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STRAIN ENERGIES OF GEM-DIFLUOROCYCLOPROPANES AND RELATED MOLECULES

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Abstract- *Ab initio* calculations using the 4-31G basis set are employed to evaluate strain energies of gem-difluoro derivatives of cyclopropane. The increased strain energies of these molecules account for the relative ease of their thermal rearrangements. Similarities between gem-difluoro, carbonyl and carbocationic centers are explored. The strain energy of hexafluorocyclopropane is almost triple that in cyclopropane while the strain in octafluorocyclobutane is less than double that in cyclobutane.

Geminal difluoro substitution profoundly affects the geometry and reactivity of a cyclopropane ring. The C_1–C_2 bond is shortened (1.464 Å) and the C_2–C_3 bond lengthened (1.553 Å) relative to the parent compound.[1,2] Gem-difluorocyclopropanes exhibit unusually low energy barriers to thermal rearrangements,[3-6] and hexafluorocyclopropane furnishes difluoromethylene upon mild heating.[7] Although the *ca* 9-10 kcal/mol decrease in activation energy for geometrical isomerization of *cis*-1,1-difluoro-2,3-dimethylcyclopropane relative to the hydrocarbon is consistent with the 4.5-5.0 kcal/mol strain increase per F substituent postulated by O'Neal and Benson,[8] other questions remain. These include: (1) Is a single fluoro substituent on cyclopropane thermodynamically destabilizing? (A minimum basis set *ab initio* MO study predicts very slight stabilization.[9]) (2) Why should the strain increments of two gem-substituted fluorines be additive, or similarly, can one assume that the extra increment of stabilization found in a compound such as 2,2-difluoropropane[10,11] is the same as that in 1,1-difluorocyclopropane? (It is clear that the incremental stabilization in 1,1-difluoroethene is much less than that in 1,1-difluoroethane.[11]) (3) Why should the activation energy simply reflect ground-state destabilization and not include transition-state effects? (One should recall the Perfluoroalkyl (R_f) Effect[12] in which substituents such as CF_3 dramatically stabilize strained rings in a kinetic sense while apparently inducing very slight thermodynamic destabilization.[13])

There are no $\Delta H_f^0(g)$ data for fluoro- and difluorocyclopropanes. Thus, a calculational study was initiated with the goal of assessing the effects of gem-difluoro substitution on strain energies of cyclopropanes. These calculations are compared, for calibration, with the experimentally-determined enthalpy of isomerization of 2,2-difluoromethylenecyclopropane to the 4,4-isomer,[6] as well as experimental enthalpies of hydrogenation for gem-difluoro derivatives of vinylcyclopropanes.[14] The destabilization and stabilization energies derived for the CF_2 fragment in various molecular environments are compared with those of the carbonyl and carbonium ion center fragments in the corresponding environments.

Methods

The Gaussian 70 program series[15] using the 4-31G basis set[16] has been employed for most of the present calculational study. The geometry of fluorocyclopropane is taken as the published structure obtained by optimization using the double zeta basis set.[2] The geometries of 1,1-difluorocyclopropane and 3,3-difluorocyclopropene use experimental parameters.[17] The geometry of 3-fluorocyclopropene is based upon comparison of fluorocyclopropane and cyclopropene.[18] The total energies of the four above compounds need not be perfectly optimized since the relevant conclusions in this work are semiquantitative. Total energies for other molecules in this study are optimized values from the literature. The energy difference between 2,2-difluoromethylenecyclopropane and its 4,4-isomer is small and must be calculated as accurately as possible in order for it to be compared with experimental data. Thus, the geometries of these two isomers were optimized by means of the gradient technique, all coordinates being simultaneously optimized employing the gradient program TEXAS[19] prior to calculation at the 4-31G level.

