group drops as the number of H atoms in the group decreases. Compared to the CH_2 group, the CH group looses about twice as much charge to each adjacent CH_3 group. Of course, the charge transfer occurs in favor of the H-richer group. This suggests that, in a way, the H atoms "retain" electrons in the groups in qualitative accord with a scheme depicting the hydrogens as electron attractors. This qualitative picture of electron retention by H atoms in CH_N groups is then the common point from which the inductive effects for the alkyl groups can be rationalized. INDO calculations[9] are in qualitative accord with such a picture.

While the mathematical isolation of the groups is relatively easy from a conceptual point of view (because it suffices to split the C–C overlap populations in halves), the attribution of the electrons within the CH_N groups reveals the artificial character of any man-made partitioning. In this sense, one conceptual advantage contained in the present scheme of charge distributions with positive carbon atoms resides in the fact that the "chemical calibration" is capable of indicating how much charge is lost by the individual C atoms in a molecule (with respect to their atomic state) without being specifically required to allocate these "lost" charges to any other specified atoms in that molecule. Fortunately, this uncertainty affecting the charge distribution in the interior of the CH_N fragments does not cause the loss of one of the most popular concepts, that of atomic charges, for discussions of chemical problems.

Intramolecular Nonbonded Attractions in Molecules?

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Abstract: Recently, Epiotis has published an analysis of bonding in the difluoroethylenes and has attempted to rationalize the bonding and energetics in these compounds by "lone-pair attractions." We have examined the source of the smaller XCX angle in 1,1-difluoroethylene (X = F) than in ethylene (X = H) by carrying out *ab initio* molecular orbital calculations on ethylene and mono- and difluoroethylenes. The orbital energies, Edmiston-Ruedenberg localized orbitals, and electron density distribution in these compounds have been examined, and model calculations simulating the fluoroethylene by changing the nuclear charges in the ethylene have been done. It is shown that the "attraction" in these compounds is not due to "lone pair" interactions but rather to changes in the nature of the C–X bonding orbital as X becomes more electronegative. Further implications of these results for rationalizing other molecular geometries are discussed.

The fact that the FCF angle in 1,1-difluoroethylene is smaller than the corresponding HCH angle in ethylene is interesting because it goes against most chemists' intuition that one would expect greater nonbonded repulsions between the more electronegative and electron-rich fluorines. A more precise analysis along the lines of electrostatics is difficult, because of the fact that the C–X bond distances are significantly different for X = H and F. Fluorine will attract its electrons more tightly than hydrogen and thus at a given XCX angle (*e.g.*, 120°), the larger F–F distance might well imply less X · · · X repulsion for X = F than for X = H.

Using valence bond ideas, Mellish and Linnett[1] found a simple hybridization explanation for the smaller FCF angle; the more electronegative fluorines cause the carbon to rehybridize and use its less tightly bound p orbitals in bonding to the fluorines while using more s character in the carbon–carbon σ bond. Rehybridization of the sp^2 carbon toward sp^n ($n > 2$) would shrink the angle between those hybrids which had acquired more p character. These hybridization arguments are useful for rationalizing molecular geometries,

but they need to be examined with actual wave functions.

From a molecular orbital viewpoint, Walsh's rules[2] have been used to rationalize molecular geometries. For AB_2 molecules of C_{2v} symmetry, one examines the orbital energy dependence on the BAB angle of the a_1 and b_1 orbitals (which have no node between the B atoms) and b_2 and a_2 orbitals (which are antibonding between the B atoms). Unfortunately, the sum of the orbital energies often does very poorly in predicting the actual BAB angle, so one has to resort to after the fact reasoning on the relative importance of the a_1 (bonding) and b_2 (antibonding) orbitals.

Epiotis[3] rationalized the fact that 1,1-difluoroethylene has a smaller XCX angle than ethylene in the following way: there is a preferential charge transfer out of a $F(p\sigma)$ antisymmetric MO, which leads to a slightly favorable "bonding" interaction between the fluorines. A similar interaction involving the $F(p\pi)$ orbitals is antibonding, but the bonding effect wins out, thus bringing the fluorines closer together. In support of his argument, he notes that the $p\pi$–$p\pi$ INDO bond order is negative and the $p\sigma$–$p\sigma$ bond order is larger than the

(1) C. E. Mellish and J. W. Linnett, *Trans. Faraday Soc.*, **50**, 657 (1954); and for a review, H. L. Bent, *Chem. Rev.*, **61**, 275 (1961).

(2) A. D. Walsh, *J. Chem. Soc., London*, 2260 (1953).
(3) N. D. Epiotis, *J. Amer. Chem. Soc.*, **95**, 3087 (1973).

$p\pi$–$p\pi$ and positive, a positive bond order implying a "bonding" interaction. However, Epiotis does not consider p_y–p_y "repulsion" which is much larger than the p_x–p_x "attraction." (The molecule is in the xy plane, with the C=C along the x axis.) For example, the Mulliken overlap population in a CNDO/2 calculation[4] between $F_1(p_y)$–$F_2(p_y)$ atomic orbitals is -0.0035; the $F_1(p_x)$–$F_2(p_x)$ population is 0.0003. Considering only the top six MO's which one might argue to be mainly "lone pair," the overlap populations are -0.0146 (p_y–p_y) and 0.0016 (p_x–p_x). Thus, the p_y–p_y bond order is repulsive in contrast to what is implied in Epiotis' Figure 5. The author's assertion that a θ(FCF) $> 90°$ in 1,1-difluoroethylene leads to a "p_x" lone pair is without theoretical justification, since even at $\theta = 120°$ the lone pairs (and the σ bond) both contain a significant amount of p_x and p_y contribution. Even if one were to argue that the lone pairs have more p_x character than p_y, the fact that the overlap population for the p_y–p_y interaction is an order of magnitude greater than the p_x–p_x implies that the net "lone pair" overlap population due to the lone pairs will be repulsive. In addition, Epiotis[3] considers only two "lone pairs" per fluorine, whereas a satisfactory theory must consider all three, since ethylene (the reference system) has none.

