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ON THE NATURE OF THE PERFLUOROALKYL (R_f) EFFECT

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Abstract—In this paper, we assess the ability of trifluoro-methyl groups to thermodynamically stabilize unsaturated and strained organic species relative to saturated analogues. Theoretical calculations with the STO-3G basis set are utilized in this analysis. The resulting theoretical data, as well as experimental calorimetric data, indicate little stabilization and perhaps some destabilization resulting from the replacement of H by CF_3 (CF_3 is unambiguously less stabilizing than methyl). This substituent effect is readily explained by dominance in CF_3-substituted compounds of an electron-withdrawing inductive effect which destabilizes the unsaturated linkages. We thus conclude that the striking thermal stability of perfluoroalkylated strained rings is completely kinetic in nature. The origins of the kinetic effect are explored.

The effects of general substituents upon the thermodynamic and kinetic stabilities of strained organic molecules[2] are often dramatic and the origins of these effects form an area of active interest.[3] For example, the recently reported tetra-butyltetrahedrane[4] is amazingly stable (m.p. 135°) despite the possibilities of a highly exothermic rearrangement to the isomeric cyclobutadiene and an exothermic, but symmetry-forbidden[5] potential decomposition to two molecules of 2,2, 5,5-tetramethyl-3-hexyne.[6] However, the effects of the Bu substituents appear to be steric rather than electronic in nature and thus involve kinetic stability only. Since steric effects are comparatively well understood, we will largely ignore them in the remainder of this paper. The isolation of crystalline material tentatively identified as tetralithiotetrahedrane[7] would furnish the most spectacular example of a predominently electronic substituent effect upon the thermodynamic stability of a strained molecule, should the compound's identity be proven conclusively.

Perfluoroalkyl groups, such as trifluoromethyl exert profound influences upon the stabilities of strained (and unsaturated) organic molecules in at least two different, if related, ways: (1) perfluoroalkylated compounds are often incredibly thermally stable compared to the parent hydrocarbons; (2) relative energies (thermodynamic stabilities) within a family of isomers may change dramatically when comparisons are made between parent and perfluoroalkylated molecules. Examples of the first type of phenomenon include the thermal stabilities of *octakis* (trifluoromethyl) cyclooctatetraene (slight decomposition after 1 hr at 400°[8]), and *hexakis* (trifluoromethyl)-3,3'-bicyclopropenyl (half-life over 2 hr at 360°[9]) compared to the parent or alkylated hydrocarbons. Examples of the second type of phenomenon include (1) the stabilization of *hexakis* (trifluoromethyl) benzene valence isomers by over 30 kcal/mole relative to the aromatic isomer when comparison is made with hexamethyl analogues,[10] and (2) the observation of greater stability for *hexakis* (pentafluoroethyl) Dewar benzene than its aromatic isomer at temperatures above 280°.[11] Lemal and Dunlap[10] have convincingly explained the observed thermodynamic effects by noting the severe nonbonded repulsions between substituents in the aromatic isomer which are largely absent in the valence isomers. These authors[10] designated "as the 'perfluoroalkyl (R_f) effect' the composite of stabilizing influences which perfluoroalkyl groups confer upon highly strained carbon frameworks." They further noted that "The R_f effect thus comprises both thermodynamic (steric in origin) and kinetic elements, where the latter include stabilization against both catalyzed and unimolecular destruction."

The primary deficiency of the above analysis is its lack of attention to the origin of the "absolute" thermodynamic effects of substituents such as CF_3 on the stabilities of strained (or unsaturated) molecules when they are compared to open-chain (saturated) analogues. The reader will recall that this comparison is the basis of the concept of molecular strain. For example, the strain energy of cyclopropane is obtained through comparison of its ΔH_f° with the sum of the values for three hypothetical unstrained CH_2 fragments.[12] In the strain energy scheme of George *et al.*,[13] eqn (1) defines the strain energy (ΔH°_{strain}) of cyclopropane.

$$\Delta H_f^\circ \text{ (cyclopropane)} = 3[\Delta H_f^\circ(CH_3CH_2CH_3) - \Delta H_f^\circ(CH_3CH_3)] + \Delta H^\circ_{strain} \quad (1)$$

For a substituted cyclopropane, eqn (2) holds:

$$\begin{aligned}\Delta H_f^\circ\Big(\overset{X}{\triangle}\Big) &= \Delta H_f^\circ(CH_3\text{–}CHX\text{–}CH_3) \\ &+ 2\Delta H_f^\circ(CH_3CH_2CH_3) - 3\Delta H_f^\circ(CH_3CH_3) \\ &+ \Delta H^\circ_{strain}\end{aligned} \quad (2)$$