Table 1. Standard gas-phase enthalpies of formation and 4–31G total energies of molecules and ions discussed in the present study

Compound	$\Delta H_f^{o}(g)$[a]	-Total E	Compound	$\Delta H_f^{o}(g)$	-Total E
CH_3^+	262[b]	39.17512[c]	CH_3F	-56.8[o]	138.85686[p]
CH_4	-17.8	40.13977[c]	C_2H_3F	-33.2	176.64989[h]
$C_2H_3^+$	269[b]	76.98983[d]	C_2H_5F	-62.9[q]	177.84230[r]
C_2H_4	12.5	77.92216[c]	3-fluorocyclopropene	----	214.38099
$C_2H_5^+$	219[b]	78.19852[d]			
C_2H_6	-20.1	79.11593[c]	cyclo-C_3H_5F	----	215.60992
cyclo-$C_3H_3^+$	257[b]	114.81364[d]	$(CH_3)_2CHF$	-70.1	216.82730[r]
cyclo-C_3H_4	66.2	115.64168[e]	CH_2F_2	-108.1	237.59180[s]
cyclo-$C_3H_5^+$	264[f]	115.95095[g]	CH_2CF_2	-80.1	275.38014
cyclo-C_3H_6	12.7	116.88350[e]	CH_3CHF_2	-119.7[q]	276.58336[s]
i-$C_3H_7^+$	191[b]	117.20864[d]	3,3-difluorocyclopropene	----	313.11794
C_3H_8	-25.0	118.09360[e]			
CH_2O	-26.0	113.69195[h]	1,1-difluorocyclopropane	----	314.34442
CH_2CO	-11.4	151.49451[h]			
CH_3CHO	-39.6	152.68475[i]	$(CH_3)_2CF_2$	----[t]	315.57310[u]
cyclopropenone	(84.2)[j]	189.23352[k]	$C_4H_4F_2$ (4)	----	352.11522
cyclopropanone	3.8[l]	190.43708[m]	$C_4H_4F_2$ (5)	----	352.11622
$(CH_3)_2CO$	-51.9	191.67699[n]			

a. Data from J.B. Pedley and J. Rylance, "Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds", University of Sussex, Sussex, England, 1977 unless otherwise noted. b. H.M. Rosenstock, K. Draxl, B.W. Steiner, and J.T. Herron, J. Phys. Chem. Ref. Data, 6, Suppl. 1, 1977. c. L. Radom, W.A. Lathan, W.J. Hehre, and J.A. Pople, J. Am. Chem. Soc., 93, 808 (1971). d. W.J. Hehre in Methods of Electronic Structure Theory, H.F. Schaefer, III (ed), Plenum, New York, 1977, p.277. e. L. Radom, W.A. Lathan, W.J. Hehre, and J..A. Pople, J. Am. Chem. Soc., 93, 5339 (1971). f. Added 6-31G* calculated energy difference (38.3 kcal/mol) between cyclopropyl and allyl cations (J.S. Binkley, R. Krishnan, D.J. DeFrees, H.B. Schlegel, J.A. Pople, "Carnegie-Mellon Quantum Chemistry Archive", Carnegie-Mellon Univ., Pittsburgh, 1980, to $\Delta H_f^{o}(g)$ value for allyl cation (226 kcal/mol).[b] g. See Ref. 21. h. L. Radom, W.J. Hehre,, and J.A. Pople, J..Am.Chem.Soc., 93, 289 (1971). i. D. Cremer, J.S. Binkley, J.A. Pople, and W.J. Hehre, J.Am.Chem.Soc., 96, 6900 (1974). j. This value is estimated from published ΔH_f^{o} data on diphenylcyclopropenone (H.P. Hopkins, Jr., D. Bostwick, and C.J. Alexander, J. Am. Chem. Soc., 98, 1355 (1976) using values for ethylene and cis-stilbene. Comparisons with molecular orbital calculations (vide infra) indicate that the experimental number is about 50 kcal/mol too high. k. A. Komornicki, C.F. Dykstra, M.A. Vincent, and L.A. Radom, J. Am. Chem. Soc., 103, 1652 (1981). l. H.J. Rodriguez, J.-C. Chang, and T.F. Thomas, J.Am.Chem.Soc., 98, 2027 (1976). m. L.A. Schaad, A. Hess, and H. Zahradnik, J.Org.Chem., 46, 1909 (1981). n. P. Kollman and S. Rothenberg, J. Am. Chem. Soc., 99, 1333 (1977). o. A.S. Rodgers, J. Chao, R.C. Wilhoit, and B.J. Zwolinski, J.Phys.Chem.Ref.Data, 3, 117 (1974). p. W.A. Lathan, L.A. Curtiss, W.J. Hehre, J.B. Lisle, and J.A. Pople, Prog. Phys. Org. Chem., 11, 175 (1974). q. S.S. Chen, A.S. Rodgers, J. Chao, R.C. Wilhoit, and B.J. Zwolinski, J. Phys. Chem. Ref. Data, 4, 441 (1975). r. W.L. Jorgensen and M.E. Cournoyer, J.Am.Chem.Soc., 100, 5278 (1978). s. W.A. Lathan, L. Radom, W.J. Hehre, and J.A. Pople, J.Am.Chem.Soc., 95, 699 (1973). t. A value of -129.8 ± 3.0 kcal/mol has been reported for $\Delta H_f^{o}(g)$ of 2,2-difluoropropane [A.D. Williamson, P.R. LeBreton, and J.L. Beauchamp, J. Am. Chem. Soc., 98, 2705 (1976)]. The authors feel that this value is too low: based upon Benson's group increment for CH_3 (-10.2 kcal/mol, ref. 26) and the previously-cited value of -104.9 kcal/mol for CF_2, one would expect a value of -125.3 kcal/mol for this molecule. u. Based upon experimental geometry: J.R. Durig, G.A. Giurgis, and Y.S. Li, J.Chem.Phys., 74, 5946 (1981).

