Hybridization Effects in Fluorocarbons

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Hybridization calculations based on experimental bond-angle data show that the carbon hybrid atomic orbitals in double bonds, carbonyls, and cyclopropyl groups containing a *gem*-difluoro group are not sp^2 hybridized as formerly thought, but are sp^3 hybridized. This is also true of the trifluoromethyl free radical. This new understanding of the hybridization in fluorocarbons makes possible an explanation of the unusual chemical reactivity of perfluoroolefins and perfluorocyclopropanes. While the carbon HAOs used in forming the C—F bonds in these compounds are sp^3 hybridized as in saturated fluorocarbons, with the C—F bonds having approximately the same bond energies, those used in forming the C—C bonds have less p character than in the corresponding hydrocarbons.

The unique chemical reactivity and unusual physical properties of fluorocarbons, due to the high electronegativity of fluorine, places these compounds in a class of their own. A theoretical understanding of some of their behavior is still lacking, however. In this paper a localized molecular orbital (LMO) theory is developed to explain the chemical reactivity of strained fluorocarbon systems containing *gem*-difluoro groups.

Bent has proposed that a rehybridization occurs at carbon centers when a substituent is replaced by one of differing electronegativity, and that more p character tends to be concentrated in carbon orbitals directed toward more highly electronegative groups.[1] On the basis of this theory one would expect that the carbon hybrid atomic orbitals (HAO's) used in forming C—F bonds should have more p character than those used in forming C—H bonds, and that the HAO's used in forming the C—C bonds in fluorocarbons should have more s character. If such hybridization changes are dramatic enough it would be expected that the effects would show up in the chemical reactivity of fluorocarbons.

Hybridization Measurement.—Numerous approaches to the calculation of hybridization at carbon centers have been taken. Perhaps the most straightforward approach to a measure of hybridization is the relationship with bond angles. The states of hybridization of carbon centers with local C_{3v}, C_{2v}, and C_s symmetry can be calculated from known bond angles,[2-4] and these procedures have been used herein. Bond-angle data can also be used to calculate the state of hybridization at trigonally, though not equivalently, hybridized carbon centers, for example, in unsymmetrically substituted olefins.[5]

During the period when good experimental bond-angle data for a multitude of compounds was becoming available from microwave and electron diffraction work it was suggested that the nmr spin–spin coupling constant $J_{^{13}\mathrm{C-H}}$ offered a direct measure of the hybridization of the carbon HAOs used in forming the C—H bonds in organic compounds.[6-8] The states of carbon hybridization in halomethanes calculated from $J_{^{13}\mathrm{C-H}}$ were found to be greatly different from those calculated from bond-angle data, and on this basis it was largely concluded that bond angles did not serve as a measure of hybridization.[7a] Recent work, however, has shown that electronegative substituents bonded to a carbon center can change the effective nuclear charge at that carbon as seen by a proton also bonded to that center without changing the carbon hybridization.[9-12] Because of this fact, in those cases where heteroatoms are bonded to carbon, as in halomethanes, $J_{^{13}\mathrm{C-H}}$ cannot be taken as a measure of the per cent s character in the C—H bond(s). It has also been observed that $J_{^{13}\mathrm{C-F}}$ is not a measure of the carbon hybridization in fluorocarbons.[7b]

There is one piece of experimental evidence which does not appear to be consistent with simple bond-angle–hybridization relationships, and that is the fact that in methylene chloride both the H—C—H and Cl—C—Cl bond angles are greater than 109°28′. The Cl—C—Cl bond angle was found by Myers and Gwinn to be 111°47′ while the H—C—H angle is 112°58′.[13] Nuclear quadrupole studies by Flygare and Gwinn showed that the Cl—C—Cl bonds are not bent.[14] For this Cl—C—Cl bond angle the assumption of normalized, orthogonal carbon HAO's requires that the H—C—H bond angle be 107°17′. The data for methylene fluoride fits with theoretical bond angles much better. The experimental values for the F—C—F and H—C—H bond angles are 108°17′ ± 6′ and 111°52′ ± 25′, respectively.[15] For this F—C—F angle the predicted H—C—H angle is 110°42′.