In this paper we examine the bonding in the fluoroethylenes with *ab initio* wave functions in the hopes of answering the following. (1) What causes "nonbonded attractions"[5] in fluoroethylenes (*cis*-1,2- and 1,1-difluoroethylene)? (2) Do these "nonbonded attractions" exist in other molecules as well and is there a general model to predict their magnitude?

Computational

The *ab initio* molecular orbital calculations were carried out with the MOLE quantum chemistry system[6] using STO-3G[7] and "double ζ"[8] basis sets and with the Gaussian 70 program[9] using STO-3G and 431G[10] basis sets. The localized orbitals were determined by minimizing the interorbital exchange repulsion, a procedure first developed by Edmiston and Ruedenberg.[11] Only the valence orbitals were localized, since it has been shown[12] that inclusion of the inner shells has a negligible effect on the shape of the localized valence orbitals.

(4) See J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970. The Mulliken overlap population is the density matrix element times the overlap integral.

(5) By nonbonded attraction, we mean a nondispersion force attraction between two atoms not directly bonded to one another (according to valence bond structures). An example of this might be the π bonding between the end carbons in *cis*-1,3-butadiene, when the phases of the occupied orbitals have the same sign between the end carbons.

(6) S. Rothenberg, P. Kollman, M. Schwartz, E. F. Hayes, and L. C. Allen, *Int. J. Quantum Chem., Symp.*, **3**, 714 (1970).

(7) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1968).

(8) We used J. Whitten's 10s Gaussians (*J. Chem. Phys.*, **44**, 359 (1966)) and S. Huzinaga's 5p Gaussians (*J. Chem. Phys.*, **43**, 359 (1965)) on C and F and Whitten's 5s sect for hydrogen. The 10s functions were contracted to four (4,3,2,1) and the 5p and 5s set contracted to 2 (4,1) with the hydrogen function scaled by $2^{1/2}$.

(9) Gaussian 70, W. J. Hehre, W. A. Latham, R. Ditchfield, M. Newton, and J. A. Pople, QCPE 236; we are grateful to Dr. John McKelvey and W. J. Hehre for the use of their CDC 7600 version of the program.

(10) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

(11) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.* **35**, 457 (1963).

(12) S. Rothenberg, personal communication.

Electronegativity changes in molecules were also simulated by changing the nuclear charges on the atoms, retaining the atomic orbital basis. In these cases only the potential energy one-electron integrals needed to be redetermined.

SCF Studies of Ethylene and Fluoroethylenes. Table I contains the results of the *ab initio* calculations on the

Table I. Total Energies of Ethylene and Fluoroethylenes

θ-(HCH), deg	E_T, au	R-(C=C), Å	R(CF), Å	θ-(FCF),[b] deg	E_T, au
		STO-3G Calculations			
	Ethylene[a]		——Fluoroethylene[b]——		
120	-77.07222	1.31	1.32	120	-174.52947
115	-77.07338				
110	-77.07103				
105	-77.06497				

R(C=C), Å	R(CF), Å	θ(CCF), deg	E_T, au
	trans-1,2-Difluoroethylene[c]		
1.32	1.40	120	-271.98025
1.32	1.40	125	-271.98076
1.32	1.40	130	-271.97493
1.31	1.32	120	-271.08092
	cis-1,2-Difluoroethylene[d]		
1.32	1.40	120	-271.97944
1.32	1.40	125	-271.98144
1.32	1.40	130	-271.97785
1.31	1.32	120	-271.97987
	1,1-Difluoroethylene[c]		
1.32	1.40	120	-271.99013
1.32	1.40	115	-271.99345
1.32	1.40	110	-271.99527
1.32	1.40	105	-271.99369
1.31	1.32	120	-271.99304
1.31	1.32	115	-271.99709
1.31	1.32	110	-271.99812
1.31	1.32	105	-271.99584
1.31	1.36	110	-272.00005
1.31	1.40	110	-271.99514

θ(HCH)	E_T, au	Compd	E_T, au
		"Double ζ" Calculations	
	Ethylene[a]	———— Fluoroethylenes[d] ————	
120	-78.00141	Monofluoroethylene	-176.84213
115	-78.00233	1,1-Difluoroethylene	-275.67898
110	-78.00026	*trans*-1,2-Difluoroethylene	-275.67280
		cis-1,2-Difluoroethylene	-275.67244

[a] R(C=C) = 1.32 Å; R(CH) = 1.09 Å. [b] All geminal angles 120°; R(CH) = 1.09 Å. [c] R(CH) = 1.09 Å; θ(CCH) = 120°. [d] All angles 120°; R(C=C) = 1.31 Å; R(CF) = 1.32 Å; R(CH) = 1.09 Å.

ethylenes and fluoroethylenes. There are a number of features of these potential surfaces which should be pointed out.

First, the calculated minimum energy XCX angle in 1,1-difluoroethylene (with the bond distances at the experimental[13] values) is 111.0° (experimental[13] 109.3) and in ethylene is 116.2° (experimental[14] 117.5), reproducing the experimental order of the bond angle.

Second, the energy of 1,1-difluoroethylene is significantly lower than that of *cis*-1,2-difluoroethylene; in addition the CCF angle in the cis-1,2 isomer is almost the same as in the trans-1,2 isomer. Epiotis[3] had used

(13) W. Edgell, P. A. Kinsey, and J. W. Amy, *J. Amer. Chem. Soc.*, **79**, 2691 (1957).

(14) L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu and J. E. Young, *J. Chem. Phys.*, **42**, 2683 (1965).

