

On the Electronic Origin of Strain Energy: QTAIM Study of Perfluorocycloalkanes

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The strain energies (SE) of the five smallest perfluorocycloalkanes ($c\text{-C}_n\text{F}_{2n}$; $n = 3, 4, 5, 6,$ and 7) were calculated by means of several homodesmotic processes using B3LYP/6-31++G(d,p) optimized molecular energies. These values were compared with the energy difference between the linear and cyclic CF_2 groups calculated by means of the quantum theory of atoms in molecules (QTAIM) applied on charge densities obtained at the same computational level. The differences between the values computed with both methods vary from 255 ($n = 3$) to 629 ($n = 7$) kJ mol^{-1} . These differences arise because QTAIM-computed SE contain the energy involved in opening the ring to give rise to nearly transferable central CF_2 fragments of linear perfluoroalkanes, whereas homodesmotic energies contain energy terms corresponding to transformation of nontransferable linear CF_2 fragments and a ring-opening energy, which depending on the process, transforms CF_2 cyclic compounds into nearly transferable or nontransferable linear CF_2 groups.

Introduction

Strain energy (SE) is one of the central topics in structural organic chemistry.^{1–3} Despite the controversy on a rigorous definition of SE,⁴ it has been usually interpreted as a destabilization arising from deviations of preferred values of valence and dihedral angles due to ring formation. This excess energy in a cyclic molecule with regard to a hypothetical reference strainless molecule is usually obtained from appropriate chemical reactions involving the molecule of interest. As can be seen in the literature, homodesmotic,⁵ diagonal,⁶ or ultradiagonal⁷ reactions are widely employed to calculate SEs.

In an original approach to the subject, by employing the quantum theory of atoms in molecules (QTAIM),⁸ Wiberg et al. computed the SE of cycloalkanes as the summation of relative energies in the cycle regarding the reference strainless compounds (linear n -alkanes).⁹ This provided a clear and concrete physical origin of SE in small cycloalkanes as the balance between the stabilization of carbon and the destabilization of hydrogens in the methylene of a cycle with respect to a standard methylene group of a linear n -alkane.

In a previous paper by the authors, the QTAIM theory was also employed to critically evaluate the computation of SEs for methyl oxiranes by using different reactions.¹⁰ This work raised two fundamental questions regarding this type of computations to deliver SE values. First, different reactions (even when they are all homodesmotic) provide different values for the SE of the same compound; second, SE obtained from homodesmotic reactions, SE_H , does not only include the energy due to ring opening, ΔE^RO , but also another energy change, ΔE^NC , due to the difference in molecular environments between the acyclic compounds in reagents and products.

We also discussed in that work¹⁰ about the shortcomings of the extension of Wiberg et al.'s procedure⁹ to compounds containing electronegative heteroatoms. The atomic energies of nearly transferable groups in the presence of an electronegative atom were found to depend on the molecular size ("size effect"),

an effect that is virtually negligible for n -alkanes. "Size effect" was later evidenced to be an undesirable artifact due to the evolution of virial ratios along homologous molecular series,¹¹ which can be suppressed¹² by employing electron densities obtained with virial scaling optimizations.¹³

Even when the size effect has been overcome, to properly include only the energy due to ring formation in SE, we should eliminate changes in the energy due to electron transfers from groups that are not present in the cycle. Whereas this is possible for cycloalkanes, where CH_2 electron population (8.000 au) coincides with its value in the central methylenes of a n -alkane,⁹ it cannot be done for heterocycles. For instance, the methylenes of oxirane are at the same time α and β to an oxygen that is only bonded to two methylene groups. The most similar situation in an acyclic compound is that of the inner methylenes in 1,2-diethoxyethane. Nevertheless, by comparing the electron populations of these methylene fragments (respectively, 7.405 and 7.340¹⁴ au at the HF/6-31++G(d,p) level), we conclude they are different indeed.

The above discussion indicates that the extension of the QTAIM treatment on the origin of SE of cycloalkanes⁹ to heterocycles is not a straightforward task.¹⁵ Thus, the SE computed as summation of differences between atomic energies in the cycle and in strainless molecules, SE^Q , does not recover the SE computed with homodesmotic, ultradiagonal, or other processes, SE_H , because of: (i) their different physical meaning, (ii) shortcomings that can affect both procedures.^{10,15} This work analyses the origin of these differences by considering a series of cyclic perfluorocycloalkanes (c -PFAs), whose SE^Q calculation is untouched by an important limitation affecting usual heterocycles: the different electron populations in cyclic and nearly transferable linear fragments. For these molecules, CF_2 cyclic fragments of symmetric conformers and the nearly transferable central CF_2 of linear perfluoroalkanes, n -PFAs, display a total population of 24.000 au. However, SE^Q and SE_H values computed for c -PFAs disagree strongly and this paper deals with the origin of these differences. Finally, it has to be mentioned that practical interest on perfluoroalkanes (PFAs) has increased

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TABLE 1: Nomenclature, Molecular Energies, Virial Ratios, γ , and Integration Errors of the Cyclic and Linear Perfluoroalkanes as Obtained from B3LYP/6-31++G(d,p) Calculations^a

	E au	ZPVE kJ mol ⁻¹	$10^6(2 - \gamma)$	$\sum E(\Omega) - E$ kJ mol ⁻¹	$10^3[\sum N(\Omega) - N]$ au	$10^3 L_{\max}(\Omega)$ au
<i>c</i> -C ₃ F ₆	-713.03876	89.4	0.97	1.8	1.5	1.9
<i>c</i> -C ₄ F ₈	-950.78601	124.0	5.61	-2.6	0.8	1.9
<i>c</i> -C ₅ F ₁₀	-1188.51282	158.9	0.20	-3.5	2.2	1.6
<i>c</i> -C ₆ F ₁₂ (chair)	-1426.22222	192.0	0.15	-4.1	4.4	2.2
<i>c</i> -C ₆ F ₁₂ (twist)	-1426.21569	192.1	0.06	-2.7	1.9	1.5
<i>c</i> -C ₇ F ₁₄	-1663.91036	224.9	1.07	0.6	2.4	1.7
<i>n</i> -C ₄ F ₁₀	-1150.45945	141.8	0.55			
<i>n</i> -C ₅ F ₁₂	-1388.16186	174.1	0.16	-2.9	0.9	2.6 (2.6)
<i>n</i> -C ₆ F ₁₄	-1625.86425	206.2	0.29	-4.1	2.6	2.6 (0.1)
<i>n</i> -C ₇ F ₁₆	-1863.56702	238.5	0.76	-1.9	2.9	1.5 (1.0)
<i>n</i> -C ₈ F ₁₈	-2101.26896	270.4	3.72	0.3	2.6	1.9 (0.3)