To the extent that the bonding at carbon centers can be described by normalized, orthogonal HAO's formed from linear combinations of atomic orbitals using a limited basis set of carbon 2s, $2p_x$, $2p_y$, and $2p_z$ AO's the bond-angle–hybridization relationship is valid. Since this assumption has served as a very useful and valuable basis for the interpretation of structure and reactivity in organic chemistry, it seemed worthwhile to apply the bond-angle–hybridization relationships to fluorocarbons, keeping in mind possible limitations in the assumption.

Hybridization in Fluorocarbons.—Table I lists the experimentally determined bond angles and the corresponding hybridization states, calculated by afore-

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(1) H. A. Bent, *J. Chem. Phys.*, **33**, 1258, 1259, 1260 (1960).

(2) P. Tarkington, *ibid.*, **19**, 528 (1951).

(3) W. H. Flygare, *Science*, **140**, 1179 (1963).

(4) W. A. Bernett, *J. Chem. Educ.*, **44**, 17 (1967).

(5) C. A. Coulson, "Victor Henri Commemoratif Volume," Maison Desoer, Liege, 1947–1948, p 15.

(6) J. Shoolery, *J. Chem. Phys.*, **31**, 1427 (1959).

(7) (a) N. Muller and D. E. Pritchard, *ibid.*, **31**, 768, 1471 (1959); (b) N. Muller and D. T. Carr, *J. Phys. Chem.*, **67**, 112 (1963).

(8) C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).

(9) D. M. Grant and W. M. Litchman, *J. Amer. Chem. Soc.*, **87**, 3994 (1965).

(10) W. J. Considine, *J. Chem. Phys.*, **42**, 1130 (1965).

(11) J. E. Huheey, *ibid.*, **45**, 405 (1966).

(12) A. W. Douglas, *ibid.*, **45**, 3465 (1966).

(13) R. J. Myers and W. D. Gwinn, *ibid.*, **20**, 1420 (1952).

(14) W. H. Flygare and W. D. Gwinn, *ibid.*, **36**, 787 (1962).

(15) D. R. Lide, Jr., *J. Amer. Chem. Soc.*, **74**, 3548 (1952).

TABLE I

BOND ANGLES AND CARBON HYBRIDIZATION IN TRIFLUOROMETHYL AND METHYL GROUPS

	∠FCF	C—F, sp	∠HCH	C—H, sp	C—F, Å	Ref
CF_3CH_3	107°18′ ± 1°	3.36			1.335 ± 0.005	*a*
$CF_3C{\equiv}CH$	107°30′ ± 1°	3.33			1.335 ± 0.01	*b*
$CF_3C{\equiv}CCF_3$	107°30′ ± 1°	3.33			1.34 ± 0.02	*c*
$CF_3C{\equiv}CCH_3$	107°32′	3.32	108°44′	3.11	1.340	*d*
CF_3CF_3	108° ± 1°30′	3.24			1.330 ± 0.015	*e*
CF_3I	108°24′ ± 1°36′	3.17			1.34 ± 0.02	*f*
CF_3CN	108°30′ ± 1°30′	3.15			1.335	*g*
CF_3Cl	108°36′ ± 24′	3.14			1.328 ± 0.002	*h*
CF_3H	108°48′ ± 45′	3.10		2.72	1.332 ± 0.008	*i*
CF_4	109°28′	3.00			1.323 ± 0.005	*j*
CH_3SiH_3			107°42′ ± 30′	3.29		*k*
CH_3GeH_3			108°25′ ± 30′	3.17		*l*
CH_3CH_3			109°45′	2.96		*m*
CH_3F		3.25	110°0′ ± 3′	2.92	1.3852 ± 0.0005	*n*
CH_3Cl			110°30′ ± 30′	2.86		*o*
CH_3Br			111°12′ ± 30′	2.76		*o*
CH_3I			111°24′ ± 30′	2.74		*o*

