

# Strainless reference states for poly- and perfluorocycloalkanes: the ultradiagonal strain energy approach

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## Abstract

It is well-established that the strain energy of cycloalkanes is affected by fluorination. While the strain energies of cyclopropane and cyclobutane are very nearly equal, perfluorination markedly increases the strain energy of the former and correspondingly decreases the latter. The numerical value for the strain energy of a given molecule is model-dependent. We discuss the strain energies of fluorinated cycloalkanes in terms of the “ultradiagonal” approach, a method earlier found useful for the understanding of fluorinated cyclopropanes and other species containing three-membered rings. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Regardless of the model used for understanding the energetics of alicyclic species, it is well-established that the strain energies of cyclopropane and cyclobutane are very nearly equal and far greater than that of any other cycloalkane [1]: we remind the reader that strain energy (SE) is the difference between the enthalpy of formation of the “real” molecule, typically taken as gaseous, and that which would be found if the groups were found in their ideal environment. That is, letting the various groups [2]<sup>1</sup> be denoted by  $G_k$  and the  $\nu_k$  are the number of each group, then (by definition, where the subscript “m” implicitly means “molar” or “per mole”)

$$\begin{aligned} SE[(G_1)_{\nu_1}(G_2)_{\nu_2} \dots, g] \\ = \Delta_f H_m^\circ E[(G_1)_{\nu_1}(G_2)_{\nu_2} \dots, g] \\ - \nu_1 \Delta_f H_m^\circ(G_1) - \nu_2 \Delta_f H_m^\circ(G_2) \dots \end{aligned} \quad (1)$$

Or, even more simply, we may write

$$\begin{aligned} SE[(G_1)_{\nu_1}(G_2)_{\nu_2} \dots, g] \\ = \Delta_f H_m^\circ [(G_1)_{\nu_1}(G_2)_{\nu_2} \dots, g] - \nu_1 E(G_1) - \nu_2 E(G_2) \dots \end{aligned} \quad (2)$$

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<sup>1</sup> We remind the reader that Benson’s approach explicitly assumes no “non-next-nearest-neighbor” interactions save some steric and ring corrections. As such, as will be acknowledged later in the current study, this approach has significant problems with fluorinated compounds.

In the current case of these small cycloalkanes, we recognize the component groups to be the simple  $\text{CH}_2$  (methylene) group and values of  $\nu$  are 3 and 4, respectively, for the two species. We recognize that the strictly  $60^\circ$  and roughly  $90^\circ$  C–C–C angles for cyclopropane and cyclobutane result in considerable destabilization over that of the idealized “tetrahedral” (i.e.  $109.5^\circ$ ) angle expected for unstrained alicyclic (and aliphatic) hydrocarbons. It is likewise well-established that perfluorination of cyclopropane considerably increases the strain energy over that of the parent hydrocarbon while perfluorination of cyclobutane decreases the strain energy from that of the parent hydrocarbon [3]. The groups in their ideal environment may be derived from a variety of sources: different model systems accompanied by either experimental, most directly calorimetric, measurements, or theoretical, quantum chemical calculational results using a large variety of computational protocols. Nonetheless, with that single size-dependent, conflicting observation, all thoughts of parallel energetics for strained hydrocarbons and their perfluorinated derivatives necessarily disappear. The reader might recall the per and  $\pi$ -fluoro effects on ionization potentials [4] (e.g. the near equality of these electron removal energies for benzene, fluorobenzene and hexafluorobenzene) and the regularities of the enthalpies of vaporization of polyfluorinated species [5] (e.g. the near equality of these liquid-to-gas transition heats for these same compounds). In both cases, fluorine more than paralleled hydrogen. That is, the effects of these substituting hydrogen by fluorine were really surprisingly small.

## 2. Thermochemical data: availability and accuracy

That there are almost no experimental thermochemical data for partially fluorinated cycloalkanes [6] might appear to generally thwart discussions of these species: however, quantum chemical calculations have been reported for many key compounds. As such, despite these seeming ambiguities and absences, the concept of strain energy remains as valuable as ever. In this vein, we will discuss some hopefully interesting features of the strain energy of poly- and perfluorinated alicyclic species. Some 20 years ago, one of the current authors introduced the rather mathematical concept of diagonal reference states for strained molecules [7,8]. By definition, this approach uses reference species that are ideally composed of only one type of group with only one type of C–C bond. For example [14], for unsubstituted alicyclic hydrocarbons, we have the groups  $-\text{CH}_2-$  or equivalently  $\text{C}(\text{H})_2$ ,  $\text{>CH-}$  or equivalently  $\text{C}(\text{H})$ , and  $\text{>C<}$  or equivalently  $\text{C}$  (and, for completeness,  $\text{CH}_3-$  or equivalently  $\text{C}(\text{H})_3$ ) that are derived from, cyclohexane, adamantane and “gaseous diamond” (and ethane). Accordingly, the manifestations of the strainless groups  $\text{C}(\text{F})_2$  (as was  $\text{C}(\text{H})_2$ ) are logically taken [3,9] from the six carbon species perfluorinated (as was parent, unsubstituted) cyclohexane. Said explicitly, numerically and simply using a defining formula