^a $L_{\max}(\Omega)$ indicates the maximum absolute value achieved for $L(\Omega)$ along each molecule. Values in parentheses refer to the atoms in the central fragment. CF₂^C in *n*-C₈F₁₈ and *n*-C₇F₁₆ and CF₂^A in *n*-C₆F₁₄ and CF₂^{AA} in *n*-C₅F₁₂.

in the past few years with the development of fluorous biphasic chemistry^{16,17} and diverse medical applications.^{18–20}

Computations

B3LYP/6-31++G(d,p) full optimizations and frequency calculations on the most stable conformers of the five smallest *c*-PFAs (*c*-C_{*n*}F_{2*n*}; *n* = 3, 4, 5, 6, and 7), and of the completely antiperiplanar conformer of the *n*-PFAs of formula *n*-C_{*n*}F_{2*n*+2} with $4 \leq n \leq 8$, were carried out using the GAMESS program.²¹ Chair and twist conformers were optimized for *c*-C₆F₁₂. All the conformers were computed with the virial scaling option¹³ until the virial ratio differed from 2 by less than 10^{-5} (Table 1). The corresponding electron densities were analyzed using Bader's QTAIM theory.⁸ The evaluation of local properties was performed using MORPHY98,^{22,23} and the integrations over the atomic basins, Ω , were carried out using the AIMPAC program series.²⁴ The quality achieved in the QTAIM integration of atomic quantities is guaranteed by several parameters. Thus, the integrated value of the Laplacian, $L(\Omega)$, that should be zero for an exact integration, has always been lower (in absolute values) than $2.6 \cdot 10^{-3}$ au (Table 1). The summation of the integrated atomic energies, $E(\Omega)$, recovers the molecular energy within the limits of 1 kcal mol⁻¹. Also, the total number of electrons in the molecule is reproduced by the summation of atomic electron populations, $N(\Omega)$, within $8 \cdot 10^{-4}$ au per C atom in the molecule (Table 1).

Results and Discussion

Optimized Geometries. The expected planar, puckered, and chair conformers were obtained for, respectively, *c*-C₃F₆, *c*-C₄F₈, and *c*-C₆F₁₂. Their main geometrical features, presented in Table 2, allow distinguishing between axial (or pseudoaxial), F_a, and equatorial (or pseudoequatorial), F_e, fluorine atoms. The twist-boat conformer of *c*-C₆F₁₂ displays *D*₂ symmetry with two kinds of carbon atoms (C_a and C_b) and three kinds of fluorine atoms (pseudoaxial, F_a, pseudoequatorial, F_e, and those bonded to C_b, F_b), as can be seen in Figure 1. A nearly envelope conformer (but with *C*₁ symmetry) is obtained for *c*-C₅F₁₀ (Figure 2) and a *C*₂ twist-chair one for *c*-C₇F₁₄ (Figure 3). The symmetry of these conformers led us to refer to their atoms by the numbering shown, respectively, in Figures 2 and 3. Conformational characteristics and geometries here obtained agree with those previously found at several computational levels.²⁵

It has to be noticed that the completely antiperiplanar conformers of *n*-PFAs, which are their global minima, present main dihedral angles that differ from 180° significantly (Table 3), displaying a helical structure (Figure 4) previously found at

TABLE 2: Main Geometrical Parameters for the Conformers of *c*-C₃F₆, *c*-C₄F₈, and *c*-C₆F₁₂^a

parameter ^b	<i>c</i> -C ₃ F ₆	<i>c</i> -C ₄ F ₈	<i>c</i> -C ₆ F ₁₂ (chair)	<i>c</i> -C ₆ F ₁₂ (twist)
C–C	1.528	1.576	1.560	1.566 ^c , 1.543 ^d
C–F _a	1.341	1.346	1.356	1.355
C–F _e		1.342	1.350	1.346
C–F _t				1.349
C–C–C	60.0	89.9	113.7	112.6 ^e , 113.4 ^f
F–C–F	112.2	110.1	108.6	109.2
C–C–F _a	118.9	113.0	108.4	107.6
C–C–F _e		114.8	108.8	109.4
C–C _b –F _b				108.3, 108.8 ^g
C–C–C–C		5.4	47.9	-58.7 ^h , 28.6 ⁱ
F _a –C–C–C	108.6	109.6	72.7	61.1 ^j
F _e –C–C–C		122.9	169.3	179.6 ^k
F _a –C–C–F _a	0.0	135.4	166.6	179.1
F _e –C–C–F _e		119.5	69.3	57.8
F _e –C–C–F _a	142.8	7.9	48.6	60.6

^a Distances in Å and angles in degrees (dihedral angles are shown in absolute values). ^b F_a refers to F in axial or pseudoaxial arrangement and F_e to equatorial or pseudoequatorial position. This difference cannot be applied to *c*-C₃F₆ fluorines. F_b refers to F atoms bonded to C_b in the twist-boat conformer of C₆F₁₂ (see Figure 1). ^c C_a–C_b. ^d C_a–C_a. ^e C_b–C_a–C_a. ^f C_a–C_b–C_a. ^g The value depends if C_a and F_b are at the same side on the middle plane of the ring (108.3) or at opposite sides (108.8). ^h C_b–C_a–C_a–C_b. ⁱ C_a–C_b–C_a–C_a. ^j F_a–C_a–C_a–C_b. ^k F_e–C_a–C_a–C_b.

several computational levels (see refs 25–26 and references therein) and rationalized as being due to F···F destabilizing 1,5-diaxial interactions.²⁷ Thus, these conformers present *C*₂ symmetry instead of the *C*_{2*h*} or *C*_{2*v*} observed, respectively, for *n*-alkanes with an even or odd number of carbons. The values of the main geometrical features alternate between compounds with an even and odd number of carbons (Table 3).