[a] W. F. Edgell, G. B. Miller, and J. W. Amy, *J. Amer. Chem., Soc.*, **79**, 2391 (1957). [b] J. N. Shoolery, R. G. Shulman, W. F. Sheehan, V. Schomaker, and D. M. Yost, *J. Chem. Phys.*, **19**, 1364 (1951). [c] W. F. Sheehan, Jr., and V. Schomaker, *J. Amer. Chem. Soc.*, **74**, 4468 (1952). [d] V. M. Laurie, *J. Chem. Phys.*, **30**, 1101 (1959). [e] J. L. Brandt and R. L. Livingston, *J. Amer. Chem. Soc.*, **76**, 2096 (1954). [f] C. Wong and V. Schomaker, *J. Chem. Phys.*, **28**, 1010 (1958). [g] M. D. Danford and R. L. Livingston, *J. Amer. Chem. Soc.*, **77**, 2944 (1955). [h] L. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, **23**, 1860 (1955). [i] S. N. Ghosh, R. Trambarulo, and W. Gordy, *ibid.*, **20**, 605 (1952). [j] C. G. Thornton, *Dissertation Abstr.*, **14**, 604 (1954). [k] R. W. Kilb and L. Pierce, *J. Chem. Phys.*, **27**, 108 (1957). [l] W. V. Laurie, **30**, 1210 (1959). [m] H. C. Allen, Jr., and E. K. Plylor, *ibid.*, **31**, 1062 (1959). [n] O. R. Gilliam, H. D. Edwards, and W. Gordy, *Phys. Rev.*, **76**, 195 (1949). [o] S. L. Miller, L. C. Aamodt, G. Dousmanis, C. H. Townes, and J. Kraitchman, *J. Chem. Phys.*, **20**, 1112 (1952).

mentioned methods,[2-5] for a number of methyl- and trifluoromethyl-containing compounds. Several interesting features are observed. In the case of trifluoromethyl groups it appears that the carbon HAO's used in forming the C—F bonds do have slightly more p character than those used in forming the C—H bonds in methyl groups, ranging from sp$^{3.00}$ to sp$^{3.36}$. There are, however, several examples where the HAO's used in forming the C—H bonds in methyl groups have a hybridization in this range when a more electropositive silicon or germanium atom is also bonded to the carbon. Second, it is observed that the hybridization of the carbon HAO's used in forming the C—F bonds in the series CF_4, CF_3H, CF_2H_2, and CFH_3 does show increasing p character (sp$^{3.00}$, sp$^{3.10}$, sp$^{3.18}$, and sp$^{3.25}$), as suggested by Bent to explain the increasing C—F bond length in this series. The C—F bond lengths will be influenced by the state of hybridization of the carbon HAO and the fluorine bonding HAO (which need not be the same in each case) and also by nonbonded interactions which will affect the degree bond orbital overlap. In general, although there appears to be slightly more p character in the carbon HAO's used in forming C—F bonds at tetrasubstituted carbons, they appear to be essentially sp^3 hybridized. Symmetry requires that the HAO's of carbon used in forming the C—F bonds in tetrafluoromethane be sp^3 hybridized.

Table II shows the bond angles and hybridization states of a number of methylene- and difluoromethylene-containing compounds. The most striking and significant conclusion to be drawn from this table is that *the carbon HAO's used in forming the C—F bonds in gem-difluoro groups remain essentially sp^3 hybridized even when that carbon center is part of a double bond, carbonyl group, or three-membered ring.* This conclusion is supported by the data on carbonyl fluoride, 1,1-difluoroethylene, tetrafluoroethylene, and difluorodiazirine. It is seen that in the corresponding hydrocarbons the carbon HAO's used in forming the C—H bonds are essentially sp^2 hybridized, as has been traditionally accepted for olefins, carbonyls, and cyclopropanes. It is also observed in the trifluoromethyl free radical that the carbon HAO's used in forming the C—F bonds are nearly sp^3 hybridized, in contrast to the approximately sp^2 hybridization of the HAO's used in forming the C—H bonds in the planar or nearly planar methyl free radical. It is worth pointing out in the case of all of the compounds in Table II containing *gem*-difluoro groups (except CF_2H_2) that within experimental error the C—F bond lengths are the same as in tetrafluoromethane and hexafluoroethane. This, when coupled with carbon sp^3 HAO's in each case, suggests that the C—F bonds in these compounds probably have about the same bond energy.

