion

Geometries. The SCF parameters for the fluoroethylenes are given in Table I and are compared with the experimental values. The bond angles and C-H bond distances in general agree well with experiment. The only major discrepancies (excluding C₂HF₃) are the value of $\theta(\text{H}_2\text{C}_1\text{C}_2)$ in C₂H₃F,² $\theta(\text{H}_3\text{C}_2\text{C}_1)$ in C₂H₃F,^{3b,4} and $\theta(\text{CCH})$ in *trans*-CHFCHF.² These differences are all in the angles involving hydrogen which are not precisely determined by experiment. For C₂HF₃, the agreement with the angles determined by Mijlhoff and co-workers⁸ is good; however, the agreement with the angles given by Bauer and associates² is not as good. This is probably because of errors in their structure since they assumed that all of the C-F bond lengths were equivalent.

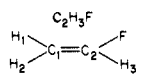
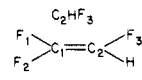
The C=C and C-F bond lengths at the SCF level are shorter than the experimental values, as expected. The SCF values for $r(\text{C}=\text{C})$ generally decrease with increasing fluorine substitution. This is especially pronounced for *gem*-difluoro substitution. The C-F bond lengths also decrease with increasing fluorine substitution and the effect is again most pronounced for *gem*-difluoro substitution. The SCF values are in agreement with the trend in $r(\text{C}=\text{C})$ determined by the Bauer group.²

There have been several theoretical calculations on the structures of the fluoroethylenes. Bock and co-workers¹³ made the most extensive comparison and determined the structures of the ethylenes with 0, 1, and 2 fluorines using a small double- ζ basis set. The C=C bond lengths at this level are too short, even in comparison with the structures determined with the DZ+D_C basis set, and the values for $r(\text{C}-\text{F})$ are all too long, even when compared to the experimental values. Optimized geometries determined with both the 4-31G¹⁴ and 3-21G¹⁵ basis sets similarly exhibited overly contracted C=C bonds and elongated C-F bonds. The trend of decreasing $r(\text{C}=\text{C})$ with increasing fluorine substitution, however, was found with each of these basis sets.¹³⁻¹⁵

Dykstra and co-workers¹⁶ optimized the structures of *cis*- and *trans*-CHFCHF with a fully polarized double- ζ basis set (DZ+P). Excellent agreement with our DZ+D_C calculations is found, except for the C-F bond length which is shorter at the DZ+P level by 0.008–0.009 Å. This again is the expected result of increasing the size of basis set and also has been observed in comparisons of DZ+D_C and DZ+P calculations on the fluoromethanes.¹²

The values for $r(\text{C}=\text{C})$ and $r(\text{C}-\text{F})$ determined at the level of a CI-SD calculation are also given in Table I. When the CI correction is included, the bonds lengthen, as would be expected from previous studies. The C=C bond lengths increase uniformly

Table I. Geometric Parameters for Fluorinated Ethylenes^a

parameter	expt 1 ^b	expt 2	expt 3	SCF	CI-SD
C ₂ H ₄					
$r(\text{C}=\text{C})$			1.339 ^c	1.325	1.342
$r(\text{C}-\text{H})$			1.086	1.076	
$\theta(\text{HCH})$			117.6	116.8	
					
$r(\text{C}=\text{C})$	1.333	1.330 ^d	1.332 ^e	1.314	1.330
$r(\text{C}-\text{F})$	1.348	1.351	1.348	1.338	1.359
					(1.51) ^f
$r(\text{C}-\text{H}_1)$	1.090	1.108	1.086	1.074	
$r(\text{C}-\text{H}_2)$	1.085	1.097	1.079	1.073	
$r(\text{C}-\text{H}_3)$	1.076	1.107	1.071	1.073	
$\theta(\text{H}_1\text{C}_1\text{C}_2)$	121.4	120.4	120.7	121.6	
$\theta(\text{H}_2\text{C}_1\text{C}_2)$	123.9	118.7	118.8	119.3	
$\theta(\text{H}_3\text{C}_2\text{C}_1)$	127.7	130.8	120.9	126.0	
$\theta(\text{FC}_1\text{C}_2)$	121.0	121.5	121.0	122.6	
CH ₂ =CF ₂					
$r(\text{C}=\text{C})$	1.316	1.340 ^g	1.315 ^h	1.307	1.323
$r(\text{C}-\text{F})$	1.324	1.315	1.323	1.310	1.330
					(1.322) ^f
$r(\text{C}-\text{H})$	1.075	1.091	1.079	1.072	
$\theta(\text{FCF})$	109.7	110.6	109.1	109.2	
$\theta(\text{HCH})$	119.3	122.0	121.9	120.6	
<i>cis</i> -CHF=CHF					
$r(\text{C}=\text{C})$	1.331	1.330 ⁱ	1.324 ^h	1.312	1.329
$r(\text{C}-\text{F})$	1.335	1.342	1.335	1.331	1.349
					(1.341) ^f
$r(\text{C}-\text{H})$	1.084	1.103	1.089	1.071	
$\theta(\text{CCF})$	123.7	122.0	122.1	122.6	
$\theta(\text{CCH})$	121.6	124.1	124.0	123.1	
<i>trans</i> -CHF=CHF					
$r(\text{C}=\text{C})$	1.329	1.320 ^j		1.311	1.328
$r(\text{C}-\text{F})$	1.344	1.338		1.336	1.354
					(1.346) ^f
$r(\text{C}-\text{H})$	1.080	1.088		1.072	
$\theta(\text{CCF})$	119.3	119.8		120.1	
$\theta(\text{CCH})$	129.3	125.0		125.5	
					