Molecular and QTAIM Energies. The total B3LYP/6-31++G(d,p) electronic energy (and also those corrected with ZPVE after frequency calculations) of *n*-PFAs is linearly correlated with the number of CF₂ groups in the compound following fitting eq 1. The corresponding fitting of ZPVE uncorrected total electronic molecular energies provides -237.70242 au for $E(\text{CF}_2)$ and -337.52732 au for $E[\text{CF}_3]$. This fitted $E[\text{CF}_2]$ energy differs from that obtained by summation of the QTAIM integrated energies of the atoms in the group (Table 4) by values that range from -35 to -93 kJ mol⁻¹ for CF₂ and from 111 to 181 kJ mol⁻¹ for CF₃. We remark that the fitted CF₂ energy is also clearly different (-89.0 kJ mol⁻¹) from that of the nearly transferable CF₂ fragment (central CF₂ of *n*-C₈F₁₈ as commented below). In contrast, molecular electronic energies are reproduced by those obtained with eq 1 and those

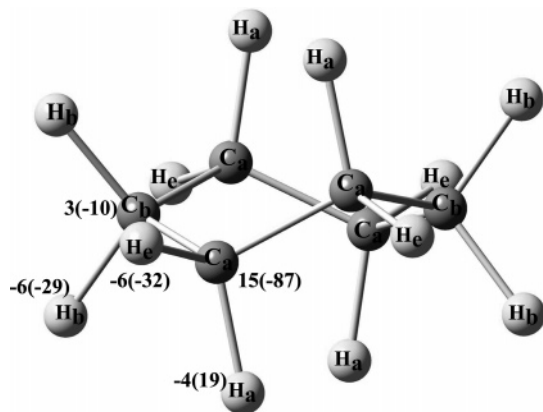


Figure 1. Structure and atom nomenclature of the D_2 twist-boat conformer of $c\text{-C}_6\text{F}_{12}$. Relative atomic electron populations (in au and multiplied by 10^3) and energies (in parentheses and kJ mol^{-1}) with regard to the nearly transferable linear CF_2 (CF_2^{C} in $n\text{-C}_8\text{F}_{18}$, Table 4). Average absolute atomic electron population and energy for C are, respectively, 4.799 and -37.23477 au, and for F, 9.601 and -100.23401 au, respectively.

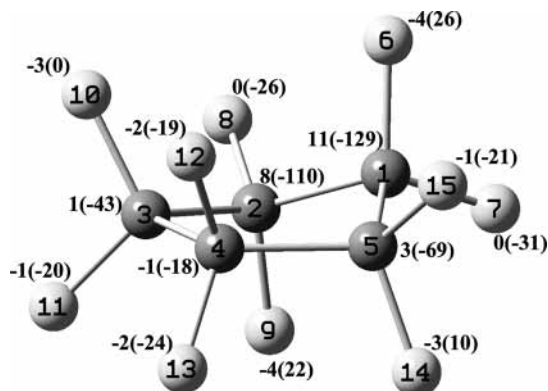


Figure 2. Structure and atom numbering for the optimized conformer of $c\text{-C}_5\text{F}_{10}$. Relative atomic electron populations (in au and multiplied by 10^3) and energies (in parentheses and kJ mol^{-1}) with regard to the nearly transferable linear CF_2 (CF_2^{C} in $n\text{-C}_8\text{F}_{18}$, Table 4). Average absolute atomic electron population and energy for C are, respectively, 4.792 and -37.23946 au and 9.604 and -100.23169 au for F. Main dihedral angles are: $\text{C1-C2-C3-C4} = -25.2^\circ$, $\text{C2-C3-C4-C5} = 5.8^\circ$, $\text{C3-C4-C5-C1} = 15.8^\circ$, $\text{C4-C5-C1-C2} = -31.5^\circ$, and $\text{C5-C1-C2-C3} = 35.2^\circ$.

parameters within 0.8 kJ mol^{-1} (Figure 5). Also, the fitted group energies are more in line with the conventionally accepted practice in the classical organic chemistry context of strain energy than the QTAIM group energies of nearly transferable groups. Nevertheless, nothing ensures that all the molecules fitted actually contain the parametrized atomic groups.

$$E[\text{CF}_3(\text{CF}_2)_n\text{CF}_3]^{n\text{-PFA}} = 2E[\text{CF}_3] + nE[\text{CF}_2] \quad (1)$$

Atomic electron populations computed for $\text{C}_n\text{F}_{2n+2}$ n -PFAs from $n = 5-8$ (Table 4) indicate, at least, the presence of four different groups in these compounds: (i) terminal CF_3 groups, (ii) CF_2 groups bonded to CF_3 (CF_3^{α}) characterized by the smallest electron population and are positively charged, (iii) CF_2 in β to a CF_3 (CF_2^{β}), which display a slight negative charge, and (iv) the central CF_2 groups in n -perfluoroheptane (CF_2^{CC}) and n -perfluorooctane (CF_2^{C}), which are neutral or nearly neutral. It has to be stressed that the group definition we are employing here follows the general rules shown in previous studies on approximate group transferability using QTAIM.^{9,28-37} This is a much stricter definition of atomic group than those