No firm conclusions can be drawn about the carbon HAO's used in forming the C—F bond at unsaturated centers bearing only a single fluorine substituent (see Table III) other than that the amount of p character is greater than that in sp^2 HAO's, ranging from sp$^{2.5}$ in fluoroethylene and *cis*-1,2-difluoroethylene to sp$^{3.32}$ in CH_3COF and sp$^{3.50}$ in HCOF. It should be pointed out in the case of hexafluorobenzene that symmetry requires the carbon HAO's used in forming the C—F bonds to be sp^2 hybridized or the C—C σ bonds to be bent.

Chemical Reactivity of Perfluoro Olefins.—The chemistry of fluoro olefins shows a number of unusual effects when compared with the behavior of the corresponding protonated olefins. Much of this work has been reviewed by Roberts and Sharts,[16] but a few examples will be cited. Tetrafluoroethylene (TFE) is observed to dimerize thermally to give octafluorocyclo-

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[16] J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 1 (1962).

TABLE II

BOND ANGLES AND HYBRIDIZATION IN DIFLUOROMETHYLENE AND METHYLENE GROUPS

	∠FCF	C—F, sp	∠HCH	C—H, sp	C—F, Å	Ref
CF_2H_2	108°17′ ± 6′	3.18	111°52′ ± 25′	2.83	1.358 ± 0.001	*a*
CF_2Cl_2	109°30′ ± 3°	3.00			1.33 ± 0.02	*b*
c-C_4F_8	109°30′ ± 3°	3.00			1.33 ± 0.02	*c*
$CF_2{=}O$	108°0′ ± 30′	3.24			1.312 ± 0.01	*d*
$CF_2{=}CH_2$	109°18′ ± 24′	3.03	121°48′	1.89	1.321 ± 0.005	*e, f*
$CF_2{=}CF_2$	110° ± 2°	2.92			1.33 ± 0.02	*g*
$CF_3\cdot$	111°6′	2.78				*h, i*
c-CF_2N_2	111°50′ ± 31′	2.69			1.315 ± 0.004	*j*
c-C_3H_4			114°42′ ± 10′	2.39		*k*
c-C_3H_6			115°12′ ± 1°	2.35		*l*
c-CH_2N_2			117° ± 2°	2.20		*m*
$CH_2{=}CH_2$			117°12′ ± 36′	2.19		*n*
$CH_2{=}C{=}CH_2$			118°12′ ± 12′	2.12		*o*
$CH_2{=}O$			119°20′ ± 30′	2.04		*p*
$CH_3\cdot$			~120°	2.00		*q, r*
$CH_2{=}C{=}O$			121°35′	1.91		*s*