MO symmetry arguments to show that in "Y" systems, such as 1,1-difluoroethylene, the lone-pair "attraction" was a compromise between σ attraction and π repulsion, whereas in "U" systems such as cis-1,2-difluoroethylene there is both σ and π "lone-pair attraction." It is clear from the results of the calculations reported here that the "attraction" in the 1,1-difluoroethylene is stronger than that in cis-1,2-difluoroethylene; thus MO symmetry arguments such as employed in ref 1 lead to incorrect conclusions on the relative energies of "Y" and "U" systems.

Pople[15] has pointed out that the exothermicity of the reaction $2CH_3F \rightarrow CH_4 + CH_2F_2$ is well reproduced by ab initio molecular orbital calculations, and our calculations on the fluoroethylenes allow us to predict that the same effect may be true there. The ΔE for the reaction $2CH_2CHF \rightarrow C_2H_4 + CH_2CF_2$ is calculated to be -4.0 kcal/mol (STO-3G) but $+2.4$ kcal/mol ("double ζ"). The above ΔE's were calculated using $\theta = 120°$ geometries for all three species. Doing a more complete geometry search leads to a $\Delta E = -4.1$ kcal/mol (STO-3G) and -1.2 kcal/mol (431G).[16] The fact that the total energy for 1,1-difluoroethylene is lower than the 1,2 isomers does appear to indicate that there is some "attractive" interaction between the fluorines. The energy difference between cis- and trans-1,2-difluoroethylenes is so small that one cannot conclude about their relative energy from these ab initio calculations unless one does a complete geometry search on these systems with a "double ζ plus polarization" basis set. From the data in ref 3, the experimental energy difference between the 1,2 isomers is about 0.3 kcal/mol with the cis more stable.

From a simple minded application of the ideas presented by Radom, et al.,[17] one would expect that the V_1 term in the rotational potential would make the cis-1,2-difluoro far less stable than the trans, due to unfavorable dipole–dipole interactions. This V_1 term is of the order of 4–8 kcal/mol for HOOH and HOOF so it appears that "orbital phase" effects[18] are strong enough to overcome the dipole interactions. What is surprising is the apparent qualitative difference between the nature of the V_1 term in single and double bonded species.

Is the Attraction between Fluorines a "Lone-Pair" Interaction? If there is really an "attractive" interaction between fluorines, one ought to try to understand the physical basis for this, since it is not clear where the attractive force is coming from. Epiotis[3] has attributed this force to "lone-pair" interactions, so one would really like to construct a model fluoroethylene system without lone pairs to see if the "attractive" force is due to the lone pairs.

(15) J. A. Pople, "Electronic Structure and Conformations of Organic Molecules," presented at G. N. Lewis award address, 1973, Berkeley, Calif.

(16) For ethylene, monofluoroethylene, and difluoroethylene, the geometries were optimized using the STO-3G basis and, at the minimum energy geometry, 431G calculations were carried out. For ethylene $R(C=C)$ and $\theta(HCH)$ were varied; for CH_2CHF, $R(C=C)$, $R(CF)$, and $\theta(CCF)$ were varied; and for CH_2CF_2, $R(C=C)$, $R(CF)$, and $\theta(FCF)$ were varied. $R(CH) = 1.09$ Å throughout and for mono- and difluoroethylene the CH_2 fragment was kept as in ethylene. The geometrical parameters found were (1) ethylene, $R(C=C) = 1.31$ Å; $\theta(HCH) = 116°$; (2) CH_2CHF, $R(C=C) = 1.31$ Å, $\theta(CCF) = 124°$, $R(CF) = 1.35$ Å; (3) CH_2CF_2, $R(C=C) = 1.31$ Å, $\theta(FCF) = 111°$.

(17) L. Radom, W. Hehre, and J. A. Pople, J. Amer. Chem. Soc., **94**, 2371 (1972).

(18) R. Hoffmann, Accounts Chem. Res., **4**, 1 (1971).

This one can do in the ethylene molecule by changing the nuclear charges of C and H to make the hydrogen more electron attracting and the carbon less electron attracting. We have done this in a number of different ways with STO-3G calculations. First, we increased all the hydrogen nuclear charges and decreased the carbon charges keeping the net charge of the molecule neutral. Second, we increased the hydrogen charges and decreased the carbon charges for only one CH_2 group, leaving the other CH_2 group with normal nuclear charges and the whole molecule neutral. Finally, we increased the hydrogen nuclear charge, keeping the carbon with its normal nuclear charge. The results are presented in Table II and show clearly that the attrac-

Table II. Nuclear Charge Effects on $\theta(HCH)$ in Ethylene and Substituted Ethylenes