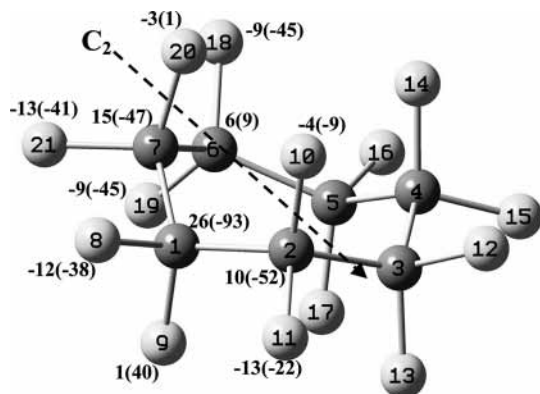


Figure 3. Structure and atom numbering for the optimized C_2 twist-chair conformer of $c\text{-C}_7\text{F}_{14}$. Relative atomic electron populations (in au and multiplied by 10^3) and energies (in parentheses and kJ mol^{-1}) with regard to the nearly transferable linear CF_2 (CF_2^{C} in $n\text{-C}_8\text{F}_{18}$, Table 4). Average absolute atomic electron population and energy for C are, respectively, 4.803 and -37.23177 au and 9.598 and -100.23484 au for F. Main dihedral angles are: $\text{C1-C2-C3-C4} = 50.2^\circ$, $\text{C2-C3-C4-C5} = -65.4^\circ$, $\text{C3-C4-C5-C6} = 76.0^\circ$, and $\text{C4-C5-C6-C7} = -33.8^\circ$.

TABLE 3: Main Geometrical Features for the Conformers of $n\text{-C}_n\text{F}_{2n+2}$ Linear Perfluoroalkanes^a

feature	$n\text{-C}_4\text{F}_{10}$	$n\text{-C}_5\text{F}_{12}$	$n\text{-C}_6\text{F}_{14}$	$n\text{-C}_7\text{F}_{16}$	$n\text{-C}_8\text{F}_{18}$
C1-C2	1.565	1.553	1.564	1.553	1.565
C2-C3	1.563	1.555	1.569	1.556	1.570
C3-C4			1.571	1.560	1.572
C4-C5					1.573
F ₁ -C1	1.341	1.338	1.341	1.338	1.342
F ₋ -C1	1.342	1.340	1.342	1.340	1.342
F ₊ -C1	1.339	1.337	1.339	1.337	1.339
C1-C2-C3	115.2	114.2	114.7	114.2	114.8
C2-C3-C4		113.8	113.8	113.6	114.1
C3-C4-C5				113.3	113.8
F ₁ -C1-C2	108.5	108.9	108.8	108.9	108.7
F ₋ -C1-C2	110.8	110.3	110.7	110.3	110.6
F ₊ -C1-C2	110.9	110.6	110.9	110.6	110.9
C1-C2-C3-C4	-167.5	-164.4	-165.4	-164.4	-163.0
C2-C3-C4-C5			-162.2	-162.9	-164.3
C3-C4-C5-C6					-160.9
F ₁ -C1-C2-C3	-171.6	-169.0	-169.4	-169.3	-170.9
F ₋ -C1-C2-C3	-52.1	-49.5	-49.9	-49.8	-51.5
F ₊ -C1-C2-C3	69.0	71.5	71.2	71.1	69.9
F-C1...C3-F ^b	17.5, 17.9	21.9, 22.5	21.0, 21.6	21.6, 22.0	21.1, 22.2
F-C2...C4-F ^b		26.7, 26.7	27.1, 27.7	27.7, 27.6	27.5, 27.6
F-C3...C5-F ^b				28.9, 28.9	29.6, 29.6

^a Distances in Å and angles in degrees. ^b Dihedral angles corresponding to 1,5-diaxial interactions. They are 0.0 for a perfectly C_{2h} (n is even) or C_{2v} (n is odd) staggered conformation. The values of both interactions are shown for every pair of carbons.

used by Benson³⁸ or Liebman,^{2,3} where the four different CF_2 groups here defined for $n\text{-C}_8\text{F}_{18}$ could be considered as four different environments of the same group. The different criterion for group definition can be considered as one of the factors that give rise to obtain different values of the strain energies of heterocycles using QTAIM and group contribution models.

Looking at the corresponding $E(\Omega)$ values (Table 4), we observe that: (i) this property varies significantly for CF_3 , CF_2^{α} , and CF_2^{β} groups along the series of molecules here considered, (ii) the energy gap between two equivalent fragments of molecules that differ in one CF_2 becomes progressively smaller as the number of carbon rises, and (iii) the only atomic groups that differ by less than 6 kJ mol^{-1} (which is close to the limits of the energy accuracy obtained when summing the atomic energies of a molecule) are the CF_2^{CC} of $n\text{-C}_7\text{F}_{16}$ and the CF_2^{C}

TABLE 5: Strain Energies, SE, Computed for (CF₂)_n Cycloperfluoroalkanes According to Homodesmotic Processes (eqs 2–4) (see text) and Their Components Due to ZPVE, SE_H^{vib}