$$E[\text{C}(\text{X})_2] = E(\text{X}-\text{C}-\text{X}) = \frac{1}{6} \Delta_f H_m^\circ[\text{cyclo}-(\text{CX}_2)_6, g] \quad (3)$$

with  $\text{X} = \text{H}$  and  $\text{F}$  for it is assumed that cyclohexanes are definitionally strainless. Relatedly, the strain energies of the cyclopropanes and cyclobutanes are definitionally found to be

$$\text{SE}[(\text{CX}_2)_n, g] = \Delta_f H_m^\circ[(\text{CX}_2)_n, g] - \frac{n}{6} \Delta_f H_m^\circ[\text{cyclo}-(\text{CX}_2)_6, g] \quad (4)$$

for  $n = 3$  and  $4$  (cyclopropane and cyclobutane) and  $\text{X} = \text{F}$  and  $\text{H}$  (perfluorinated and unsubstituted cycloalkanes). The enthalpies of formation of all three cycloalkanes appear to be in good order; certainly, the case for the reference species cyclohexane is most assuredly so.

However, a more thorough analysis of the enthalpy of formation of perfluorocyclohexane suggests potential problems. The primary literature reference to this quantity [10] used a method earlier developed by the same authors [11,12] wherein no auxiliary substances were used in the oxygen combustion process. This method was evaluated as part of a review [13] on the calorimetry of fluorinated species as only moderately precise. The calorimetric reviewers noted that the use of a steel bomb and crucible produces both ferrous and ferric fluorides. As the crucible was open, there was the additional ambiguity of how much of the compound was in the liquid state and how much as the gas. The final combustion gases were assumed to be  $\text{CO}_2$ ,  $\text{CF}_4$ ,  $\text{F}_2$  and unburned compound. While corrections were made for the unburned material and determination of

the other products were made, there exists the possibility of other fluorocarbon products as well. As such, we share the judgment of the authors of the later review [13] that the literature combustion process [10–12] was not adequately defined.

Accordingly, the results reported for  $\Delta_c H_m^\circ[\text{cyclo}-(\text{CF}_2)_6, \ell]$  and hence  $\Delta_f H_m^\circ[\text{cyclo}-(\text{CF}_2)_6, g]$  lack the generally desired accuracy for calorimetric studies. Nonetheless, that all of the diverse methods [3,9] for obtaining the value of  $E[\text{C}(\text{F})_2]$  within the diagonal (and ultradiagonal) approach resulted in consonant numbers suggests that these numbers and associated analyses are fundamentally valid. For the case in which  $\text{X} = \text{H}$  we are not surprised. For  $\text{X} = \text{F}$  we are relieved.

## 3. The meaning of $E[\text{C}(\text{X})_2]$ and other strainless group quantities

It is now to be recalled in the above analysis, by  $E[\text{C}(\text{X})_2]$ , we really meant to write  $E[\text{C}(\text{X})_2(\text{CX}_2)_2]$ , i.e. each  $\text{CX}_2$  group is bonded to two other, identical  $\text{CX}_2$  groups. We have learned the salutary lesson that the strain energy of 1,1-difluorocyclopropane is greater than that of cyclopropane and that three times that increase does not result in the strain energy of perfluorocyclopropane: the thermochemical effects of sequential *gem*-difluorination are not additive [3]. How then do we define the enthalpies of formation of the various strainless groups? Or, perchance, do we even need strainless groups? Ultradiagonal reasoning was introduced for such variously substituted three-membered ring species [14] wherein the strain energy of the latter was defined in terms of the enthalpy of formation of variously substituted cyclohexanes: so doing we recognize cyclohexanes as the formal dimers of cyclopropanes. Again, these cyclohexanes were assumed to be strainless and so there is the simple relation

$$\text{SE}(\text{cyclo-ABC}) = \Delta_f H_m^\circ[(\text{cyclo-ABC}, g)] - \frac{1}{2} \Delta_f H_m^\circ[(\text{cyclo-ABCABC}, g)] \quad (5)$$

wherein A, B and C are the three 1-carbon constituents (ring carbon with two affixed groups) of the cyclopropane. In this defining [14] and subsequent studies [15,16] for ultradiagonal reasoning, we chose the cyclohexane wherein the bonding pattern is the same as the cyclopropane. That is, the group A is attached solely to B and C, the group B to C and A, and the group C to A and B, and so cyclo-ABCABC is the cyclohexane of choice and not cyclo-ABCCBA wherein there are both A–A and C–C bonds. Despite this mathematical foundation, in [14] and the subsequent papers [15,16], we always had the self-imposed limitation of two of the groups A, B and C being chosen to be the same.