$r(\text{C}=\text{C})$	1.309	1.341 ^k		1.307	(1.323) ^f
$r(\text{C}-\text{F}_1)$	1.336	1.316		1.304	(1.315) ^f
$r(\text{C}-\text{F}_2)$	1.336	1.316		1.310	(1.321) ^f
$r(\text{C}-\text{F}_3)$	1.336	1.342		1.331	(1.342) ^f
$r(\text{C}-\text{H})$	1.073	1.100		1.070	
$\theta(\text{F}_1\text{C}_1\text{C}_2)$	125.4	124.0		126.0	
$\theta(\text{F}_2\text{C}_1\text{C}_2)$	125.4	123.1		122.8	
$\theta(\text{F}_3\text{C}_2\text{C}_1)$	118.8	120.0		121.2	
$\theta(\text{HC}_2\text{C}_1)$	127.2	124.0		123.1	
C ₂ F ₄					
$r(\text{C}=\text{C})$	1.311			1.307	1.320
$r(\text{C}-\text{F})$	1.319			1.306	1.322
$\theta(\text{FCF})$	112.5			112.6	

^a Bond distances in Å, bond angles in degrees. ^b Reference 2.

^c Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619. ^d Reference 4. ^e Reference 3b.

^f Corrected values obtained by subtracting 0.008 Å from the CI-SD value. See text. ^g Reference 5. ^h Reference 3a. ⁱ Reference 6.

^j Reference 7. ^k Reference 8. ^l Estimated from the SCF values with use of correction values of +0.016 Å for $r(\text{C}=\text{C})$ and +0.011 Å for $r(\text{C}-\text{F})$. See text.

by ~ 0.016 Å, whereas the CF bond lengths show a slightly larger increase of ~ 0.019 Å.¹⁷ The smallest increases for both values are found for C₂F₄.¹⁸ The correlation correction gives exactly

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Table II. Total Energies (au) of the Fluoroethylenes Determined at the Optimum SCF Geometry (DZ+D_C)

molecule	SCF(DZ+D _C)	SCF(DZ+P)	CI-SD(DZ+D _C)	CI-SDQ(DZ+D _C)
C ₂ H ₄	-78.042 712	-78.050 701	-78.295 362	-78.318 555
C ₂ H ₃ F	-176.912 823	-176.929 856	-177.251 795	-177.286 675
CH ₂ CF ₂	-275.785 037	-275.814 166	-276.207 838	-276.255 453
<i>cis</i> -CHFCHF	-275.771 009	-275.798 143	-276.193 007	-276.240 925
<i>trans</i> -CHFCHF	-275.771 357	-275.797 942	-276.193 450	-276.241 486
C ₂ HF ₃	-374.635 360	-374.674 803		
C ₂ F ₄	-473.492 467	-473.544 715	-474.074 774	-474.151 803