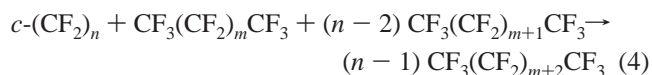
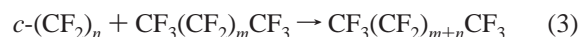
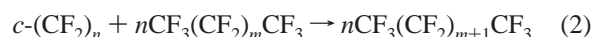
	process (eq)	<i>m</i>	SE _H	ΔSE _H	SE _H ^{vib}	ΔSE _H ^{vib}	SE ^{Q^d}	SE ^{f^d}	ΔE _H ^{RO}	ΔE _H ^{NC}	ε _H	
<i>c</i> -C ₃ F ₆	(2)	2	172.4	6.0	-7.4	0.8	-85.4	179.9				
		3	172.5		-7.1				61.3	-246.6	-5.8	
		4	175.4		-7.3				96.8	-274.3	5.2	
		5	169.4		-6.6				85.4	-256.7	4.7	
		3	173.4		-7.3							
	(3)	2	173.4	-7.3					53.7	-231.8	1.4	
		3	172.4	-7.0								
	(4)	2	172.4	-7.2								
		3	174.4	-7.2					67.3	-247.4	1.5	
		4	171.4	-6.8					85.4	-258.7	4.9	
<i>c</i> -C ₄ F ₈	(2)	2	57.1	7.9	-4.9	1.0	-296.6	62.2				
		3	57.2		-4.6				264.4	-328.8	-2.6	
		4	61.1		-4.8				311.8	-365.7	12.0	
		5	53.1		-3.9				296.6	-342.3	11.4	
		2	57.1		-4.6							
	(3)	2	57.1	-4.6								
		4	57.2	-4.7								
	(4)	3	60.1	-4.7					282.3	-338.8	8.4	
		4	55.1	-4.1					296.6	344.3	11.5	
		2	-4.3	9.9	-2.3	1.3	-450.4	-1.9				
<i>c</i> -C ₅ F ₁₀	(2)	3	-4.3		-1.9				410.4	-411.0	-3.0	
		4	0.6		-2.2				469.6	-457.1	15.2	
		5	-9.3		-1.1				450.5	-427.8	14.4	
		2	-4.3		-2.0							
		3	-0.4		-2.1				440.1	-430.2	11.6	
	(4)	4	-7.4		-1.3				450.5	-429.9	14.6	
		2	-21.8	11.9	-1.4	1.5	-558.6	-20.2				
		3	-21.7		-0.9				510.4	-493.2	-3.6	
	<i>c</i> -C ₆ F ₁₂ ^b	(2)	4	-15.9		-1.2				581.4	-548.5	18.3
			5	-27.8		0.1				558.6	-513.4	17.3
2			-21.7		-1.0							
3			-16.8		-1.2				551.9	-521.6	14.7	
4			-25.8		-0.1				558.6	-515.4	17.5	
(4)		2	-4.6	11.9	-1.4	1.5	-539.9	-3.1				
		3	-4.5		-0.9				491.7	-493.2	-5.1	
		4	1.3		-1.2				562.7	-548.5	16.8	
<i>c</i> -C ₆ F ₁₂ ^c		(2)	5	-10.6		0.1				539.9	-513.4	15.8
			2	-4.5		-1.0						
	3		0.3		-1.2				533.2	-521.6	13.1	
	4		-8.6		-0.1				539.9	-515.4	15.9	
	2		16.3	13.9	-0.8	1.8	-605.4	17.3				
	(4)	3	16.4		-0.2				549.1	-575.4	-9.6	
		4	23.2		-0.6				632.0	-639.9	15.9	
		5	9.3		1.0				605.4	-599.0	14.8	
	(4)	2	16.4		-0.3							
		3	22.2		-0.5				602.5	-613.1	12.2	
4		11.3		0.8				605.4	-601.0	14.9		

^a Maximum variations observed for both quantities in every compound (ΔSE_H and ΔSE_H^{vib}), and SE^f values as well as the components of SE_H^Q are also shown. All values in kJ mol⁻¹. ^b Chair conformer. ^c Twist-boat conformer. ^d SE^Q and SE^f values do not depend on the process and are common for each compound.

The irregular geometry of the *c*-C₅F₁₀ conformer gives rise to different values of atomic electron population and energies for each atom. We notice that C atoms with the largest atomic populations are the most stabilized (C1 and C2). The twist-boat conformer of *c*-C₆F₁₂ presents two different CF₂ groups (Figure 1 and Table 4). The one with pseudoaxial and pseudo-equatorial fluorines being the most stabilized and electron populated. Finally, four different CF₂ groups are present in the optimized conformer of *c*-C₇F₁₄, as some are equivalent because of its C₂ symmetry (Figure 3). The largest destabilization and smallest electron population corresponds to the CF₂ group whose carbon atom (C6) is on the C₂ axis.

Homodesmotic Strain Energies. Several homodesmotic processes can be employed to calculate the SE_H of *c*-PFAs here considered using the total molecular energies and ZPVEs of the *n*-PFA shown in Table 1. Some of these processes are summarized by eqs 2–4. The SE_H computed with 2 ≤ *m* ≤ 5 (when all the linear compounds involved in the process belong to the series *n*-C₄F₁₀–*n*-C₈F₁₈) differ for a same cycle as much as 6–14 kJ mol⁻¹ (Table 5). These differences are larger than

those originated by ZPVE corrections, ΔSE_H^{vib}, which are always less than 2 kJ mol⁻¹ (Table 5).



It is also noticeable that *c*-C₅F₁₀ and both conformers of *c*-C₆F₁₂ display negative SE_H values, with the chair conformer of *c*-C₆F₁₂ presenting the most negative ones. A plausibly negative strain energy has been discussed for perchlorocycloalkanes in a previous work,⁴⁰ bearing in mind that SEs are defined as relative to some strainless species, which need not have the lowest energy of species composed by the groups contained therein.

The sequence of SE_H values obtained for equivalent processes (same equation and same *m* value) follows the same order