[a] Reference 15. [b] R. L. Livingston and D. H. Lyon, *J. Chem. Phys.*, **24,** 1283 (1956). [c] H. P. Lemaire and R. L. Livingston, *J. Amer. Chem. Soc.*, **74,** 5732 (1952). [d] V. W. Laurie and D. T. Pence, *J. Chem. Phys.*, **37,** 2995 (1962). [e] W. F. Edgell, P. A. Kinsey, and J. W. Amy, *J. Amer. Chem. Soc.*, **79,** 2691 (1957). [f] W. V. Laurie and D. T. Pence, *J. Chem. Phys.*, **38,** 2693 (1963). [g] Reference 37. [h] R. W. Fessenden and R. H. Schuler, *ibid.*, **43,** 2704 (1965). [i] M. T. Rogers and L. D. Kispert, **46,** 3193 (1967). [j] J. L. Hencher and S. H. Bauer, *J. Amer. Chem. Soc.*, **89,** 5527 (1967). [k] P. H. Kasai, R. J. Myers, D. F. Eggers, Jr., and K. B. Wiberg, *J. Chem. Phys.*, **30,** 512 (1959). [l] O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Cryst.*, **17,** 538 (1964). [m] L. Pierce and V. Dobyns, *J. Amer. Chem. Soc.*, **84,** 2651 (1962). [n] L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitso, and J. E. Young, Jr., *J. Chem. Phys.*, **42,** 2683 (1965). [o] A. G. Maki and R. A. Toth, *J. Mol. Spectry.*, **17,** 136 (1965). [p] M. G. Krishna Pillai, *J. Annamallai Univ.*, **25,** 126 (1964). [q] T. Cole, H. O. Pritchard, N. R. Davidson, and H. M. McConnell, *Mol. Phys.*, **1,** 406 (1958). [r] L. Andrews and G. C. Pimentel, *J. Chem. Phys.*, **47,** 3637 (1967). [s] A. P. Cox, L. F. Thomas, and J. Sheridan, *Spectrochim. Acta*, **15,** 542 (1959).

TABLE III

BOND ANGLES AND CARBON HYBRIDIZATION IN FLUOROMETHYLENE GROUPS

	∠FCC	∠FCH	∠FCO	C—F, sp	C—F, Å	Ref
$CH_2{=}CHF$	120°54′	115°24′		2.53	1.334 ± 0.002	*a*
cis-$CHF{=}CHF$	122°	114°		2.49	1.335 ± 0.002	*b*
$CH_3CF{=}O$	110°44′ ± 1°		121°22′ ± 1°	3.32	1.348 ± 0.015	*c*
$CHF{=}O$		109°54′ ± 3°	122°46′ ± 30′	3.50	1.338 ± 0.005	*d*

[a] B. Bak, D. Christensen, L. Nygard, and J. R. Anderson, *Spectrochim. Acta*, **13,** 120 (1958). [b] See footnote *f*, Table II. [c] L. Pierce and L. C. Krishner, *J. Chem. Phys.*, **31,** 875 (1959). [d] R. F. Miller and R. F. Curl, Jr., *ibid.*, **34,** 1847 (1961).

butane,[17] with a standard heat of reaction of −50 kcal/mol,[18] while the corresponding reaction with ethylene (which has a theoretical heat of reaction of −18.7 kcal/mol, *vide infra*) has not been observed. Hexafluoro-1,3-butadiene undergoes thermal cyclization to form hexafluorocyclobutene,[19] while in the protonated analog the equilibrium lies on the side of the more stable 1,3-butadiene.[20] Perfluoropropene, chlorotrifluoroethylene, and 1,1-dichloro-2,2-difluoroethylene also dimerize thermally to four-membered-ring systems.[16] Neither of the 1,2-difluoroethylenes nor 1,1-difluoroethylene has been observed to dimerize. TFE also codimerizes with many nonfluorinated olefins, often more readily than it dimerizes with itself.[16] The heats of addition of halogens and halogen acids to perfluoroolefins are observed to be more exothermic than in the case of the corresponding hydrocarbon systems.[21] The heat of polymerization of TFE is 17 kcal/mol more exothermic than that of ethylene.[22]

It is clearly seen that the *gem*-difluoro group ($CF_2{=}$), or more specifically the group ($CF_2{=}CF{-}$), has a very marked effect on the position of olefin–cyclobutane equilibria. The greater exothermicity in going from C=C bonds to C—C bonds in fluorocarbon systems is large enough to offset the effects of ring strain. Two possible alternative explanations for this behavior have been clearly summarized by Schlag and Peatman,[23] namely, that the instability of the fluoro olefin system is due to (a) the C—F bonds being weaker than those in saturated systems (because the carbon HAO's are sp^2 hybridized) or (b) the C=C bond is weaker than a normal C=C double bond.