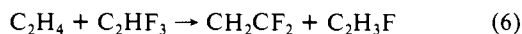
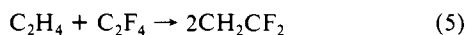
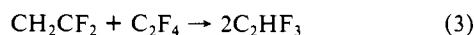
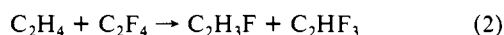
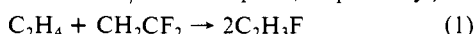
Table III. Isodesmic Reaction Energies

eq	ΔH°/ΔE (kcal/mol)			
	3-21G ^a	DZ+D _C	DZ+P	ΔH°(exptl) ^b
1	5.0/4.6	1.7/1.3	3.6/3.2	1.1 ± 1.9
2	-5.0/-6.4	-6.7/-8.1	-4.4/-5.8	-5.0 ± 3.1
3	7.7/6.9	5.2/4.4	6.4/5.8	3.6 ± 5.2
4	-17.7/-17.9	-13.6/-13.8	-14.7/-14.9	-9.8 ± 4.0
5	-22.6/-24.2	-20.3/-21.9	-19.1/-20.7	-14.6 ± 2.3
6	-12.7/-13.3	-11.8/-12.4	-11.0/-11.6	-8.6 ± 3.5

^aTotal energies determined at the optimum 3-21G geometry. The energies for C₂H₄, C₂H₃F, and CH₂CF₂ are from ref 15. The energies for C₂HF₃ and C₂F₄ are -372.545 89 and -470.855 34 au, respectively (this work). ^bCalculated from experimental ΔH_f^o values in Table IV.

the same trends that are observed at the SCF level: *the values for r(C=C) and r(C-F) decrease with increasing fluorine substitution.* The C=C bond lengths at the CI level are in excellent agreement with those determined by the Bauer group.² The C-F bond lengths are all somewhat longer than the experimental values. This is probably because of errors at the SCF level where the C-F bonds are 0.008 Å too long as compared to the DZ+P calculated values. When this correction is applied to the CI values (except for C₂F₄), the C-F bond lengths are now in excellent agreement with experiment (Table I). We also have estimated *r(C=C)* and *r(C-F)* for C₂HF₃ using a correction of +0.016 Å for *r(C=C)* and a correction of +0.011 Å for *r(C-F)* (0.019–0.008 Å) to give the values in Table I. The *r(C=C)* and *r(C-F)* values for each fluoroethylene that we consider to be most accurate are italicized.

Energetics. The total SCF energies of the fluoroethylenes were determined at the SCF (DZ+D_C) optimized geometries with the DZ+D_C basis set and with a basis set that included polarization functions on all atoms (DZ+P).¹¹ The values, which are listed in Table II, were used to calculate the energies of the isodesmic reactions in eq 1–6. The results are given in Table III. (The SCF isodesmic ΔE values calculated with the DZ+P basis set with use of the most accurate geometries from Table I rather than the DZ+D_C optimized geometries gave very similar results: 2.6, -7.0, 5.2, -14.8, -21.8, -12.2 kcal/mol for eq 1–6, respectively.)



To properly compare the theoretical results to experiment, the calculated ΔE values need to be converted to ΔH values. The required zero-point energies for the fluoroethylenes were calculated with the 3-21G basis set¹⁹ and scaled values are given in Table IV. The calculated isodesmic reaction energies corrected for zero-point energy differences are compared with experiment and 3-21G results in Table III.

(18) The largest errors would be expected for C₂F₄ because the basis set size is the smallest considering the number of electrons. The CI at the SD level also recovers the smallest percentage of correlation energy for C₂F₄, again due to the large number of electrons.

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The calculated ΔH° values for reactions 1–4 and 6 with both of our basis sets agree well with experiment. The 3-21G results are less satisfactory. The DZ+P results for reactions 1 and 4 are slightly outside the experimental errors. The greatest discrepancy between theory and experiment appears in reaction 5. The error is 4.5 kcal/mol with the DZ+P basis set and 5.7 kcal/mol with the DZ+D_C basis set. Among the five isodesmic equations, the neglect of correlation energy is also likely to produce the largest error for eq 5.

Because of the large number of fluorine valence electrons, CI-SD calculations do not recover as much of the correlation energy as that found for systems with fewer valence electrons. This occurs because higher order excitations play a larger role, simply because of the very large number of such excitations. Furthermore, size consistency problems can become significant. This will be especially true for isodesmic reactions involving C₂F₄. We therefore do not recommend applying a CI correction involving only single and double excitations to the isodesmic energies. (Such problems, however, are not expected to play a major role in the calculations of geometries.) For example, using the CI energies given in Table III, we calculate ΔH° = -27.0 kcal/mol at the CI-SD level and -23.8 kcal/mol at the CI-SDQ level for isodesmic reaction 5. The latter calculation includes an estimate for quadrupole excitations using Davidson's formula.²⁰ Thus, inclusion of higher order excitations gives a result in the right direction, but a large error is still present.