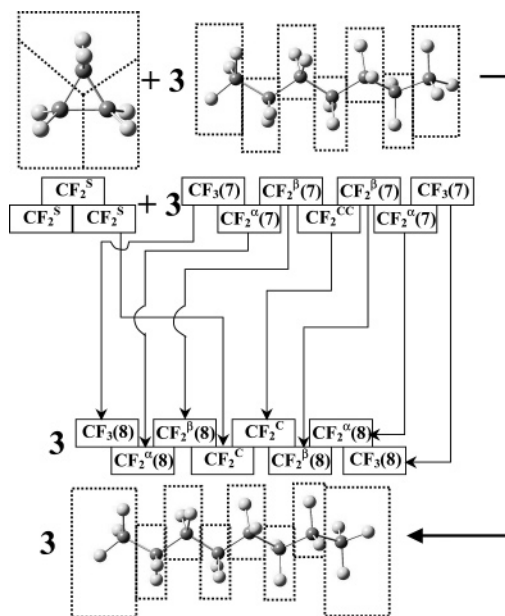
obtained for cycloalkanes.^{1,41} Thus, $SE_H(c-C_3F_6) > SE_H(c-C_4F_8) > SE_H(c-C_7F_{14}) > SE_H(c-C_5F_{10}) > SE_H(c-C_6F_{12}, \text{chair})$. Nevertheless, the SE_H obtained for $c-C_3F_6$ is much larger than that for $c-C_4F_8$ (114–116 kJ mol⁻¹), whereas the SE_H generally accepted values of cyclopropane and cyclobutane^{1,29} differ by less than 5 kJ mol⁻¹. This result agrees with previous calculations of SE_H carried out for $c-C_3F_6$ and $c-C_4F_8$,^{42,43} where it is also found that perfluorination increases the SE_H of cyclopropane and decreases that of cyclobutane.^{42–44} Thus values of 226 kJ mol⁻¹ for $c-C_3F_6$ and from 61 to 75 kJ mol⁻¹ for C_4F_8 were reported by Liebman et al.⁴² on the basis of Benson's group increments and experimental $\Delta H_f(\text{gas})$ values for both molecules. HF/6-311G** optimizations lead to SE_H values of 472 and 65 kJ mol⁻¹ for $c-C_3F_6$ depending on the linear compounds used as references for the homodesmotic process.⁴³ Finally, diagonal and ultradiagonal SE_H values of 259 kJ mol⁻¹ were computed at the same computational level assuming a zero SE for perfluorocyclohexane,⁴³ which is not confirmed by our calculations. Nevertheless, as commented above, the diverse SE_H are relative to different reference strainless species.

Moreover, the difference between SE_H values of $c-C_7F_{14}$ and $c-C_5F_{10}$ is significantly larger than that between the SE_H s of $c-C_7H_{14}$ and $c-C_5H_{10}$ (0.4 kJ mol⁻¹ from experimental data¹ and 1.2 kJ mol⁻¹ using MP2/6-31+G* calculations⁴¹). Finally, SE_H values calculated for the twist-boat conformer of $c-C_6F_{12}$ are approximately equal to those obtained for $c-C_5F_{10}$.

QTAIM Strain Energies. In contrast with the multiple SE_H values associatable to a given cyclic compound, QTAIM provides a unique SE^Q value for each ring. It is defined as the difference between the summation of group energies in the cycle and those of the nearly transferable fragments of the corresponding linear groups, which are taken as the strainless reference. Another way to obtain a unique value of SE for each ring consists of using fitted values for the group energies of the strainless reference. The energy of each group is obtained by fitting a series of electron molecular energies of linear compounds to the number of groups of each kind presented by them. Hereafter, the values computed with this reference are named SE^f .

We observe that the election of the strainless reference is not meaningless. In fact, SE^f values display similar evolution and values to SE_H ones for the series here considered (Table 5). In contrast, SE^Q values differ a lot from SE_H ones (hundreds of kJ mol⁻¹); they even display opposite signs in several cases ($c-C_3F_6$, $c-C_4F_8$, and $c-C_7F_{14}$) and follow a different sequence of relative values for the series (Table 5). On the contrary, SE^Q values only contain the energy involved in ring opening.

Why are SE^Q values so different from SE_H and SE^f ? The calculation of SE_H using the group energies provided by QTAIM and listed in Table 4 gives insight about this question. Let's consider, for instance, one molecule of $c-C_3F_6$ experiencing the eq 2 process with $m = 5$ (Figure 6). We observe that reagents are made up by: three specific CF_2 three-membered ring groups, six specific CF_3 groups of $n-C_7F_{16}$, six specific CF_2^α groups of $n-C_7F_{16}$, six specific CF_2^β groups of $n-C_7F_{16}$, and three specific CF_2^C group of $n-C_7F_{16}$. The products are made up by: six specific CF_3 groups of $n-C_8F_{18}$, six specific CF_2^α groups of $n-C_8F_{18}$, six specific CF_2^β groups of $n-C_8F_{18}$, and six nearly transferable CF_2^C groups. Therefore, none of the groups is common to reagents and products. Also, only six groups are strictly involved in the ring opening process (the three specific CF_2 three-membered ring groups of reagents and three of the six nearly transferable CF_2^C groups). The difference between the energy of these groups (85.4 kJ mol⁻¹) is the one implied



3 [$CF_2^S \rightarrow CF_2^C$]	3(28.5)	$\Delta E^{RO} = 85.4$
3 [$CF_2^{CC} \rightarrow CF_2^C$]	3(-3.8)	$\Delta E^{NC} = -256.7$
6 [$CF_2^\alpha(C_7F_{14}) \rightarrow CF_2^\alpha(C_8F_{16})$]	6(-10.2)	
6 [$CF_2^\beta(C_7F_{14}) \rightarrow CF_2^\beta(C_8F_{16})$]	6(-6.0)	
6 [$CF_3(C_7F_{14}) \rightarrow CF_3(C_8F_{16})$]	6(-24.8)	

Figure 6. Scheme indicating the transformation of molecular groups experienced within homodesmotic process (eq 2) for perfluorocyclopropane with $m = 5$ and which of them belong to ΔE^{RO} and ΔE^{NC} . The energy variation associated to each change is shown in parentheses (in kJ mol⁻¹).

in the ring-opening process, ΔE_H^{RO} , and in this process (but not in all, see below) is just the opposite to SE^Q . The difference between the energies of the remaining groups (-256.7 kJ mol⁻¹) is an energy term included in SE_H and due to the presence of linear compounds in reagents, ΔE_H^{NC} . The summation of ΔE_H^{NC} and ΔE_H^{RO} differs only from $-SE_H$ in an error term originated in the numerical computation of $E(\Omega)$ in each molecule. This error term is given by the summation of the errors in the molecular energy listed in Table 1 once they are multiplied by the stoichiometric coefficients in eq 2.