RESULTS AND DISCUSSION

Table 1 lists $\Delta H_f^0(g)$ as well as total energies (4 31G) of hydrocarbons, fluorocarbons, carbonyl compounds, and carbonium ions relevant to this work. It quickly became apparent that the STO-3G basis set gives very unreliable results for gem-difluoro compounds. One example is the 18.6 kcal/mol discrepancy in the heat of hydrogenation of 1,1-difluoroethene apparent in Table 2. In contrast, the 4 31G values are within 1-2 kcal/mol of experimental data.

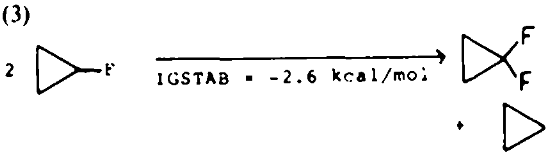
Table 3 lists calculated enthalpies of hydrogenation of simple cyclopropanes using the 4-31G basis set. The implication is that there is 4.6 kcal/mol of destabilization in fluorocyclopropane and 11.7 kcal/mol of destabilization in 1,1-difluorocyclopropane in fair quantitative agreement with the conclusions of O'Neal and Benson.[8] This 11.7 kcal/mol strain energy increase is in reasonable agreement with the 9.7 kcal/mol decrease in the geometric isomerization barrier in *cis*-1,1-difluoro-2,3-dimethylcyclopropane. Thus, it appears that kinetic destabilizations in these species reflect thermodynamic stabilizations.

One may also compare 4–31G values for incremental geminal stabilization (IGSTAB, as defined in Ref. 11) for 1,1-difluoroethane, 1,1-difluoroethene, and 1,1-difluorocyclopropane according to eqns 1 3.