θ-(HCH)a	Z-(C1)	Z-(C2)	Z-(H1a,b)	Z-(H2a,b)	$\epsilon_1(a_1)$, aub	$\epsilon(b_2)$, auc	E_T, au
			STO-3G				
120	5.6	5.6	1.2	1.2	-0.517	-0.552	-66.68300
115	5.6	5.6	1.2	1.2	-0.531	-0.548	-66.68787
110	5.6	5.6	1.2	1.2	-0.545	-0.541	-66.68854
105	5.6	5.6	1.2	1.2	-0.558	-0.533	-66.68524
120	5.8	5.8	1.1	1.1	-0.524	-0.504	-71.79021
115	5.8	5.8	1.1	1.1	-0.538	-0.499	-71.79311
110	5.8	5.8	1.1	1.1	-0.551	-0.493	-71.79223
105	5.8	5.8	1.1	1.1	-0.564	-0.484	-71.78744
120	6.2	6.2	0.9	0.9	-0.525	-0.426	-82.52526
115	6.2	6.2	0.9	0.9	-0.536	-0.420	-82.52485
110	6.2	6.2	0.9	0.9	-0.547	-0.414	-82.52131
105	6.2	6.2	0.9	0.9	-0.558	-0.405	-82.51439
120	5.6	6.0	1.2	1.0	-0.516	-0.489	-71.88456
115	5.6	6.0	1.2	1.0	-0.521	-0.490	-71.88675
110	5.6	6.0	1.2	1.0	-0.526	-0.490	-71.88703
105	5.6	6.0	1.2	1.0	-0.531	-0.489	-71.88536
120	5.8	6.0	1.1	1.0	-0.523	-0.479	-74.43285
115	5.8	6.0	1.1	1.0	-0.529	-0.478	-74.43428
110	5.8	6.0	1.1	1.0	-0.534	-0.476	-74.43383
105	5.8	6.0	1.1	1.0	-0.539	-0.473	-74.43145
120	6.2	6.0	0.9	1.0	-0.524	-0.441	-79.80034
115	6.7	6.0	0.9	1.0	-0.530	-0.437	-79.80027
110	6.2	6.0	0.9	1.0	-0.535	-0.432	-79.79869
105	6.2	6.0	0.9	1.0	-0.541	-0.426	-79.79546
120	6.0	6.0	1.2	1.0	-0.695	-0.640	-77.54197
115	6.0	6.0	1.2	1.0	-0.700	-0.640	-77.54391
110	6.0	6.0	1.2	1.0	-0.706	-0.639	-77.54402
105	6.0	6.0	1.2	1.0	-0.710	-0.638	-77.54221
120	6.0	6.0	1.4	1.0	-0.856	-0.796	-78.03693
115	6.0	6.0	1.4	1.0	-0.860	-0.797	-78.03819
110	6.0	6.0	1.4	1.0	-0.864	-0.798	-78.03977
105	6.0	6.0	1.4	1.0	-0.867	-0.799	-78.03955
			"Double ζ"				
120	5.6	5.6	1.2	1.2	-0.583	-0.592	-67.55739
115	5.6	5.6	1.2	1.2	-0.597	-0.586	-67.56095
110	5.6	5.6	1.2	1.2	-0.611	-0.579	-67.56113
105	5.6	5.6	1.2	1.2	-0.625	-0.571	-67.55780
			1,1-Difluoroethylene "H1a,b = F1a,b"				
120	6.4	6.0	8.8	1.0	-0.419	-0.417	-267.46240
115	6.4	6.0	8.8	1.0	-0.424	-0.414	-267.46471
110	6.4	6.0	8.8	1.0	-0.422	-0.413	-267.46400

a HCH angle; when both ends of the molecule had changed nuclear charges, both ends had their HCH angle varied; if only one end had altered charges, the other HCH angle was fixed at 120°. b Highest occupied a_1 orbital energy (no node between geminal H's). c Highest occupied b_2 orbital energy (node between geminal H's).

tive interaction in fluoroethylenes is an *electronegativity* effect and *not* due to "lone-pair" interactions since there are no lone pairs in our model system. As one

increases the H nuclear charge, making it more electronegative, the HCH angle shrinks and as one decreases the H nuclear charge the HCH angle increases. One "double ξ" search with ethylene found the same trend.

We carried out the same type of calculation with 1,1-difluoroethylene (Table II), and *decreasing* the C–F electronegativity difference increased the FCF angle, as expected from our previous results. Thus, we have shown that the smaller XCX angle in 1,1-difluoroethylene than in ethylene is due mainly to electronegativity differences and *not* to lone-pair interactions (results are summarized in Table III).

Table III. Minimum Energy Angles for Ethylene and 1,1-Difluoroethylene

System	θ(XCX)
Ethylene: STO-3G; normal nuclear charges	116.2
$Z(C_1) = Z(C_2) = 5.6$; $Z(H_1) = Z(H_2) = 1.2$	111.6
$Z(C_1) = Z(C_2) = 5.8$; $Z(H_1) = Z(H_2) = 1.1$	113.7
$Z(C_1) = Z(C_2) = 6.2$; $Z(H_1) = Z(H_2) = 0.9$	118.0
$Z(C_1) = 5.6$; $Z(C_2) = 6.0$; $Z(H_1) = 1.2$; $Z(H_2) = 1.0$	111.8
$Z(C_1) = 5.8$; $Z(C_2) = 6.0$; $Z(H_1) = 1.1$; $Z(H_2) = 1.0$	113.7
$Z(C_1) = 6.2$; $Z(C_2) = 6.0$; $Z(H_1) = 0.9$; $Z(H_2) = 1.0$	117.6
$Z(C_1) = Z(C_2) = 6.0$; $Z(H_1) = 1.2$; $Z(H_2) = 1.0$	112.3
$Z(C_1) = Z(C_2) = 6.0$; $Z(H_1) = 1.4$; $Z(H_2) = 1.0$	108.5
Ethylene: double ξ; normal nuclear charges	116.0
$Z(C_1) = Z(C_2) = 5.6$; $Z(H_1) = Z(H_2) = 1.2$	112.3
1,1-Difluoroethylene: normal nuclear charges	111.0
$Z(C_1) = 6.4$; $Z(C_2) = 6.0$; $Z(F) = 8.8$; $Z(H) = 1.0$	113.7

It should also be pointed out that the Mulliken overlap population is more repulsive for the "pseudoethylenes" (H's more electronegative) than ethylene at θ(HCH) = 120°, despite the fact that the optimum energy angle is smaller for the former system. Thus one should use Mulliken overlap populations with considerable caution in interpreting "bonding" interactions.