The energy difference between *cis*- and *trans*-1,2-difluoroethylene has been determined quite precisely from experiment.²¹ Contrary to simple chemical intuition, the *cis* isomer is more stable than the *trans* isomer by 0.93 ± 0.03 kcal/mol (ΔΔH_f^o). There have been numerous theoretical studies of this energy difference,^{13,14,16,22} with the most extensive one being that of Dykstra and co-workers.¹⁶ At the DZ+D_C level (Table II) the *trans* structure is more stable by 0.22 kcal/mol. There is essentially no correlation correction with this basis set, ΔE(CI-SD) = 0.28 kcal/mol and ΔE(CI-SDQ) = 0.35 kcal/mol (Table II). As expected from previous results,¹⁶ improvement of the basis set leads to a better ΔE. At the DZ+P level the *cis* isomer is correctly calculated to be more stable than the *trans*, but by only 0.13 kcal/mol.

The experimental heats of formation of *cis*- and *trans*-1,2-difluoroethylene are not known precisely (Table IV). The *trans* isomer is predicted experimentally to be 10.7 ± 3.9 kcal/mol less stable than CH₂CF₂. With the DZ+D_C basis set, the energy difference is 8.6 kcal/mol, favoring CH₂CF₂. Again there is essentially no correlation correction for this energy difference, ΔE(CI-SD) = 9.0 kcal/mol and ΔE(CI-SDQ) = 8.8 kcal/mol. Improvement of the basis set leads to a small change in ΔE, which is 10.1 kcal/mol with the DZ+P basis set. After correcting for zero-point energy differences, our best estimates of the heats of formation are -70.0 kcal/mol for *trans*-CHFCHF and -71.0 kcal/mol for *cis*-CHFCHF.

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Table IV. Heats of Formation, Zero-Point Energies, and Dipole Moments

ethylene	ΔH_f° ^a	ZPE ^b	$\mu, ^c$ D			
			(DZ+D _C)	(DZ+P)	(CI-SD)	exptl
C ₂ H ₄	12.5 ± 0.3	30.9 (30.9)				
C ₂ H ₃ F	-33.2 ± 0.4	27.1	1.92	1.67	1.73	1.43
CH ₂ CF ₂	-80.1 ± 0.8	22.9 (22.1)	1.82	1.44	1.62	1.38
<i>trans</i> -CHFCHF	-69.4 ± 3.1 ^d	22.8 (22.5) ^e				
<i>cis</i> -CHFCHF	-70.8 ± 3.1 ^d	23.1 (22.7)	3.26	2.87	2.94	2.42
C ₂ HF ₃	-117.2 ± 2	18.5	1.79	1.52		1.40
C ₂ F ₄	-157.9 ± 0.4	13.3 (13.3)				

^a In kcal/mol. Unless noted otherwise, from: Pedley, J. B.; Rylance, J. "Sussex-N.P.L. Computer Analyzed Thermochemical Data: Organic & Organometallic Compounds"; University of Sussex: Sussex, Brighton, 1977. ^b 3-21G calculated values multiplied by 0.90, in kcal/mol. Experimental values in parentheses were calculated from vibrational frequency data: Shimanouchi, T. "Tables of Molecular Vibrational Frequencies", NSRDS-NBS 39: U.S. Government Printing Office: Washington, DC, 1972. ^c Calculated dipole moments at the SCF minimum geometry (DZ+D_C). Experimental values from: Nelson, R. D., Jr.; Lide, D. R., Jr.; Maryott, A. A. "Selected Values of Electric Dipole Moments for Molecules in the Gas phase"; NSRDS-NB10: U.S. Government Printing Office: Washington, DC, 1967. McClellan, A. L. "Tables of Experimental Dipole Moments"; W. H. Freeman: San Francisco, 1963; Vol. 1. ^d Jochims, H. W.; Lohr, W.; Baumgärtel, H. *Nouv. J. Chim.* **1979**, 3, 109. ^e Reference 21b.

The effects of fluorination of the geometries and stabilities of ethylenes and the diverse explanations for these effects have been reviewed elsewhere.¹ Among the various proposals to account for the relative stabilities of the three C₂H₂F₂ isomers are nonbonded attraction,^{22e,f,23} conjugative destabilization,²⁴ resonance stabilization,^{21c,25} hyperconjugation,²⁶ as well as electrostatic^{13,14} and other electronic effects.²⁷ It is not our intention to try to sort out and pinpoint the specific electronic effects that determine fluoroethylene geometries and energies. Rather, we seek to identify the requirements for a basis set that are crucial for reasonably accurate calculations of geometries and energies. It is noteworthy, however, the whatever the actual electronic reasons might be, the relative stabilities of the fluoroethylenes appear to be entirely a consequence of their relative π -bond strengths.