(1) $2CH_3CH_2F \xrightarrow[\text{IGSTAB = 4.6 kcal/mol}]{} CH_3CHF_2 + CH_3CH_3$

(2) $2CH_2CHF \xrightarrow[\text{IGSTAB = 0.8 kcal/mol}]{} CH_2CF_2 + CH_2CH_2$

(3)



The 11.7 kcal/mol destabilization calculated for 1,1-difluorocyclopropane is also in reasonable agreement with destabilization enthalpies determined for compounds **1** (14.2 kcal/mol), **2** (13.8 kcal/mol), and **3** (12.1 kcal/mol) obtained by comparison of their

Table 2. Experimental and calculated enthalpies of hydrogenation (kcal/mol) of fluorinated ethylenes which indicate the reliabilities of the STO–3G and 4–31G basis sets for these species.[a] (Values are based upon data in Table 1)

	EXPERIMENTAL	STO-3G[b]	4-31G[c]
CH_2CH_2	-32.6	-32.6	-32.6
CH_2CHF	-29.7	-25.3	-31.8
CH_2CF_2	-39.6	-21.0	-38.5

a. The STO-3G basis set is adequate for predicting IGSTAB for saturated species such as:

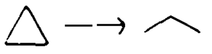
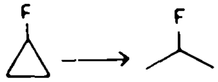
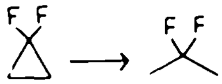
$$2\ CH_3F \longrightarrow CH_2F_2 + CH_4$$

where the discrepancy with experiment is about 2 kcal/mol, and agrees to within 1 kcal/mol of the 4-31G values for IGSTAB of CH_3CHF_2 and $(CH_3)_2CF_2$.

b. The actual STO-3G value for ethylene is -71.9 kcal/mol; all values are scaled to the experimental value.

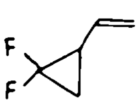
c. The actual 4-31G value for ethylene is -42.0 kcal/mol; all values are scaled to the experimental value.

Table 3. Calculated (4 31G) heats of hydrogenation (kcal/mol) of substituted cyclopropanes based upon data in Table 1

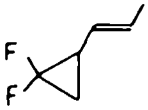
	EXPERIMENTAL	4-31G[a]
	-37.7	-37.7
	----	-42.3
	----	-49.4

a. The actual 4-31G value for cyclopropane is -52.3 kcal/mol; all values are scaled to the experimental value.

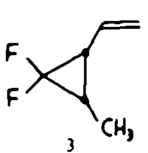
experimental enthalpies of hydrogenation with those of the corresponding hydrocarbons.[14]



1



2



3

It is important to explore how well the 4-31G calculations compare with experimental data for these gem-difluoro systems. Such a comparison can be made for the equilibrium in eqn 4. Calculationally, geometric optimizations for **4** and **5** were carried out as described in the Methods section and the energy values reported are 4-31G values and the calculated structures are shown in Fig. 1. Optimization is crucial for this equilibrium since the energy difference is small. In the other molecules investigated the conclusions can be more qualitative. It is clear that the 4-31G basis set is quite adequate for the present study. It is also worth noting that the rearrangement of 2-fluoromethylenecyclopropane to the 4-fluoro isomer is slightly more exothermic ($\Delta H = -2.5$ kcal/mol)[20] than the difluoro equilibrium. This at first seems surprising when one considers that the corresponding rearrangement in the dimethyl series ($\Delta H = -1.2$ kcal/mol)[20] is about twice as exothermic as the monomethyl equivalent (-0.5 kcal/mol).[20] Part of the reason for this disparity is that IGSTAB is greater for cyclopropyl than for vinyl when a CF_2 increment is present.