Finally, one may compare the strain energy of a substituted cyclopropane to the parent in the manner of eqn (3), where a negative value for $\Delta\Delta H^\circ_{strain}$ is equated to a decrease in the strain energy of the substituted cyclopropane.

$$\Delta\Delta H^\circ_{\text{strain}} = \left[\Delta H^\circ_f\left(\overset{X}{\Delta}\right) - \Delta H^\circ_f(\text{cyclopropane})\right]$$
$$- [\Delta H^\circ_f(CH_3CHxCH_3) - \Delta H'_f(CH_3CH_2CH_3)] \quad (3)$$

In the case of the bridgehead carbons of bicyclobutane or the carbons in tetrahedrane, Me_3CH and Me_3CX are employed as standards suitable also for cyclopropene and acetylene ("bicycloethane"). The use of isodesmic[14] equations such as 3 are well suited to theoretical studies where calculated total energies can be employed in place of ΔH°_f and inherent errors due to inadequacies in the chosen basis set as well as arising from electron correlation largely cancel.[14]

We shall employ such isodesmic equations to assess the "absolute" thermodynamic effects of CF_3 groups upon strained and unsaturated linkages.

We note that there is a dearth of thermochemical data for CF_3-substituted molecules. (Caloimetric determinations of ΔH°_f of fluorine-containing organic compounds are particularly difficult.[15]) For the moment, one may compare the stabilizing ability of CF_3 upon unsaturated molecules with that of CH_3 employing eqns (4) and (5).[16]

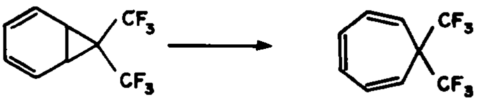
$$\Delta H^\circ_f(CH_2{=}CHCF_3) + \Delta H^\circ_f(CH_3CH_3) \rightarrow \Delta H^\circ_f(CH_2{=}CHCH_3) + \Delta H^\circ_f(CH_3CF_3) \quad (4)$$

$$\Delta H^\circ_f(C_6H_5CF_3) + \Delta H^\circ_f(CH_3CH_3) \rightarrow \Delta H^\circ_f(C_6H_5CH_3) + \Delta H^\circ_f(CH_3CF_3) \quad (5)$$

Equation (4) is exothermic by 6.3 kcal/mole and eqn (5) is exothermic by 2.8 kcal/mole clearly indicating that Me confers better stabilization (thermodynamically) than trifluoromethyl on unsaturated linkages. If one employs a double bond stabilization parameter of 2.5 kcal/mole for the Me group,[17] the CF_3 group is seen to be slightly destabilizing or at best nonstabilizing when attached to the vinyl group. Alternatively, one may use eqn (6), an approach analogous to eqn (3), to estimate an "absolute" substituent effect for CF_3. Although there is no experimental value

$$\Delta\Delta H^\circ_{\text{strain}} = [\Delta H^\circ_f(CH_2{=}CHCF_3) - \Delta H^\circ_f(CH_2{=}CH_2)] - [\Delta H^\circ_f(CH_3CH(CF_3)CH_3) - \Delta H^\circ_f(CH_3CH_2CH_3)] \quad (6)$$

for the heat of formation of 2-methyl-1,1,1-trifluoropropane, it may reasonably be estimated at −190 kcal/mole,[18] The destabilization estimated by eqn (6) is 6 ± 4 kcal/mole. Similar effects would be anticipated for cyclopropanes. In this regard, we note that CF_3 groups do not stabilize a norcaradiene relative to the isomeric tropylidene (eqn 7[19]) in marked contrast to the effect of cyano groups (eqn 8[20]).



(7)

(8)

Methodology. In order to obtain the total calculated energies of molecules investigated in this study, we have performed calculations employing the GAUSSIAN 70 package[21] at the STO-3G level[22] using published geometries[23] for the hydrocarbons and monosubstituting them by a standard CF_3 group whose structural parameters[24] are taken from the literature.[25] Comparisons between strain energies of substituted and parent strained (unsaturated) molecules are made in the manner of eqn (3). The standard for a carbon having two bonds with other carbons (e.g. cyclopropane and ethylene) is the methylene group in propane, for carbon having three bonds to other carbons (e.g. tetrahedrane and acetylene), isobutane is employed as the standard.