From the D_π° values of 59.1, 62.8, and 52.3 kcal/mol for CH₂CH₂, CH₂CF₂, and CF₂CF₂,²⁸ respectively,

$$D_\pi^\circ(\text{CF}_2=\text{CF}_2) + D_\pi^\circ(\text{CH}_2=\text{CH}_2) - 2D_\pi^\circ(\text{CH}_2=\text{CF}_2) = -14.2 \text{ kcal/mol}$$

Within experimental error, this result is identical with the enthalpy of isodesmic reaction 5. Similarly,

$$D_\pi^\circ(\text{CH}_2=\text{CF}_2) - D_\pi^\circ(\text{c-CHF=CHF})^{29} = 8.4 \text{ kcal/mol}$$

This difference compares to the above DZ+D_C computed value of 8.8 kcal/mol for the difference in energy (ΔE) between *cis*-CHFCHF and CH₂CF₂.

Ionization Potentials and Dipole Moments. The ionization potentials of the fluoroethylenes are all known experimentally and

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(29) $D_\pi^\circ(\text{c-CHF=CHF})$ is not known experimentally. The value for $D_\pi^\circ(\text{CH}_2=\text{CH}_2) - D_\pi^\circ(\text{c-CHF=CHF})$ was equated to the difference in activation energies for the *cis*-*trans* isomerizations of CHD=CHD and CHF=CHF (4.7 kcal/mol)³⁰ (the difference in π -bond energies between CF₂=CH₂ and CH₂=CH₂, 3.7 kcal/mol, is equivalent within experimental error to the computed difference in their rotational barriers, 3 kcal/mol³¹). Thus, $D_\pi^\circ(\text{c-CHF=CHF}) \cong 54.4$ kcal/mol.

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Table V. Ionization Potentials in eV

ethylene	DZ+D _C	DZ+P	exptl ^a
C ₂ H ₄	10.27	10.26	10.51 ^b
C ₂ H ₃ F	10.58	10.48	10.56
CH ₂ CF ₂	10.95	10.74	10.69
<i>cis</i> -CHFCHF	10.84	10.64	10.44
<i>trans</i> -CHFCHF	10.84	10.64	10.38
C ₂ HF ₃	11.17	10.85	10.54
C ₂ F ₄	11.48	11.05	10.56

^a Reference 32. ^b Levin, R. D.; Lias, S. G. "Ionization Potential and Appearance Potential Measurements 1971-1981"; NSRDS-NBS 71: U.S. Government Printing Office: Washington, DC, 1982. See this reference for other values for the fluoroethylenes.

are about 10.5 eV.³² The calculated IP's from Koopmann's theorem are given in Table V and show excellent agreement with experiment considering the approximations involved. As expected, the DZ+P values show slightly better agreement. Although the fluoroethylene IP's are about equal, one trend is evident. For the C₂H₂F₂ isomers, the highest IP corresponds to the most stable isomer (CH₂CF₂) and the lowest IP corresponds to the least stable isomer (*trans*-CHFCHF). The differences in the IP's are similar to the differences in the ΔH_f° 's for the isomers. The IP(CH₂CF₂) is 7.1 kcal/mol higher than IP(*trans*-CHFCHF), which approaches the difference of 10 kcal/mol in ΔH_f° 's. The IP difference between the *cis* and *trans* isomers is 1.4 kcal/mol, which compares to the difference in ΔH_f° 's of 0.9 kcal/mol.²¹

The experimental and calculated dipole moments, which were determined at the minimum SCF geometry (DZ+D_C), are given in Table IV. The DZ+D_C values are roughly 30% high, whereas the DZ+P values are about 15% high. As expected, including correlation lowers the dipole moment, but the effect is slightly smaller than that found by improving the basis set.

Conclusions

This study demonstrates that the geometries of the fluoroethylenes exhibit simple trends. The DZ+D_C basis set gives a good description of the structure of the fluoroethylenes with errors like those typically found in other SCF calculations with good basis sets. Correlation corrections at the CI-SD level provide a uniform correction and give very good structural parameters in comparison to experiment. We expect that our structures are accurate to within $\pm 1^\circ$ for bond angles and ± 0.01 Å for bond lengths, which are typical experimental errors. Finally, we have demonstrated the adequacy of the DZ+D_C basis set for predicting reasonable, consistent geometries and energies for these fluorocarbons. This basis set is still of a modest enough size that it can be applied to larger fluorocarbon systems.

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