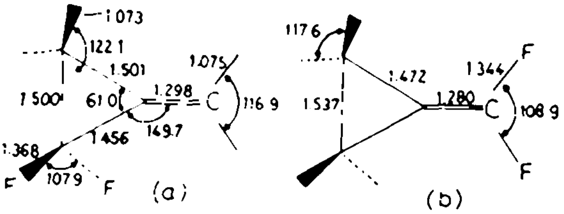
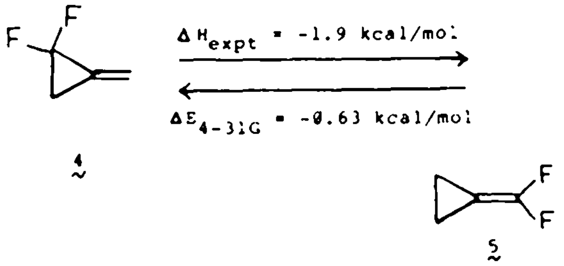


Fig. 1. Calculated structures of (a) 2,2-difluoromethylenecyclopropane, (b) 4,4-difluoromethylenecyclopropane.

(4)

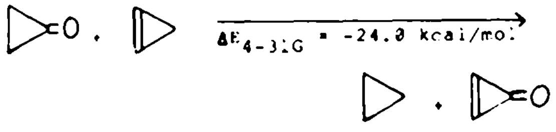


4

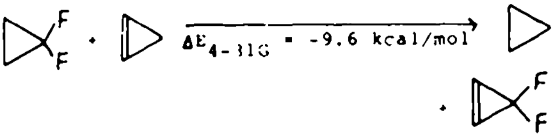
5

There are some other noteworthy points which may be mentioned here. For example, the calculated exothermicity of eqn 5 provides one measure of the aromaticity of cyclopropenone. A similar relation in eqn 6 indicates that 3,3-difluorocyclopropene has about 40% of the aromatic stabilization of cyclopropenone. The values can be compared with the corresponding eqn 7 for cyclopropenium cation.

(5)



(6)



(7)

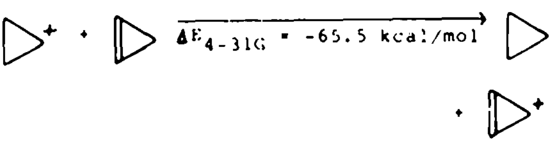


Table 4 lists calculated (4–31G) "Et stabilization energies"[21] for corresponding carbonium ions, carbonyls, gem-difluoro and monofluoro compounds. The discrepancy between experimental and theoretical values for cyclopropenone is apparently due to errors in the determination of the enthalpy of combustion.

A recent experimental determination of $\Delta H_f^0(g)$ for hexafluorocyclopropane (-233.8 kcal/mol),[22] when combined with three recently-derived $C(F)_2(C)_2$ enthalpy increments of -104.9 kcal/mol[23] each, indicates a strain energy of 80.9 kcal/mol. Bernett[24] had some time ago calculated a strain energy of 68.6 kcal/mol for this molecule using a value of -98.1 kcal/mol for the $C(F)_2(C)_2$ increment. An STO-3G calculation based upon the experimental geometry[25] of this molecule predicts a strain energy of 60.2 kcal/mol which underestimates the value much as the minimal basis set does for 1,1-difluorocyclopropane. (The standard Gaussian 70 program cannot calculate hexafluorocyclopropane at the 4-31G level.) The use of the $C(F)_2(C)_2$ fragment ignores the possibility of special effects arising from perfluorination in hexafluorocyclopropane. It is therefore interesting to evaluate the strain energy of this molecule using perfluorinated acyclic molecules as models. Equation (8) indicates a value of 76.7 kcal/mol for the strain energy of hexafluorocyclopropane using this approach (the analogous equation for hydrocarbons yields a value of 27.4 kcal/mol for cyclopropane). This value is in substantial agreement with the value derived from the $C(F)_2(C)_2$ increment. The discrepancy is only 1.4 kcal/mol per CF_2 and indicates that "non-next-nearest-neighbor" corrections[26] in the acyclic model compounds (e.g. C_3F_8) are small. However, it is quite clear that "non-next-nearest-neighbor" corrections in hexafluorocyclopropane are significant. For example, one might predict a strain energy in hexafluorocyclopropane of ca 63 kcal/mol by adding three 11.7 kcal/mol increments (Table 3) to the strain energy of cyclopropane. It is not yet clear what the source of the extra strain in hexafluorocyclopropane is. The strain energy of octafluorocyclobutane [$\Delta H_f^0(g)$ for this molecule as well as C_2F_6 and C_3F_8 are obtained from footnote *a*, Table 1] is calculated to be 50.5 kcal/mol using the $C(F)_2(C)_2$ increment and 45.3 kcal/mol using an equation analogous to 8. The discrepancy between these