DISCUSSION OF RESULTS

Table 1 lists the calculated total energies and strain energies of trifluoromethyl derivatives of cyclopropane, ethylene, bicyclobutane, and tetrahedrane as well as parent hydrocarbons and saturated model compounds. It is obvious that the calculated stabilizations (strain reductions) are not large. When one considers that the STO-3G calculations provide results which appear to overstate stabilizations by substituents such as Me_3 and OMe_3 by 2–5 kcal/mole,[3] it is apparent that stabilizations by CF_3 are small at best and perhaps negative (i.e. destabilizations) in some cases. This is certainly consistent with the earlier discussions of eqns (4)–(6).

Table 1. Calculated (STO-3G) total energies (au) and strain energies (kcal/mole) of unsaturated and strained hydrocarbons, their saturated model compounds, and corresponding trifluoromethyl derivatives

Molecule	Total Energy	Strain Energy	Relative Energy
Ethane	-78.30618[a]	——	——
Propane	-116.88581	——	——
Isobutane	-115.46499	——	——
Cyclopropane	-115.66554	27.4	——
Ethylene	-77.07095	22.3	——
Bicyclobutane	-152.99802	65.6	——
Tetrahedrane	-151.70784	148.8	——
1,1,1-Trifluoroethane	-370.68983	——	——
2-Methyl-1,1,1-trifluoro-propane[b]	-447.84686	——	——

Table 1. (*Contd*)

Molecule	Total Energy	Strain Energy	Relative Energy
2,2-Dimethyl-1,1,-trifluoropropane[b]	-486.41416	———	
Trifluoromethylcyclopropane:			
C-F over ring face	-446.62879	26.0	0
C-F anti to ring face	-446.62603		1.7
C-F eclipsing cyclopropyl C_1C_2	-446.62730		0.9
3,3,3-Trifluoropropene			
C-F eclipsing C=C	-408.03554	19.8	0
C-F perpendicular to C=C-C plane	-408.03491		0.4
C-F anti to C=C	-408.03420		0.8
1-Trifluoromethyl bicyclobutane[b]			
C-F anti to C_1C_3	-483.96316	57.1	0
C-F syn to C_1C_3	-483.96101		1.3
Trifluoromethyltetrahedrane[b]	-482.67320	139.4	

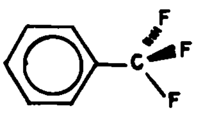
a. W.A. Lathan, L.A. Curtiss, W.J. Hehre, J.B. Lisle, and J.A. Pople, Prog. Phys. Org. Chem., 11, 175 (1974)

b. geometry analogous to corresponding hydrocarbon

The most stable conformer of 3,3,3-trifluoropropene is calculated to have a C–F bond eclipsing the olefinic linkage, in accord with experiment.[25] This is consistent with the negligible operation of hyperconjugative effects in this molecule and so is in accord with the prevailing view of fluorine hyperconjugation.[26] The calculated stabilization (2.5 kcal/mole) may be compared to the calculated stabilization for propene (6.6 kcal/mole) which is itself over 4 kcal/mole greater than the experimental value.[17] The calculated stabilization in trifluoromethylcyclopropane (C–F eclipsing face of the ring) is smaller still. Although the calculated stabilizations of 8.7 kcal/mole and 9.4 kcal/mole in 1-trifluoromethylbicyclobutane and trifluoromethyltetrahedrane, respectively, might seem to be significant, they would appear to be overstated by at least 5 kcal/mole (see earlier discussions) and perhaps more due to reduced "F-strain"[27] when comparing these "pinned back" species with Me_3CCF_3. The high *p*-character (*ca.* 96%[28]) of the central bond in bicyclobutane does not appear to cause any significant hyperconjugative interaction with the substituent, unlike what happens in the case of the substituent CH_2^+.[29]

Table 2 lists the calculated total energies of benzene, benzvalene, Dewar benzene, prismane, and 3,3'-bicyclopropenyl as well as the substituted derivatives 1–8 along with their relative energies. It is quite clear that these are no significant stabilizations or destabilizations compared to trifluoromethyl benzene.

These results substantiate Lemal and Dunlap's sug-



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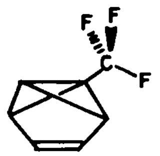

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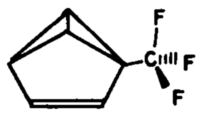

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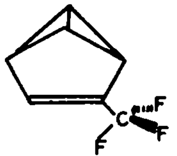

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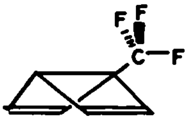

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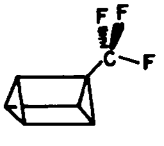

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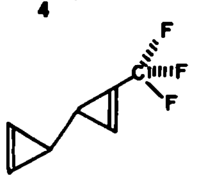