The process represented by eq 2 with $m = 4$ is an example where ΔE_H^{RO} (96.8 kJ mol⁻¹) and $-SE^Q$ (85.4 kJ mol⁻¹) do not coincide. It is easy to demonstrate that the energy difference (11.4 kJ mol⁻¹) should be, as it is, three times the difference between the energy of the nearly transferable CF_2^C group and that of the corresponding specific group in $n-C_7F_{16}$ (3.8 kJ mol⁻¹, Table 4).

The values obtained for SE^Q are negative for all the cycles here studied (Table 5), as the specific CF_2 cyclic groups are always more stabilized than the near transferable linear one (Table 4). The larger the cycle, the more negative SE^Q is. This does not keep in line with the evolution sequence of SE_H . Nevertheless, when SE^Q values are divided by the number of CF_2 groups in the molecule, we obtain the largest stabilization per CF_2 groups corresponding to the chair conformer of $c-C_6F_{12}$ (-93.1 kJ mol⁻¹) that is close to the average found in $c-C_5F_{10}$ (-90.1 kJ mol⁻¹) and $c-C_7F_{14}$ (-86.5 kJ mol⁻¹). Finally, the stabilization gained by a CF_2 group in $c-C_4F_8$ (-74.1 kJ mol⁻¹) is much larger than in $c-C_3F_6$ (-28.5 kJ mol⁻¹).

Looking at the atomic components of CF₂ stabilization in the cycles and at the differences between the atomic populations in the cycle and the nearly transferable linear CF₂ (Table 4 and Figures 1–3), we observe that: (i) All the carbon atoms gain stability in the cycles (C6 in *c*-C₇F₁₄ being the only exception). (ii) Most of the fluorine atoms of *c*-C_{*n*}F_{2*n*} compounds with *n* > 4 are more stabilized than in the nearly transferable linear CF₂, and they lose electron population that is gained by the carbons. (iii) Perfluorocyclobutane presents a specific behavior with pseudoequatorial fluorines stabilized more than the destabilization displayed by axial fluorines. In this case, the carbon atoms lose electron population (with regard to the CF₂^C fragment) gained by the fluorines (more by those in pseudoequatorial disposition). (iv) CF₂ groups of perfluorocyclopropane display also specific characteristics, as their atomic electron populations coincide with those of the CF₂^C fragment. In contrast, carbons are stabilized, whereas fluorines are destabilized, giving rise to the lowest value of ΔE^{RO} in the series.

Theoretical Approach to the Relations between the Diverse SE Here Considered. Strain energies, SE, are computed using a homodesmotic, diagonal, or other chemical process, SE_H, using eq 5, where ν_{*i*}^H refers to the stoichiometric coefficients of reactant *i* in process H (positive for products and negative for reagents), and E_{*i*}^{el} and E_{*i*}^{vib} denote, respectively, the electronic (including nuclear–nuclear repulsion) and vibrational molecular energy of reactant *i*. According to QTAIM the electronic molecular energy can be obtained by adding the atomic energies, E_{*i*}(Ω). Because of the numerical procedure employed to compute E_{*i*}(Ω) values, their summation differs from the electronic molecular energy in term ε_{*i*}, usually employed as one of the parameters that estimate the quality assignable to the QTAIM-computed atomic properties and calculated by eq 6. By replacing E_{*i*}^{el} in eq 5, we obtain eq 7. Equation 7 becomes eq 11 when we introduce: the vibrational contribution to strain energy, SE_H^{vib} (defined by eq 8), the total error affecting the computation of SE_H with atomic energies, ε_H (defined by eq 9), and the homodesmotic strain energy computed with QTAIM atomic energies, SE_H^Q (defined by eq 10).

$$SE_H = -\sum_i \nu_i^H (E_i^{\text{vib}} + E_i^{\text{el}}) \quad (5)$$

$$\epsilon_i = [\sum_{\Omega} E_i(\Omega)] - E_i^{\text{el}} \quad (6)$$

$$SE_H = -\sum_i \nu_i^H \{ [\sum_{\Omega} E_i(\Omega)] + E_i^{\text{vib}} - \epsilon_i \} \quad (7)$$

$$SE_H^{\text{vib}} = -\sum_i \nu_i^H E_i^{\text{vib}} \quad (8)$$

$$\epsilon_H = \sum_i \nu_i^H \epsilon_i \quad (9)$$

$$SE_H^Q = -\sum_i \nu_i^H \sum_{\Omega} E_i(\Omega) \quad (10)$$

$$SE_H = SE_H^{\text{vib}} + SE_H^Q + \epsilon_H \quad (11)$$

The SE_H^Q term can be split by considering different criteria. One of them is distinguishing between atoms involved (Ω_{RO}) and not involved (Ω_{NC}) in ring opening, as indicated in eq 12. This allows definition of the ring-opening energy, ΔE_H^{RO}, and the term due to other noncyclic groups, ΔE_H^{NC}, involved in the homodesmotic process (eqs 13 and 14, respectively). By using these terms, eq 11 transforms into eq 15.

$$SE_H^Q = -\sum_i \nu_i^H \left[\sum_{\Omega_{RO}} E_i(\Omega_{RO}) + \sum_{\Omega_{NC}} E_i(\Omega_{NC}) \right] \quad (12)$$

$$\Delta E_H^{RO} = \sum_i \nu_i^H \sum_{\Omega_{RO}} E_i(\Omega_{RO}) \quad (13)$$

$$\Delta E_H^{NC} = \sum_i \nu_i^H \sum_{\Omega_{NC}} E_i(\Omega_{NC}) \quad (14)$$

$$SE_H = SE_H^{\text{vib}} + \epsilon_H - [\Delta E_H^{RO} + \Delta E_H^{NC}] \quad (15)$$