Electron Density Differences. If there are some attractive forces between the fluorines in 1,1-difluoroethylene and *cis*-1,2-difluoroethylene, perhaps the electron density distribution in these compounds might reveal the nature of this attraction. We have used the wave functions from our STO-3G calculations in
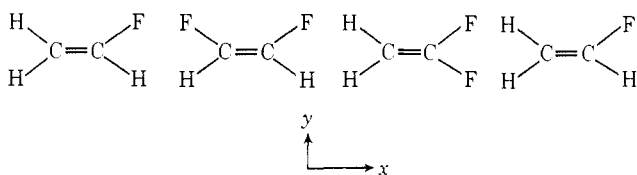
and compared the electron densities in the $+x$, $+y$ quadrant. If there is F · · · F attraction in *cis*-1,2- and 1,1-difluoroethylenes, then one might expect charge build-up along the $+x$ axis ($y = 0$) in 1,1-difluoroethylene and along the $+y$ axis ($x = 0$) in *cis*-1,2-difluoroethylene (compared to monofluoroethylene). In neither case does one actually find an increase of charge directly between the fluorines in the difluoroethylenes relative to monofluoroethylene.

If one compares the electron density in "pseudoethylene" ($Z(C) = 6.0$ and $Z(H_1) = 1.2$) and ethylene

one finds that in "pseudo-ethylene" there is charge build-up around the more electronegative hydrogens but nonetheless charge lost along the $+x$ axis (along the line bisecting the XCX angle). However, if one compares the charge lost along the $+x$, $+y$ axis and various intermediate directions extending from the carbon, one notes that there is more charge loss on the "outside" of the C–X bond than the "inside." Thus one might speculate that the "hydrogens" move in the direction where more charge remains. This is similar to the Mellish–Linnett analysis which implies charges in carbon hybridization, so an examination of the localized orbitals of these molecules can shed further light on this problem.

Localized Orbitals in Fluoroethylenes. We have used the Edmiston–Ruedenberg[11] method to determine the localized valence orbitals in these molecules. The orbitals for C–H and C–F bonds turn out to look like the classical chemical picture of a two-electron bond, with most of the charge density built-up between the nuclei.

The localized orbitals for the C=C linkage turn out to be the "banana bond" representation of the double bond. Table IV presents the directionality and per

Table IV. Localized Orbitals in Substituted Ethylenes

Molecule[a]	Bond[b]	C hybrid[c]		F hybrid Direction
		% s	Direction	
Ethylene	C–H	37.2	57.5	
	C–C	37.4	56.4	
Pseudo-ethylene;	C–H₁	34.6	55.3	
$Z(H_1)_{a,b} = 1.2$;	C–H₂	37.8	58.8	
other charges normal	C–C₁*	39.4	59.2	
	C*–C₁	37.6	53.7	
Monofluoroethylene	C₁–F	39.6	57.6	61.1
	C–H_gem	39.2	55.0	
	C–H_cis	37.1	57.9	
	C–H_trans	37.5	58.2	
	C–C₁*	41.6	55.9	
	C*–C₁	34.6	57.6	
1,1-Difluoroethylene;	C₁–F	41.1	54.8	62.5
θ(FCF) = 120°	C–H	37.9	58.7	
	C–C₁*	47.4	55.7	
	C*–C₁	31.2	59.0	
1,1-Difluoroethylene;	C₁–F	39.7	54.8	
θ(FCF) = 110°	C–H	38.2	58.9	
	C–C₁*	50.4	55.8	
	C*–C₁	29.8	59.5	
cis-1,2-Difluoroethylene	C–F	39.8	57.9	61.1
	C–H	39.9	56.0	
	C–C	38.4	57.2	
trans-1,2-Difluoroethylene	C–F	40.2	58.3	
	C–H	39.5	55.7	
	C–C	38.6	57.1	
Difluoromethane	C–H	31.9	56.4	
	C–F	35.9	53.5	55.0

[a] For ethylene and "pseudo-ethylene" $\theta = 120$, R(C=C) = 1.32 Å, and R(CH) = 1.09 Å; for the fluoroethylenes, unless noted otherwise, $\theta = 120°$, R(C=C) = 1.31 Å, R(CF) = 1.32 Å, and R(CH) = 1.09 Å. [b] Asterisk denotes the carbon hybrid reported. [c] Per cent s character determined by summing the squares of the coefficients of the carbon AO contribution to the localized orbital and dividing this into the square of the carbon 2s AO coefficient.

cent s character of the hybrid orbitals which contribute to the various localized orbitals. For the C=C linkage, the per cent s character is expressed for the "σ" bond; that is the per cent s contribution to the banana bond orbital is doubled to translate our results on per cent s

character for the σ hybrid, assuming the π bond is pure p. The "direction" for a carbon hybrid refers to its angle with respect to the x(C=C) axis. The "direction" for an F hybrid refers to its orientation with respect to the x axis (the molecule is in the xy plane).

Comparing ethylene and "pseudo-ethylene," one finds that valence bond "rehybridization" arguments well describe the localized orbitals. As one makes H more electronegative, the C–H' ($Z = 1.2$) hybrid has less s character and points more toward the x axis. This calculation at θ(H'CH') = 120° predicts that the H'CH' angle will be smaller than the HCH angle in ethylene, a prediction which is borne out by the geometry optimization. Similarly for 1,1-difluoroethylene at θ(FCF) = 120° the hybrid points significantly inward (54.8°), thus predicting a much smaller FCF angle. In both ethylene and 1,1-difluoroethylene, like water, the hybrid points somewhat inward relative to the line between the atoms. In cis- and trans-1,2-difluoroethylenes, the C–H hybrid points more inward than the C–F, so one would expect the CCH angle to be larger than the CCF by about 2°. A microwave study by Laurie and Pence[19] found θ(FCC) = 122.1° and θ(HCC) = 124° and our calculations are in agreement with their findings. However, the direction of the localized orbitals is less successful in rationalizing the geometrical parameters in monofluoroethylene, where one would expect θ(CCF) to be smaller than θ(CCH$_{gem}$). Laurie[20] found these angles to be approximately identical. In general, however, the directions of the localized orbitals do foreshadow geometry variations and might be useful in speeding up geometry searches in *ab initio* calculations or in giving insight into the minimum energy geometry when the cost of a search is prohibitive.