Table 4. Comparison of 4–31G ethyl stabilization energies[a]

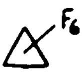
	$-\overset{|}{\underset{|}{C}}{}^{+}$	$>C{=}O$	$>CF_2$
Methyl	-29.6	-10.4	-9.7
Vinyl	-9.4	2.2	-5.9
Cyclopropyl	-9.5	-9.6	-4.1
Isopropyl	20.3	9.1	7.6
Cyclopropenyl	56.0	14.4	5.5

a. Examples:

$$CH_2{=}CH^+ + CH_3CH_3 \longrightarrow CH_3CH_2^+ + CH_2{=}CH_2$$
$$CH_2{=}C{=}O + CH_3CH_3 \longrightarrow CH_3CHO + CH_2{=}CH_2$$
$$CH_2{=}CF_2 + CH_3CH_3 \longrightarrow CH_3CHF_2 + CH_2{=}CH_2$$

two values is only 1.3 kcal/mol per CF_2. Bernett[24] had calculated a value of 32.0 kcal/mol for the strain in this molecule.

(8) $3\ C_3F_8 \xrightarrow{\Delta H\ =\ 76.7\ kcal/mol}$



$+\ 3\ C_2F_6$

It is interesting to note that the loss of CF_2 from 1,1-difluorocyclopropane as well as hexafluorocyclopropane is not only a manifestation of their strain, but also the anomalous stability of CF_2, a ground-state singlet. While the difference in the strain energies of 1,1-difluorocyclopropane and hexafluorocyclopropane is 45.2 kcal/mol, the difference in activation energies for CF_2 extrusion is only 17.8 kcal/mol. This is because the transition states are late on the reaction coordinate and, thus, largely reflect the stabilities of the product olefins. These relationships are depicted in Fig. 2.

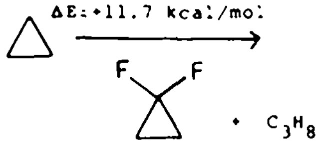
CONCLUSIONS

The lowered energies of activation for rearrangement of gem-difluorocyclopropanes appear to almost entirely reflect enhanced strain in these compounds. The discrepancies between the lowering of the isomerization barrier (9.7 kcal/mol) for *cis*-1,1-difluoro-2,3-dimethylcyclopropane, the calculated increased strain in 1,1-difluorocyclopropane (11.7 kcal/mol), and the experimentally-determined increased strain of **1** and **2** (14.2–13.8 kcal/mol) are generally within the limits of calculational and experimental "noise". The relative activation energies for CF_2 extrusion from 1,1-difluorocyclopropane and hexafluorocyclopropane, on the other hand, closely parallel destabilization energies of the product olefins.

While one would like to extrapolate stabilization or destabilization energies from one ring or unsaturated molecular system to another, this approach may not be always acceptable. For example, eqns (9) and (10) indicate the relative stabilities of geminal fluoro substituents on vinyl and cyclopropyl carbons relative to the more favorable substitution on the middle carbon in propane. (The reason that the vinyl site is more destabilized than the cyclopropyl site involves decreased IGSTAB in the former which is only partially compensated for by stronger, shorter C–F bonds).