Depending on the homodesmotic process, ΔE_H^{RO} defined by eq 13 may contain in the products atoms that belong to the nearly transferable linear groups, Ω_{RO}^t, or to specific linear groups, Ω_{RO}^s. So, in general, we can write eq 16, where the first summation extends to products, p, and the second to reagents, r. As the only reagent involved in ring opening is the cycle, no atom included in the second summation belongs to a nearly transferable linear group. Also, the summation can be reduced to the atoms in the cycle, Ω_c, and ν_{*r*}^H is –1. Considering a certain homodesmotic process, HT, where all the Ω_{RO} atoms of the products belong to nearly transferable linear groups, ΔE_{HT}^{RO} coincides with the definition given for a SE computed using nearly transferable linear groups as the strainless reference, SE^Q, as is written in eq 17. The energy of a specific atom in a linear compound can be related to that of the corresponding nearly transferable atom by eq 18. Then the ΔE_H^{RO} term of any process can be related to SE^Q by eq 19.

$$\Delta E_H^{RO} = \sum_p \nu_p^H \left[\sum_{\Omega_{RO}^t} E_p(\Omega_{RO}^t) + \sum_{\Omega_{RO}^s} E_p(\Omega_{RO}^s) \right] - \sum_r |\nu_r^H| \sum_{\Omega_{RO}^s} E_r(\Omega_{RO}^s) \quad (16)$$

$$\Delta E_{HT}^{RO} = \left[\sum_p \nu_p^H \sum_{\Omega_{RO}^t} E_p(\Omega_{RO}^t) \right] - \left[\sum_{\Omega_c} E(\Omega_c^s) \right] = -SE^Q \quad (17)$$

$$E_p(\Omega_{RO}^s) = E_p(\Omega_{RO}^t) + \delta E_p(\Omega_{RO}) \quad (18)$$

$$\Delta E_H^{RO} = -SE^Q + \left[\sum_p \nu_p^H \sum_{\Omega_{RO}^s} \delta E_p(\Omega_{RO}) \right] \quad (19)$$

The second term on the right-hand side of eq 19 will be named in what follows as nontransferability contribution to ring-opening energy, ΔE_H^{RONT}. This term is different for each process and may be positive or negative depending on the groups considered. Thus, eq 15 becomes eq 20.

$$SE_H = SE_H^{\text{vib}} + \epsilon_H + SE^Q - [\Delta E_H^{\text{RONT}} + \Delta E_H^{NC}] \quad (20)$$

Finally, we should look for a relationship between SE_H and the strain energy obtained using fitted group energies, SE^f. The term SE^f is defined as the difference between the energy of the cycle, E_c, and the summation of the fitted energies of the corresponding groups resulting from ring opening, E_G^f. It is given by eq 21, where n_G is the number of G groups in a cycle. In this case, the balance of molecular electronic energies included in eq 5 is given by eq 22, where ε_f represents the error introduced by the fitted value in this calculation. Therefore, eq 23 confirms that SE_H and SE^f only differ by small terms and should be very similar, as shown in Table 5. In fact, the largest difference between SE^f and SE_H is 10.5 kJ mol^{–1} (process eq 2 with *m* = 5 for *c*-C₃F₆), whereas it does not exceed 4.3 kJ mol^{–1} for the chair conformer of *c*-C₆F₁₂.

$$SE^f = E_c - \sum_G n_G E_G^f \quad (21)$$

$$\sum_i v_i^H E_i^{el} = SE^f + \epsilon_f \quad (22)$$

$$SE_H = SE^f + SE_H^{vib} - \epsilon_f \quad (23)$$

As commented in a previous section, group energies obtained by fitting equations such as eq 1 correspond neither to specific nor to nearly transferable groups. They are a certain average of the diverse group energies in the series of molecules. By comparing the equations obtained by inserting eq 21 in eq 23 and eq 17 in eq 20, and taking into account eqs 6 and 9, we get eq 24. The summation in the first term on the right-hand side represents the nearly transferable energy of the groups resulting from ring opening, $\sum_G n_G E_G^t$. Thus, we finally get eq 25, which indicates the average character of fitted group energies and how they include the main causes (energy differences due to transformation of noncyclic reagents, nontransferability of groups obtained by ring opening) that make SE^Q and SE_H so different. The average character is even more clear, considering molecules, like perfluorocycloalkanes, where all the linear fragments obtained by ring opening, are equivalent, and we can write eq 26.

$$\sum_G n_G E_G^f = \left[\sum_p v_p^H \sum_{\Omega_{RO}^t} E_p(\Omega_{RO}^t) \right] + \Delta E_H^{RONT} - \Delta E_H^{NC} - \epsilon_f - \sum_{i \neq c} \epsilon_i \quad (24)$$

$$\sum_G n_G E_G^f = \left[\sum_G n_G E_G^t \right] + \Delta E_H^{RONT} - \Delta E_H^{NC} - \epsilon_f - \sum_{i \neq c} \epsilon_i \quad (25)$$

$$E_G^f = E_G^t + \left[(\Delta E_H^{RONT} - \Delta E_H^{NC} - \epsilon_f - \sum_{i \neq c} \epsilon_i) / n_G \right] \quad (26)$$

Conclusions

Homodesmotic strain energies SE_H include an energy term, ΔE_H^{NC} , that QTAIM atomic energies show as due to the balance between noncyclic fragments and that should not be present in SE. Moreover, this term varies depending on the particular homodesmotic process selected to compute SE_H and gives rise to the multiplicity of SE_H values that can be obtained for a same cycle. For example, six different values of SE_H (ranging from 9.3 to 23.2 kJ mol⁻¹) are obtained in this work for the seven homodesmotic processes considered for *c*-C₇F₁₄. In contrast, SE computed by using the exclusively energy of the cyclic molecule and the energy of nearly transferable linear fragments, SE^Q , provides a unique value for each cycle that only contains energy due to ring opening. The computation of SE replacing the energy of the nearly transferable linear fragment with the energy obtained by fitting the molecular energies to the number of CF₂ groups, SE^f , introduces an averaged ΔE_H^{NC} term as a mean of different groups included in the fitting. Thus, SE^f value is unique for each cycle but includes energy that is not due to ring opening. It has to be remarked that SE^Q values span a different range and display different trends to those computed with homodesmotic, diagonal, or other processes. So, on first view, SE^Q values can be considered surprising despite their physical meaning.

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