When one examines the per cent s character in the carbon hybrids in the fluoroethylenes, one finds that the carbon hybrids in the C–F bonds have more s character than those in the C–H bonds, in contrast to the usual VB description of the bonding. Of course, in these same systems, the s character of the hybrid used in the C–C bond is also higher, so one might argue that one has fractionally less s character (relative to the total s character used in all the hybrids around a given carbon) in the C–F bond.

However, a precise comparison between the "per cent s character" derived from localized MO's and that inferred from valence bond perfect pairing arguments is difficult, since the VB theory constrains the C hybrids to be totally 25% s and 75% p, whereas the more flexible MO theory can use, and actually does, flexible amounts of s and p character for bonding around a given atom. For example, one can see all the bonds around a given carbon in H_2CCF_2 have more than 30% 2s character.

One has noted that in X–C–H, as X is made more electronegative, the ^{13}C–H coupling constant increases. This has been interpreted[1] in terms of more "p character" in the C–F bond and more "s character" remaining in the C–H bond. As one can see clearly from Table IV (cis-1,2- and trans-1,2-difluoroethylene vs. ethylene), the fact that the C–F bond has more "s character" than the C–H does not preclude the C–H bond in the fluoroethylenes from having more "s

character" than the C–H bond in ethylene (the product of the coefficients of the carbon 2s and hydrogen 1s orbital is also greater in the fluoroethylenes than in ethylene), thus making the increased $J(^{13}$C–H) still explicable in terms of the s character in the C–H bond.

A Mechanism for θ(XCX) Shrinkage is X Is Made More Electronegative. A simple molecular orbital explanation for the smaller XCX angle when X is made more electronegative comes from consideration of the nature of the a_1 and b_2 orbitals of the system, which are depicted in the Scheme I. By comparing the least

Scheme I. AO's Which Contribute to a_1 and b_2 MO's of CH_2 Fragment
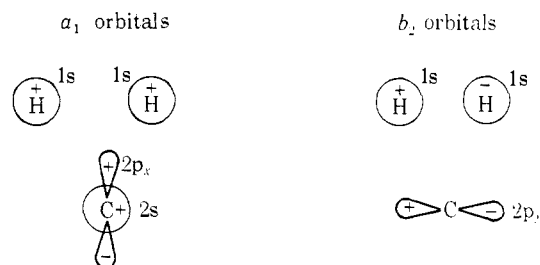
tightly bound orbital energies of the "pseudo-ethylenes" in Table II with those for ethylene ($\theta = 120°$; $\epsilon(a_1) = -0.525$; $\epsilon(b_2) = -0.461$), one finds that the b_2 orbital is considerably stabilized by electronegativity changes and the a_1 relatively little affected. For example, at the same geometry for pseudo-ethylene ($Z(H) = 1.2$, $Z(C) = 5.6$), the b_2 orbital has been stabilized relative to ethylene by 0.087 au and is lower than the a_1 orbital ($\epsilon(a_1) = -0.517$, $\epsilon(b_2) = -0.548$). The more tightly bound and virtual b_2 and a_1 orbitals behave similarly; the b_2 orbitals are significantly stabilized by an electronegativity increase on the external atoms and the a_1 orbitals are relatively little affected. The electronegative atom is withdrawing more electrons from the p_y AO on the carbon than from the carbon s and p_x because a function with a node between the fluorines builds up more charge *at* the more electronegative fluorines. In this way, the carbon s and p_x orbitals contribute relatively more to the C–F bonding than the p_y and the fluorines move in toward the x axis to take advantage of the location of higher electron density. In comparing ethylene and pseudo-ethylene ($Z(H_{1a,b}) = 1.2$, all other charges normal), one finds that the carbon to which the more electronegative H's are bound loses 0.078 electron from its 2s orbital, 0.041 from its p_x, and 0.153 from its p_y and gains 0.163 in its p_z orbital. The crucial factor in determining the BAB angle is *not* the s character in the A–B bonding orbitals but the relative amounts of p_x and p_y atomic orbital occupancy. Comparing ethylene and 1,1-difluoroethylene, the carbon to which the fluorines are bonded loses a total of 0.419 electron; the 2s atomic orbital loses 0.087, the p_x 0.066, and the p_y 0.301 and the p_z orbital gains 0.035 when fluorines replace hydrogens. The other carbon is much less perturbed by the fluorine addition, gaining a total of 0.068 electron.

We summarize our results as follows. (1) The smaller XCX angle in 1,1-fluoroethylene is due to a larger withdrawal of charge from the carbon p_y AO than the p_x, thus causing the fluorines to move in toward the position of higher electron density (we found similar results in our examination of the electron den-

(19) V. Laurie and D. T. Pence, *J. Chem. Phys.*, **38**, 2693 (1963).
(20) V. Laurie, *J. Chem. Phys.*, **34**, 291 (1961).

sities in the fluorocarbons). (2) The orbital energy differences between the b_2 and a_1 orbitals may give some insight into the trends in BAB angles in different molecules. For example, comparing the "double ζ" wave functions for ethylene and 1,1-difluoroethylene, one finds for the highest occupied orbitals $\epsilon(b_2) - \epsilon(a_1) = 0.08$ in ethylene and 0.02 in 1,1-difluoroethylene.