In a recent theoretical paper directed towards understanding fluorinated species, in the particular variously fluori-

nated cyclopropanes [9], we allowed A, B and C to be different. They are to be chosen from the groups CH<sub>2</sub>, CHF and CF<sub>2</sub>. For these three-membered ring species, we were fortunate that we did not have to define individual group energies. Unlike the pure hydrocarbon case of aliphatic and alicyclic species, the energy of a fluorinated group is very sensitive to its environment [17,18]. Not needing to define individual group energies for the cyclopropanes was fortunate since there are a total of 18 groups of the general type A(B)(C) wherein all three of the A, B and C may be the same or different: by A(B)(C) we mean to consider an A group that is bonded to (i.e. has nearest neighbors) a B and a C group. We remind the reader while A(B)(C) equals A(C)(B), neither equals B(A)(C) or any of the remaining permutations of A, B and C. We would need to know the energy of each group  $E[A(B)(C)]$  should we wish to determine the strain energy of these species whether we use the ultradiagonal or some more traditional strain energy approach. What can we do? Cutting the number to three corresponding to CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>, CHF(CHF)<sub>2</sub> and CF<sub>2</sub>(CF<sub>2</sub>)<sub>2</sub> — derived from the diagonal reference species — seems too severe for understanding our fluorinated species. So, what do we do for arbitrarily fluorinated cycloalkanes?

#### 4. A simplified analysis

Let us simplify the analysis for the current study by assuming there are but two components, A and B. In the current case, consider CH<sub>2</sub> and CF<sub>2</sub> (these components are simpler than CHF since we do not get into stereochemical questions such as *cis*- versus *trans*-orientations of two CHF groups and besides, or maybe partially because of this, there has been generally more interest in the experimental literature in partially fluorinated cycloalkanes containing CF<sub>2</sub> groups than those containing CHF groups). From these two components, we have six groups CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>, CH<sub>2</sub>(CH<sub>2</sub>)(CF<sub>2</sub>), CH<sub>2</sub>(CF<sub>2</sub>)<sub>2</sub>, CF<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>, CF<sub>2</sub>(CH<sub>2</sub>)(CF<sub>2</sub>) and CF<sub>2</sub>(CF<sub>2</sub>)<sub>2</sub>. Before we go onto arbitrary sized rings for which these groups will be explicitly necessary, let us first define the energies of these various groups.

The values of the energy contribution of the first and last groups,  $E[\text{CH}_2(\text{CH}_2)_2]$  and  $E[\text{CF}_2(\text{CF}_2)_2]$  are easily found by accepting the earlier defining relations within the ultradiagonal approach

$$E[\text{CH}_2(\text{CH}_2)_2] = \frac{1}{6} \Delta_f H_m^\circ [\text{cyclo}-(\text{CH}_2)_6, g] \quad (6)$$

$$E[\text{CF}_2(\text{CF}_2)_2] = \frac{1}{6} \Delta_f H_m^\circ [\text{cyclo}-(\text{CF}_2)_6, g] \quad (7)$$

However, no such simple relation exists for any of the other groups. For example, consider the following relation between CH<sub>2</sub>(CF<sub>2</sub>)<sub>2</sub> and a plausible (and earlier-used) cyclohexane, the 1,1,2,2,4,4,5,5-octafluoro species 1,2,4,5-cyclo-(CH<sub>2</sub>)<sub>2</sub>(CF<sub>2</sub>)<sub>4</sub>

$$E[\text{CH}_2(\text{CF}_2)_2] = \frac{1}{2} \Delta_f H_m^\circ [\text{cyclo}-(\text{CH}_2)_2(\text{CF}_2)_4, g] \quad (8)$$

This putative equality is unequivocally false, or otherwise useless. It is likewise in error for any other multiplicative factor of the group enthalpy. We recognize the fluorinated cyclohexane, or more properly its enthalpy of formation, to be expressible in terms of groups as

$$\begin{aligned} \Delta_f H_m^\circ [\text{cyclo}-(\text{CH}_2)_2(\text{CF}_2)_4, g] \\ = 2E[\text{CH}_2(\text{CF}_2)_2] + 4E[\text{CF}_2(\text{CH}_2)(\text{CF}_2)] \end{aligned} \quad (9)$$