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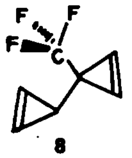

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Table 2. Calculated (STO-3G) total energies (au) and relative energies (kcal/mole) of benzene and its valence isomers as well as trifluoromethylated derivatives

Molecule	Total Energy	Calc'd Rel. Energy (C_6H_6)	Exp'tl Rel. Energy*	Calc'd Rel. Energy ($C_6H_5CF_3$)
benzene	-227.89128	0	0	——
trifluoromethyl benzene (1)	-558.85410	——	——	0
benzvalene	-227.78248	68.2	67.5	——
1-trifluoromethyl benzvalene (2)	-558.74709	——	——	67.1
2-trifluoromethyl benzvalene (3)	-558.74393	——	——	69.1
3-trifluoromethyl benzvalene (4)	-558.74772	——	——	66.7
Dewar benzene	-227.76544	78.9	59.5	——
1-trifluoromethyl Dewar benzene (5)	-558.72826	——	——	78.9
Prismane	-227.74379	92.5	91.2	——
trifluoromethyl prismane (6)	-558.70859	——	——	91.2
3,3'-bicyclopropenyl	-227.66341	142.9	119 (est.)	——
1-trifluoromethyl-3,3'-bicyclopropenyl (7)	-558.62811	——	——	141.7
3-trifluoromethyl-3,3'-bicyclopropenyl (8)	-558.62591	——	——	143.1

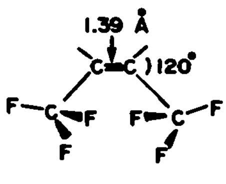
* Experimental relative energies are those reported for hexamethyl derivatives of benzvalene, Dewar benzene, and prismane (see J.F.M. Oth, Angew. Chem., Int. Ed. Engl., 7, 646 (1968). The value of ΔH_f° for 3,3'-bicyclopropenyl was estimated as:

$$2\ \Delta H_f^\circ\ \text{(cyclopropene)} + \Delta H_f^\circ\ \text{(bicyclopropyl)} - 2\ \Delta H_f^\circ\ \text{(cyclopropane)}$$

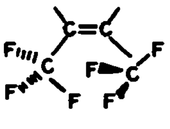
gestion that the dominant factor in the relative thermodynamic stabilities of the *hexakis* (trifluoromethyl) benzene valence isomers compared to the aromatic isomer is the instability of the latter caused by nonbonded repulsion of CF_3 groups. The results discussed earlier suggest to us that all five $(CCF_3)_6$ species are destabilized relative to open chain analogues, or Me analogues.

The steric strain in *hexakis* (trifluoromethyl) benzene approaches the resonance energy of the aromatic ring, even when one neglects the destabilization introduced by the CF_3 groups (eqn 5). In order to further investigate this effect, we have calculated total energies of model structures, namely, conformers (9–11) of "1,1,1,4,4,4-hexafluoro-*cis*-2-butene" in which the olefinic linkage is assumed to be 1.39 Å and perfect trigonal (120°) geometry is assumed at the olefinic termini. The 0,0 conformer of model "1,1,1,4,4,4-hexafluoro-*trans*-2-butene" (12) is included for comparison. The results are presented in Table 3. The (0, 0) conformer of the model *cis* compound is extremely high in energy since the two closest fluorine atoms are well within the van der Waals repulsion region.

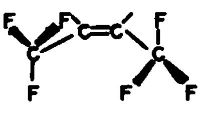
The rotational potential surface of 1,1,1,4,4,4-hexafluoro-*cis*-2-butene is qualitatively similar to but more exaggerated than that of *cis*-2-butene.[30] Furthermore, the lowest energy interaction (9) cannot exist without some very high energy interactions in *hexakis*



9 (180, 180)



10 (0, 180)



11 (−90, 90)

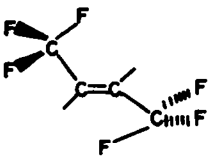


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Table 3. Calculated (STO-3G) total energies (au) and strain energies of structures 9–11 (C_2–C_3, 1.39 Å; trigonal (120°) geometry about C_2 and C_3) which are taken as models for *ortho-bis* (trifluoromethyl) benzene. The *trans*-structure (12) is assumed to be strain-free for this purpose

Structure	Total Energy	Steric Strain
9 (180,180)	-738.98016	5.8
10 (0,180)	-738.96981	12.3
11 (-90, +90)	-738.96796	13.5
12 (trans isomer)	-738.98941	0