More General Implications of These Results. Before proceeding further, we might inquire what Walsh's rules have to say about the geometries of the system; can one predict the relative geometry of ethylene and 1,1-difluoroethylene by examining the sum of orbital energies as a function of XCX angle? The answer is clearly no: the sum of orbital energies is still decreasing as one increases the FCF angle to $120°$; the sum of orbital energies of ethylene has its minimum at $\theta(\text{HCH})$ less than $105°$. These results are not too surprising since Walsh's rules are usually not quantitatively useful.[21a] Our results and analysis predict for a general AB_2 fragment that the BAB angle will decrease as B becomes more electronegative. A trivial extension of our results is to the bond angles in CH_2, CF_2, and CH_2F_2. As expected, the bond angle in $CF_2(^3B_1)$ is about $10°$ smaller than that in $CH_2(^3B_1)$.[21b] In addition the FCF angle in CH_2F_2 is smaller than the HCH.[21c] The fact that $\theta(\text{ClCCl})$ in 1,1-dichloroethylene is between the angles found for 1,1-difluoroethylene and ethylene is consistent with the order of electronegativity $F > Cl > H$. Comparing H_2CO, Cl_2CO and F_2CO,[22] one finds the XCX angle for $X = H$, Cl and F to be 118, 111, and 108 degrees.

Consider the bond angles in Li_2O, H_2O, and H_2S.[23] The minimum energy bond angle decreases in this series (180, 105, 92) as the external atom becomes more electronegative. The highest occupied a_1–b_2 orbital energy gap is 0.061 au for Li_2O, 0.154 au for H_2O, and 0.123 au for H_2S (all at the experimental geometries), with the a_1 lying lower. In H_2S there is a low-lying a_1 orbital at -0.95 au; the next orbital energy in H_2O is -1.36 au. In a qualitative way, the BAB angle correlates with the a_1–b_2 orbital energy gap but we can see this correlation fails if we only consider the top two MO's of H_2O and H_2S. A simple ionic model also rationalizes the fact that Li_2O had a greater bond angle than H_2O.

A comparison of H_3O^+, NH_3, and CH_3^- shows that the bond angle decreases (112, 107, 105)[24] as the external atom becomes more electronegative (relative to the central atom). In this case, one would expect that the more tightly held the e orbital (antibonding) is relative to the a_1 orbital (bonding) the smaller the HXH angle, and this is indeed the case; the $\Delta\epsilon$ (a_1–e) is 0.20, 0.27, and 0.30 au for H_3O^+, NH_3, and CH_3^-.

A most intriguing set of geometry variations is found in the alkaline earth dihalides MX_2. As one goes down the periodic table for $X = F$ (BeF_2, MgF_2, . . .), the bond angle shrinks, and, if one takes a given metal and goes to heavier halogens, the bond angle widens. Both of these trends are consistent with the bond angle dependence on electronegativity mentioned above; as the external atom becomes more electronegative relative to the central atom, the bond angle shrinks. Unfortunately, the highest occupied b_2 and a_1 orbitals are nearly degenerate in BeF_2[25] and CaF_2[26] and one sees no clear trend in the orbital energy differences in these systems, unlike the AH_3 molecules discussed in the previous paragraph. Hayes[27] has rationalized the geometry trends in these systems invoking increased d orbital participation in the bonding and Büchler, et al.,[28] have stated that an ionic polarizability model is satisfactory for a qualitative explanation of these trends. These are reasonable explanations, but the above discussion indicates that electronegativity effects lead one to expect the same trend.

The series of alkali metal oxides M_2O is interesting because the angle *decreases* as one makes the external atom less electronegative. Li_2O is definitely linear and Cs_2O has a bond angle of $\sim135°$.[29] This trend is opposite to the trend observed in all of the molecules discussed previously; here the less electronegative the external atom the smaller the bond angle. Here, a simple ionic model taking into account the polarizabilities of the end atoms does the best job at rationalizing the structural properties of the alkali oxides, although it might be interesting to examine further the electronic structure of Li_2O, Na_2O, and K_2O and see if there are any specific orbital effects contributing to the bending of M_2O from linearity.

Bingham and Dewar[30] have pointed out that simple electronegativity arguments do not explain the difference in geometries in substituted methyl radicals. However, an examination of the nature of the C–C bonding orbitals in $C(CH_3)_3$ compared to $C(CF_3)_3$ might reveal that the methyl carbon is *less* electronegative relative to the radical carbon in the latter case, thus allowing one to rationalize the structural differences in terms of the arguments presented above.

This discussion of "general implications" is tentative and as pointed out in the above cases other explanations for the structural changes exist. However, the same type of reasoning employed here for the fluoroethylenes might provide a general way of looking at all these cases.

Summary and Future Issues

One can briefly summarize the conclusions of this paper. We have shown: (1) that the smaller BAB angle in 1,1-difluoroethylene than in ethylene is due to a preferential charge withdrawal from the b_2 symmetry AO (p_y orbital) on the carbon, thus pulling the fluorines in to

(21) (a) R. J. Buenker and S. D. Peyerimhoff, *Chem. Rev.*, **74**, 127 (1974); (b) J. F. Harrison and C. W. Eakers, *J. Amer. Chem. Soc.*, **95**, 3467 (1973); (c) S. P. Porto, *J. Mol. Spectrosc.*, **3**, 248 (1959).

(22) "Tables of Interatomic Distances and Angles," *Chem. Soc., Spec. Publ.* (1965).

(23) The orbital energies for Li_2O taken from R. J. Buenker and S. Peyerimhoff, *J. Chem. Phys.*, **45**, 3682 (1966); those from H_2O from P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 6101 (1970), and those for H_2S from M. E. Schwartz, *J. Chem. Phys.*, **51**, 4182 (1969). All calculations were of "double ζ" quality and as Rauk, *et al.*,[24] show, there is relatively little basis set dependence or orbital energies beyond the "double ζ" level.

(24) NH_3: A. Rauk, E. Clementi, and L. C. Allen, *J. Chem. Phys.*, **53**, 4133 (1970); H_3O^+: P. Kollman and C. F. Bender, *Chem. Phys, Lett.*, **21**, 271 (1973); CH_3^-; R. Kari and I. Csizmadia, *J. Chem. Phys.*, **50**, 1443 (1969).