Cox has suggested that the double-bond strength is the same in fluorinated and nonfluorinated olefins, but that the C—F bonds in perfluoro olefins are weaker than in saturated fluorocarbons.[24] Peters has also made this assumption, theorizing that the C—F bond should be weaker because the fluorine should be less able to remove p electrons from an sp^2-hybridized carbon HAO than from an sp^3-hybridized carbon HAO;[25] *i.e.*, he assumed *a priori* that the carbon HAO's in fluoro olefins are sp^2 hybridized, although at one point in his argument he envisions nonorthogonal carbon HAO's.

Hine has suggested that on the basis of double bond–

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(17) B. Atkinson and A. B. Trenwith, *J. Chem. Soc.*, 2082 (1953).

(18) A. S. Rodgers, *J. Phys. Chem.*, **71,** 1996 (1967).

(19) M. Prober and W. T. Miller, Jr., *J. Amer. Chem. Soc.*, **71,** 598 (1949).

(20) W. P. Hansen and W. D. Walters, *J. Phys. Chem.*, **67,** 1328 (1963).

(21) C. R. Patrick, *Advan. Fluorine Chem.*, **2,** 1 (1961).

(22) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **86,** 622 (1964).

(23) E. W. Schlag and W. B. Peatman, *ibid.*, **86,** 1676 (1964).

(24) J. D. Cox, *Tetrahedron*, **18,** 1337 (1962).

(25) D. Peters, *J. Chem. Phys.*, **38,** 561 (1963).

no bond resonance the C—F bonds attached to an unsaturated carbon should be weaker than those attached to a saturated carbon atom.[26] This also assumes, however, that the unsaturated carbon is sp^2 hybridized and not sp^3 hybridized.

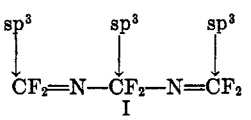
Schlag and Kaiser have concluded from a study of the heat of *cis–trans* isomerization of perfluorobutene-2 that the low activation energy, relative to butene-2, was due to the C=C bond being weaker in the perfluoro case.[27] They argued that, if the strain were in the C—F bonds rather than in the C=C bond, the activation energies should be about the same.

LMO Theory of Strained Fluorocarbons.—From the available structural data it appears that *the attachment of two fluorines to normally sp^2-hybridized carbon centers changes the hybridization to sp^3.* Such a hybridization change in olefins and cyclopropanes can be visualized in either of two equivalent LMO descriptions. For every possible σ—π bond description of the double bond there is an *equivalent* bent bond LMO description,[28] and for every Walsh-type[29] description of the cyclopropyl ring there is an *equivalent* bent bond LMO description.[4] The hybridization in ethylene is essentially sp^2, *i.e.*, three sp^2 HAO's and an unhybridized p orbital at each carbon in the σ—π bond description or, equivalently, two sp^2 HAO's and two sp^5 HAO's at each carbon in the equivalent bent bond description (the sp^5 HAO's used in forming the C=C bond). The angle between two sp^5 HAOs is 101°32′.[4] It is here suggested that the hybridization of the carbon HAO's in tetrafluoroethylene, and in other olefins containing *gem*-difluoro groups, is essentially sp^3, *i.e.*, two sp^3 HAO's (used in forming the C—F bonds) and an sp HAO along with any unhybridized p orbital (the former used in forming the σ bond and the latter the π bond), or, equivalently, four sp^3 HAO's at each carbon in the bent bond LMO description.[28b] The angle between two sp^3 HAO's is, of course, 109°28′.

From available thermochemical data it is possible to calculate the strain energies in tetrafluoroethylene and perfluorocyclobutane. Using a value of -98.1 kcal/mol for the standard heat of formation of a saturated $-CF_2-$ group,[30–32] the strain energy in tetrafluoroethylene is found to be 41.2 kcal/mol, while that in ethylene is 22.39 kcal/mol.[32,33] From the heat of formation of perfluorocyclobutane[18,34] its strain energy is found to be 32.0 kcal/mol, compared with 26.2-kcal/mol strain energy in cyclobutane.[35] With both the completely fluorinated and protonated four-membered rings having sp^3 carbon hybridization similar strain energies are not too surprising. A difference of about 3.9 kcal/mol would be expected based on the differences in the potential barrier to rotation in ethane and perfluoroethane.[36,37]