(trifluoromethyl) benzene. As a result of these interactions, *hexakis* (trifluoromethyl) benzene adopts a shallow chair structure in which the substituents alternate above and below (12°) the pseudo plane of the molecule.[31] This may be contrasted with hexamethyl benzene which has a strain energy of only 6–7 kcal/mole. This latter species maintains a planar ring but has its methyl groups alternating above and below the ring plane by 10°.[32]

The results reported in this paper indicate that CF_3 groups provide little (if any) stabilization and provide in certain cases some destabilization of strained (unsaturated) molecules relative to saturated model compounds. The little experimental data available supports this view. Thus, the remarkably thermally stable molecule *octakis* (trifluoromethyl)-cyclooctatetraene is probably destabilized energetically relative to saturated model compounds. While energies of $(CCF_3)_6$ isomers relative to the aromatic member of the family are well explained by steric strain in the last species[10] we feel that all members are destabilized relative to the hexamethyl series and possibly even the parent species. The dominant effect of the CF_3 group is inductive electron withdrawal which is destabilizing for unsaturated[17] and strained molecules.[3] However, not surprisingly CF_3 groups stabilize negative charges and so CF_3COOH and CF_3CH_2OH are stronger (gas phase) acids than CH_3COOH and CH_3CH_2OH.[33]

If trifluoroalkyl groups do not lower the strain energy of strained molecules, how do they confer stability? Obviously, resistance to attack by various species is explicable in the manner of saturated fluorocarbons: "...fluorine atoms in a saturated fluorocarbon form an almost impenetrable sheath which must give excellent protection from chemical attack to the carbon backbone."[34] More puzzling, however, is the increased stability with respect to unimolecular thermal reactions despite apparent weakening of the bonds in the carbon skeleton which are the ones most susceptible to rupture. For example, note that the value of E_a is higher (and the pre-exponential factor A lower) in unimolecular thermal decomposition of trifluoromethyl cyclopropane than for decomposition of methylcyclopropane.[35] This occurs despite the conclusions developed here that the Me group is more stabilizing, thermodynamically, than the trifluoromethyl group. We feel this relates to the way the requisite collisions between perfluoroalkylated molecules distribute their energy between translational modes (external energy) and vibrational modes (internal energy). The hard, repulsive nature of nonbonded fluorine–fluorine interactions should cause collisions between perfluoroalkyl molecules to be less intimate (occur at greater separations and over shorter contact times) than collisions between permethylated analogues. As such there should be little coupling to vibrational modes and the collisions should be relatively elastic. Since the molecules absorb little internal energy, they are subject to little decomposition of the carbon skeleton. The weak interactions (because of low polarizability, for example) between fluorocarbons are evidenced by their low boiling points (e.g. BP CF_4 (MW 88) = –182°; BP CH_4 (MW = 16) = –184°) as well as other physical properties.[34]

Another way of viewing this behavior is as follows: upon collision, nuclear positions and electron densities are distorted from normal. One can view, the distorted molecule as being in a superposition of various stationary states of the undistorted compound (i.e. various vibrationsl, rotational, and electronic states).

There is insufficient energy in these collisions to produce electronically excited states and so collisions produce either higher rotational and vibrational states or no change (elastic scattering). Translational energy can be transferred into vibrational modes. In the fluorocarbons however, the steep repulsive nonbonded potential associated with tightly-bound electrons causes little distortion upon collision and therefore comparatively little vibrational excitation.

Another factor may well be the relative ease with which any vibrational excitation in a perfluoroalkyl system may be "siphoned" from the carbon skeleton to the substituents. The C–F stretching frequency is between 1000 and 1400 cm^{-1} while the C–H stretching frequency is close to 3000 cm^{-1}.[36] In toto, perfluorocarbon chemistry exemplifies the poor translational–vibrational energy interconversion which characterizes nonhydrogen containing species.[37]

Finally, we briefly note that the comparative inertness conferred on molecules by fluorination is well chronicled to transcend the aforementioned fluorocarbons. This effect even applies to molecular fluorine. Simple examples are the reactions: $F + X_2 \rightarrow XF + X$ vs $X + F_2 \rightarrow XF + F$[38] for X=Cl and Br and $R + X_2 \rightarrow RX + X$ for R=H and O and X = F, Cl and Br.[39] In each of these cases, the reaction exothermicity provides inadequate explanation of the relative reaction rates: the general rule is seemingly the relative inertness of F_2 compared to the heavier halogens.

Summary. In summary we find that trifluoromethyl groups thermodynamically destabilize unsaturated and strained organic species relative to saturated analogues. As such, we conclude that the striking thermal stability of perfluoroalkylated strained rings is completely kinetic in nature.

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