Relatedly, using the earlier-used 1,1,4,4-tetrafluorocyclohexane, we write

$$\begin{aligned} \Delta_f H_m^\circ [\text{cyclo}-(\text{CH}_2)_4(\text{CF}_2)_2, g] \\ = 2E[\text{CF}_2(\text{CH}_2)_2] + 4E[\text{CH}_2(\text{CH}_2)(\text{CF}_2)] \end{aligned} \quad (10)$$

We now borrow the earlier concept of “bond-diagonal” from the diagonal approach [7,8] to convey that while a reference species has only one type of bond, it does not have only one type of group (e.g. adamantane for alicyclic hydrocarbons). Accordingly, using the enthalpy of formation of such a bond-diagonal species, 1,1,3,3,5,5-hexafluorocyclohexane, we write

$$\begin{aligned} \Delta_f H_m^\circ [\text{cyclo}-(\text{CH}_2)_3(\text{CF}_2)_3, g] \\ = 3E[\text{CH}_2(\text{CF}_2)_2] + 3E[\text{CF}_2(\text{CH}_2)_2] \end{aligned} \quad (11)$$

#### 5. Mathematical and chemical equations and their solutions

We now have five equations for six unknowns. No unique solution exists. We need another equation. What is our sixth and last equation? From the elementary properties of linear equations and determinants, it can be proven that any equation that treats the two groups CH<sub>2</sub> and CF<sub>2</sub> equivalently (as do the above five equations, taken in toto) fails to provide a mathematical unique solution.<sup>2</sup> Alternatively, one may supplement ultradiagonal reasoning by the explicit use of the diagonal philosophy of reference species. Accordingly, the following species are used to define reference group energies: cyclo-(CH<sub>2</sub>)<sub>6</sub>, cyclo-(CF<sub>2</sub>)<sub>6</sub>, 1,4-cyclo-(CH<sub>2</sub>)<sub>4</sub>(CF<sub>2</sub>)<sub>2</sub> and 1,2,4,5-cyclo-(CH<sub>2</sub>)<sub>2</sub>(CF<sub>2</sub>)<sub>4</sub>, and also 1,3,5-cyclo-(CH<sub>2</sub>)<sub>3</sub>(CF<sub>2</sub>)<sub>3</sub>. Should we opt to use any other “poly-*gem*-difluoro-substituted cyclohexane”, i.e. any species of the type cyclo-(CH<sub>2</sub>)<sub>n</sub>(CF<sub>2</sub>)<sub>6-n</sub>, its enthalpy of

<sup>2</sup> More precisely, we generate a matrix with five rows and six columns corresponding to the above equations. Any new linear equation of the type

$$\begin{aligned} k_1 E[\text{CH}_2(\text{CH}_2)_2] + k_2 E[\text{CH}_2(\text{CH}_2)(\text{CF}_2)] \\ + k_3 E[\text{CH}_2(\text{CF}_2)_2] + k'_3 E[\text{CF}_2(\text{CH}_2)_2] \\ + k'_2 E[\text{CF}_2(\text{CH}_2)(\text{CF}_2)] + k'_1 E[\text{CF}_2(\text{CF}_2)_2] = k \end{aligned}$$

wherein  $k_1 = k'_1$ ,  $k_2 = k'_2$  and  $k_3 = k'_3$  can be shown to be a linear combination of the aforementioned equations. As such, the new set of equations is linearly dependent and a unique numerical solution for the unknown group increments does not exist in this case either.

formation is either inconsistent or redundant with the others already chosen.<sup>3</sup> It seems unfair that we are forced to treat hydrogen and fluorine, methylene and difluoromethylene, differently and to invent, de novo, a group increment. We are endeavoring to find a chemically motivated, mathematically soluble, equation and/or group increment. So doing must be left to the subject of a later paper [19].<sup>4</sup>

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<sup>3</sup>This may be derived simply by brute force manipulation of the enthalpies of formation of the various poly-*gem*-difluoro-substituted cyclohexanes and their use to derive groups, or as reference species, per se. For example, the enthalpy of formation of cyclo-(CH<sub>2</sub>)<sub>5</sub>(CF<sub>2</sub>) is inseparably related to those of cyclo-(CH<sub>2</sub>)<sub>6</sub> and 1,4-cyclo-(CH<sub>2</sub>)<sub>4</sub>(CF<sub>2</sub>)<sub>2</sub>.

<sup>4</sup>This logical situation of incompleteness or inconsistency appears to us to be very reminiscent of that for the choice of Euclidean versus non-Euclidean geometry and explicitly Euclid's parallel postulate. Why should not Gödel's theorem encompass the analysis of the thermochemistry of fluorinated and strained species? Why cannot we get back from the ashes what we thought we had irretrievably lost? For metaphysical and metamathematical (can we, therefore, infer "metachemical"?) discussions of Gödel's theorem, consider, reference [19].