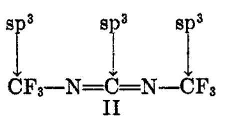
From a theoretical standpoint it would be expected that an sp^3-hybridized ethylene would be more "strained" than ethylene with sp^2–sp^5 hybridization. The increased C—H bond strength of the sp^2 C—H bonds relative to sp^3 C—H bonds [the overlap integrals using STO's are 0.734 (1.084 A) and 0.678 (1.107 Å), respectively] more than offsets the increased bond strength which would result from sp^3 bent C=C bonds rather than sp^5 bent C=C bonds [S = 0.454 and 0.449 (1.333 Å), respectively, compared with 0.650 (1.536 Å) for the sp^3 C—C bond in ethane]. Tetrafluoroethylene, having essentially sp^3 hybridization, would be expected to show a larger strain energy than ethylene, even though its C=C bent bonds should be slightly stronger than those of ethylene (the C=C bond length appears to be equal to, or slightly less than that in ethylene[37]), because its C—F bonds have not, because of the effects of Bent's rule, undergone the sort of strengthening that C—H bonds do relative to a saturated, straight-chain analog. While ethylene has stronger C—H bonds and weaker C—C bonds than $\lbrace CH_2—CH_2 \rbrace_n$, tetrafluoroethylene can be expected to have C—F bonds which have essentially the same bond energy as those in $\lbrace CF_2—CF_2 \rbrace_n$, and C—C bonds that are weaker. An sp^2–sp^5-hybridized TFE would be expected to have *both* weaker C—F and C=C bonds than the sp^3 case. The decrease in p character in the carbon HAO's forming the C—F bond in going from sp^3 to sp^2 would presumably lead to a decrease in the ionic contribution to the C—F bond.[1]

The driving force for the dimerization of TFE to perfluorocyclobutane, and for the dimerization and cycloaddition reactions of the CF_2=CF- group in general, can be seen to be the relief of double-bond strain, C—F bond strength remaining essentially constant. In the case of ethylene, while dimerization would lead to relief of double-bond strain, it would also lead to an increase in C—H bond "strain," or decrease in C—H bond energy, making this reaction less favorable than in the fluorinated system. The facile fluoride ion-catalyzed isomerization of perfluoro-2,4-diazapenta-1,4-diene (I) to the corresponding bis(trifluoromethyl)carbodiimide (II)[38] can also be understood from a hybridization standpoint. In going from I to II



$$\overset{\overset{sp^3}{\downarrow}}{C}F_2=N-\overset{\overset{sp^3}{\downarrow}}{C}F_2-N=\overset{\overset{sp^3}{\downarrow}}{C}F_2$$

I



$$\overset{\overset{sp^3}{\downarrow}}{C}F_3-N=\overset{\overset{sp^3}{\downarrow}}{C}=N-\overset{\overset{sp^3}{\downarrow}}{C}F_3$$

II

there are in the bent bond description no hybridization changes at the carbons and, therefore, no increase in double-bond strain (other factors equal). In the protonated analogs there would be increased strain in going from the bisazomethine (with sp^2–sp^5 hybridized CH_2= groups) to the carbodiimide because of the hybridization changes. An analogous rearrangement has been reported for 1,4-perfluoropentadiene.[39]

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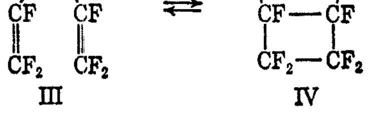
A hybridization situation similar to that between TFE and ethylene may exist between cyclopropane and perfluorocyclopropane. While sp^2–sp^5 hybridization serves as a model for cyclopropane,[4] the carbons of perfluorocyclopropane may be more nearly sp^3 hybridized. The C—C bonds in perfluorocyclopropane would be bent by about 24°44′, while those in cyclopropane are bent by about 20°46′. Although the C—C bonds in perfluorocyclopropane would still (based on overlap integral calculations assuming equal intraatomic distances) be slightly stronger than in cyclopropane the C—F bonds would not be strengthened as would the C—H bonds. Perfluorocyclopropane would be expected to show a larger strain energy than cyclopropane.