(25) S. Rothenberg and H. F. Schaeffer III, *J. Amer. Chem. Soc.*, **95**, 2095 (1973).

(26) D. R. Yarkony, W. H. Hunt, and H. F. Schaeffer III, *J. Chem. Phys.*, in press.

(27) E. F. Hayes, *J. Phys. Chem.*, **70**, 3740 (1966).

(28) A. Büchler, J. L. Stauffer, and W. Klemperer, *J. Amer. Chem. Soc.*, **86**, 4544 (1964).

(29) R. C. Spiker and L. Andrews, *J. Chem. Phys.*, **58**, 713 (1973).

(30) R. C. Bingham and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **95**, 7182 (1973).

take advantage of the greater charge remaining in the $C(2p_x)$; (2) this decrease in bond angle in AB_2 systems as B becomes more electronegative is expected to be a general result, not dependent on the presence of "lone pairs" on the external atoms. This dependence of geometry on electronegativity has been previously discussed in terms of "rehybridization," but we have shown that it is equally explicable using MO concepts. The MO description is probably a superior one because one can often relate the bond angle trends to differences in b_2 and a_1 orbital energies, which can be measured in photoelectron spectroscopy.

Interesting future issues include the following. (1) An attempt to understand the geometry of the alkali oxides, which appear to be an exception to the general electronegativity rule. (2) Geometry changes in rigid ring systems[31] on electronegative substitution may well be made explicable by considering the geometry variations in the model system
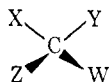
as X, Y, Z, and W undergo electronegativity changes. (3) Attempts to quantify the orbital energy differences and their changes with angle might involve the IC–SCF procedure[32] for determining the orbital energies and Bartell's second-order Jahn–Teller formalism[33] for examining their angle dependence. (4) Finally, we have not given a definitive answer to the question posed in our title. As Pople pointed out,[12] the experimental evidence is clear in terms of increased C–F bond strength in fluoromethanes with increased fluorine sub-

stitution and this can be explained simply by noting that successive fluorine substitution makes the C–F bonds more ionic and, thus, stronger. Therefore, one does not have to invoke "nonbonded attraction" to explain the exothermicity of reactions like $2CH_3F \rightarrow CH_4 + CH_2F_2$ and $2CH_2CHF \rightarrow C_2H_4 + CH_2CF_2$.[34] In comparing the Mulliken populations on the carbon for ethylene, monofluoroethylene, and 1,1-difluoroethylene, one finds a near linear decrease in charge, indicating that in monofluoroethylene the C–F carbon finds it energetically favorable to donate as much charge as the carbon in ethylene to a fluorine substituent. Thus, the evidence appears strong that in AB_2 molecules (or fragments) "nonbonded attractions" are more likely to be due to changes in the nature of the A–B bonds than to specific $A \cdots A$ "attractive forces."

(31) C. M. Weeks, W. L. Duax, and M. E. Wolff, *J. Amer. Chem. Soc.*, **95**, 2865 (1973); and P. A. Kollman, D. D. Giannini, W. L. Duax, S, Rothenberg, and M. E. Wolff, *ibid.*, **95**, 2869 (1973).

(32) S. T. Elbert, S. R. Langhoff, and E. R. Davidson, *J. Chem. Phys.*, **57**, 2005 (1972).

(33) L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968).

(34) Compilations of thermochemical data ((1) D. R. Stull and H. Prophet, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 37 (1971), and (2) "Thermochemistry of Organic and Organometallic Compounds," J. D. Cox and G. Pilcher, Ed., Academic Press, New York, N. Y., 1970) indicate that the reactions $2CH_3F \rightarrow CH_4 + CH_2F_2$ and $2C_2H_3Cl \rightarrow C_2H_4 + CH_2CCl_2$ are exothermic by 13.7 and 4.2 kcal/mol, respectively. There are no data on vinyl fluoride (C_2H_3F), but from the above it is very likely that $2C_2H_3F \rightarrow C_2H_4 + CH_2CF_2$ is exothermic, indicating an energetic driving force for geminal C–F bonds. This effect does not continue through CF_4, since the heats for the reactions, $2CH_2F_2 \rightarrow CHF_3 + CH_3F$ and $2CHF_3 \rightarrow CH_2F_2 + CF_4$ are -2.8 and $+2.3$ kcal/mol. It should also be noted that further support for the fact that there is no attraction in *cis*-1,2-difluoroethylene (compared to 1,1-difluoroethylene) comes from the fact that the enthalpy for the reaction $2CH_2CF_2 \rightarrow C_2H_4 \rightarrow C_2F_4$ is $+15.5$ kcal/mol.

A Model Calculation of the Intramolecular Vibration Spectrum of Liquid Water

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Abstract: The eigenfrequency spectrum corresponding to intramolecular vibrations in the Weres–Rice model of water is calculated. Additional assumptions, beyond those fundamental to the water model, must be employed to convert the calculated spectrum to a form which can be compared with experimental data. It is shown that the spectrum predicted by the Weres–Rice model is not in disagreement with the observed infrared and Raman spectroscopic data.

The analysis of the vibration–rotation spectrum of an isolated molecule has been used successfully, for many years, to obtain information about its structure. Indeed, much of our knowledge of chemical bonding is derived from studies of this kind. In contrast, the available studies of infrared and Raman spectra of liquids, wherein molecules interact strongly, have not

yielded much direct information about their structure. In part this failure merely reflects the inadequacy of current theories of the liquid state. However, in part it also stems from the nature of the recorded spectra, which generally only show broad features which are difficult to correlate with properties of the liquid structure. Spectroscopic studies of the liquid state are,