(9) $CH_3CF_2CH_3 + CH_2{=}CH_2 \xrightarrow{\Delta E\ =\ +13.5\ kcal/mol} CH_2{=}CF_2 + C_3H_8$

(10) $CH_3CF_2CH_3$ +



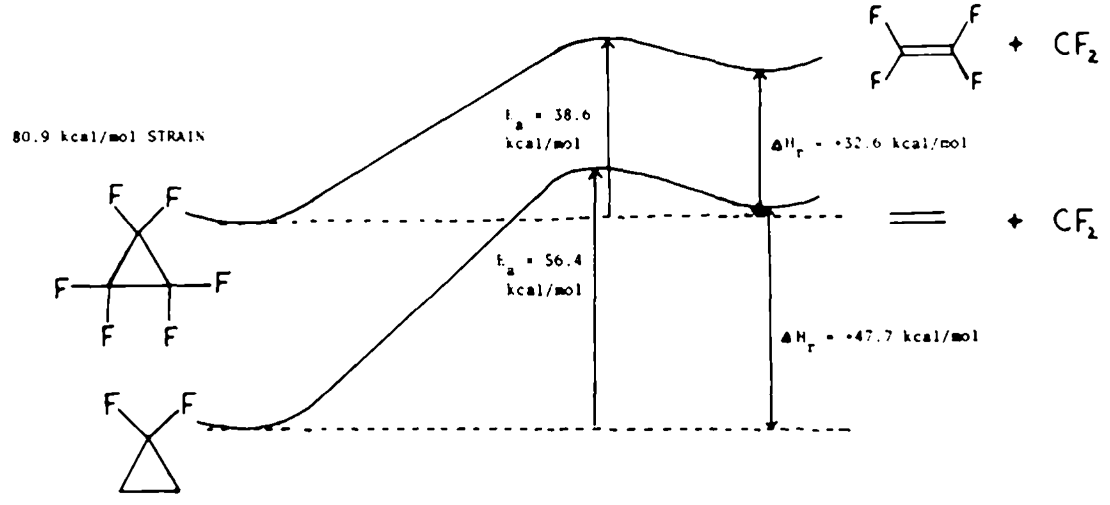
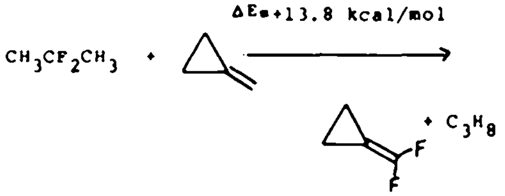


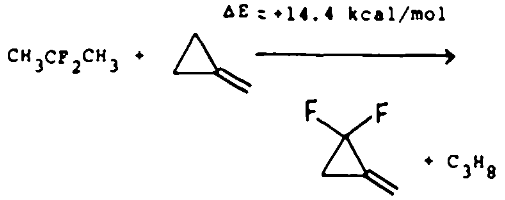
Fig. 2. Plot of the reaction coordinate diagrams for extrusion of CF_2 from 1,1-difluorocyclopropane and hexafluorocyclopropane.

Using these values, one would predict that the conversion of **4** to **5** (eqn 4) should be endothermic by 1.8 kcal/mol rather than exothermic. What is the source of the disparity? Equation 11 indicates that **5** is quite consistent with 1,1-difluoroethylene in its calculated destabilization.[27] However, eqn 12 indicates that there is an extra 2.7 kcal/mol destabilization increment in **4** possibly due to a geometry which forces the C–C bond pooposite to the CF_2 to be shorter than the adjacent bonds in contrast to the situation in 1,1-difluorocyclopropane.

(11)



(12)



There are many similarities between the gem-difluoro, carbonyl and carbocationic molecular fragments. The aromatic stabilization in cyclopropenone appears to be about 40% of that in cyclopropenium cation while 3,3-difluorocyclopropene appears to have about 15% of the stabilization of the cation.

The strain energy of hexafluorocyclopropane obtained using the $C(F)_2(C)_2$ increment or eqn 8, is almost triple that in cyclopropane. It does not appear to be an additive function involving three cyclopropyl CF_2 increments. The strain in octafluorocyclobutane is less than double that in cyclobutane. This is a manifestation of the general behavior of cyclobutanes as ameliorated cyclopropanes.

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