Chemical Reactivity of Perfluorocyclopropanes.—Although little is known of the chemistry of perfluorocyclopropanes, Mitsch and Neuvar have studied the kinetics of the thermal isomerization of perfluorovinylcyclopropane, which rearranges to perfluorocyclopentene.[40] The activation energy for this isomerization was found to be 15.0 kcal/mol lower than for the corresponding hydrocarbon. These workers attributed this difference to the added strain in the perfluoro system. Atkinson and McKeagan have studied the thermal decomposition of perfluorocyclopropane to TFE and $:CF_2$ and observed this compound to be much less stable than cyclopropane.[41] Using their value of −31 kcal/mol for the heat of reaction and the heats of formation for $:CF_2$[42] and TFE,[32] the strain energy in perfluorocyclopropane is found to be 68.6 kcal/mol, compared with 27.5 kcal/mol in cyclopropane.[35] These results suggest that at temperatures below which $:CF_2$ is split out (*ca.* 250°) ring-opening reactions of perfluorocyclopropanes may be very facile; that, unlike cyclopropanes which undergo both substitution and addition reactions, perfluorocyclopropanes may only undergo addition reactions; and that because of the large strain energy perfluorocyclopropane may behave similarly to perfluoroolefins in undergoing dimerization, addition, and cycloaddition reactions. Perfluorocyclopropane reportedly reacts with hydrogen fluoride to give the 1,3-ring-opened addition product.[43]

A qualitative estimation of strain energies suggests for III that only in the case of $n = 1$ would the thermal equilibrium lie on the side of the diene. In the case of $n = 0$ [20] and $n = 2$ [44] the equilibrium has been observed to lie on the side of the cyclic isomer. In view of the above high strain energies such compounds as perfluorocyclopropene, perfluorobicyclo[1.1.0]butane, and perfluorospiropentane should be highly strained and very reactive. The synthesis of 1,2-bis(trifluoromethyl)-3,3-difluorocyclopropene and 1,3-bis(trifluoromethyl)-2,2,4,4-tetrafluorobicyclobutane has been reported but no data is available on their strain energies.[45]



III IV

Mitsch and Neuvar have also compared the uv spectra of perfluorobutadiene, perfluorocyclopropylethylene, and perfluoropropene and concluded that the perfluorocyclopropyl moiety has π-electronic character and can enter into conjugation with unsaturated systems. Additional evidence on this point would be desirable, however. The Walsh descriptions suggest no difference in the relative conjugative abilities of the cyclopropyl and perfluorocyclopropyl groups. On the other hand the bent bond descriptions suggest that the sp^5 HAO's of the cyclopropyl ring should overlap more effectively with adjacent unsaturated groups than would the sp^3 HAO's in the perfluorocyclopropyl ring. Transformation of the Walsh description of perfluorocyclopropane to a SO description, *via* the method of Hall and Lennard-Jones,[28a] shows that the highest occupied SO's in the plane of the perfluorocyclopropyl ring have less p character than do those in cyclopropane. It should be remembered, however, that these are not "exact" quantum mechanical descriptions of the two-ring systems and based on bond angles they are probably more similar in hybridization than the above descriptions indicate. There are similar differences in the predicted conjugative abilities of the vinyl and perfluorovinyl groups.

Conclusions

In conclusion, it can be said that the widely accepted theory of sp^2-hybridized carbon HAO's in double bond, carbonyl, and cyclopropyl groups breaks down when they contain a *gem*-difluoro group. In such cases the high electronegativity of fluorine causes the hybridization of the carbon HAO's of the *gem*-difluoro group to be essentially sp^3. With these views in mind the chemical reactivity of resultant highly strained fluorocarbon systems becomes much more readily understandable.

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