

Enthalpy of Formation of Carbocycles: A Precise Theoretical Determination of Experimentally Imprecise Measurements.

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ARTICLE INFO

Keywords:

carbocycles
enthalpy of formation
strain energy
composite methods

ABSTRACT

Despite being one of the best-known families of organic compounds, the fact that hydrocarbons exhibit a rich variety of structures owing to branching, cyclization, and the presence of multiple bonds, means that many of their properties are yet to be determined accurately, or even at all. Among cyclic hydrocarbons, those with three-membered rings are particularly interesting because of their strain energy. In this paper, we report accurate calculations of the enthalpy of formation of three-membered carbocycles, whose experimental values have not been obtained by direct measurement of the heat of combustion. For this purpose, we used several accurate composite methods to obtain the gas-phase enthalpies of atomization and derived from them the gas-phase enthalpies of formation, using experimentally determined accurate values for the atoms. Moreover, to minimize the inaccuracy that can possibly arise in this procedure, we also used homodesmotic reactions designed to balance systematic errors in the geometric and electronic structure of some of the species. A careful analysis of the results shows that some of the indirectly derived values reported in the literature are far from the most accurate theoretical outcomes, and we suggest that these new ones should be adopted.

1. Introduction

Hydrocarbons constitute the simplest family of organic chemicals. Their properties have been studied in multiple original papers and review articles but owing to the possibility of cyclization and multiple bonds, the sheer complexity of the manifold of C_nH_m structures causes that many properties of some of these species have not been determined accurately [1,2].

Among the hydrocarbons, carbocycles with saturated and unsaturated bonds attracted a lot of attention. In particular, the study of thermochemical properties of carbocycles containing three-membered rings (among others) has been the subject of many publications [3–16], since ring strain [17,18] (an important factor for obtaining better fuels [19,20]) and aromaticity/antiaromaticity [21,22] are important considerations in the building up of more complex structures, and the understanding of their isomerization and conformation [23–25].

Computational chemistry is particularly well-suited for the study of thermochemical properties of small- and medium-size systems,

especially enthalpies of formation, which in many cases are not experimentally available [5-16,26-33]. Following this approach, in this paper we seek to determine precisely and accurately the enthalpy of formation of some three-membered cyclic hydrocarbons studied previously by one of us [3], for which experimental results were (and mostly still are) not available.

The chemical species studied in this work are shown in Fig. 1. All of them are hydrocarbons that contain at least one C3-ring. The largest species studied in this paper is $C_{11}H_{10}$, [4.4.1]propellatetraene. In the name of brevity, we limited ourselves to the structures studied previously by Liebman (also a coauthor in the present study) and Greenberg [3] (from now on abbreviated as LG89) for which no direct calorimetric data is available, and the enthalpies of formation were derived from other sources (hence the abbreviation DRV in LG89 [3]). We also included the parent compounds, cyclopropane and cyclopropene, and, in some cases, when isodesmic or homodesmotic reactions [31] were employed, the auxiliary molecules needed. The species used are reported in each case in the specific section and full calculated data is

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<https://doi.org/10.1016/j.ctta.2023.100121>

Received 13 September 2023; Accepted 3 October 2023

Available online 5 October 2023

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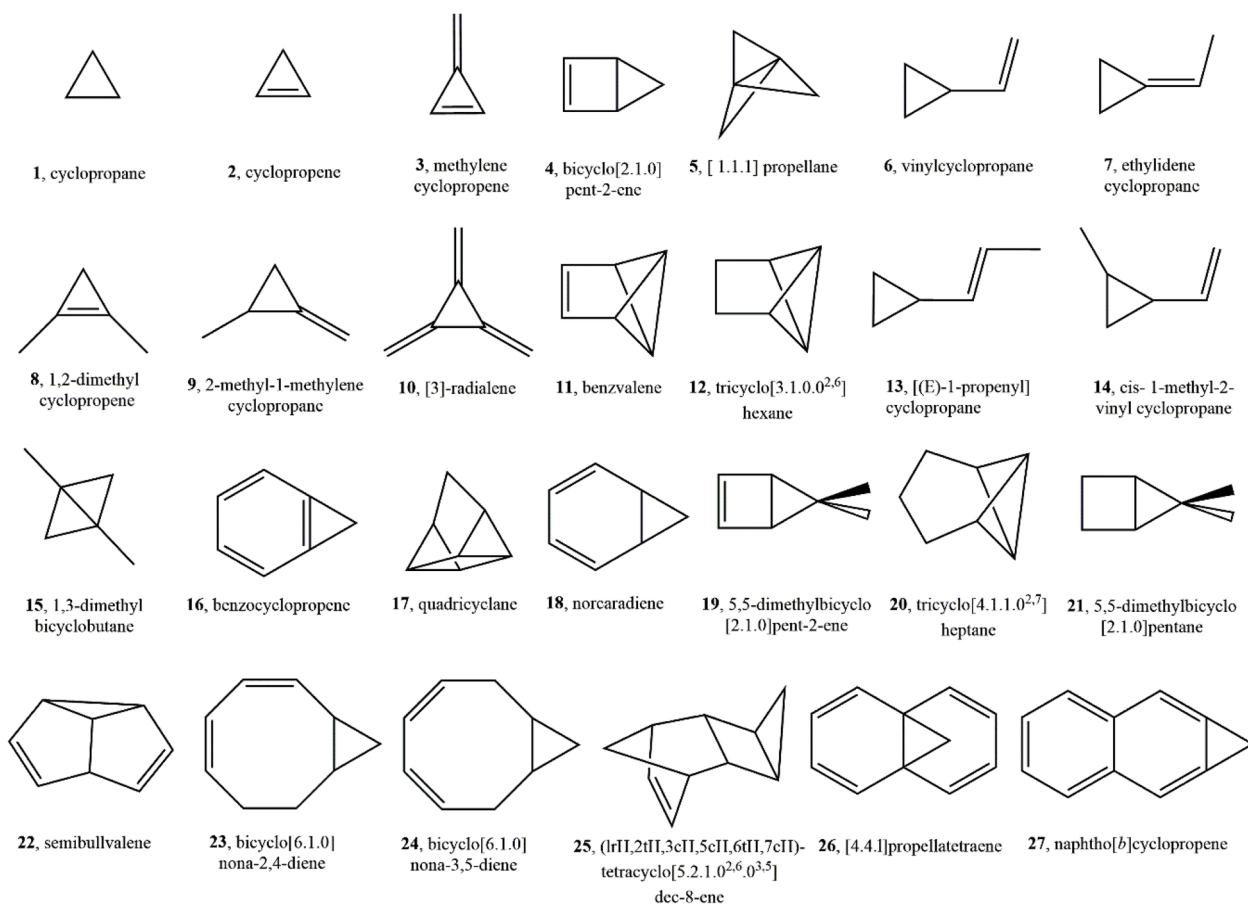


Fig. 1. Schematic structures and names of the species studied in this work.

Table 1

Enthalpy of formation (kJ mol^{-1}) of cyclopropane (1) and cyclopropene (2) using atomization, homodesmotic and isodesmic reactions with different computation schemes)

SPECIES		Name	Procedure	CBS-QB3	G4	W1BD	SVECV	jChS	DRV ^a	Other			FINAL ^e	
Nr	Global									ATct ^b	Theor ^c	Exptl ^d	μ	$\pm 2\sigma$
1	C ₃ H ₆	Cyclopropane	Atomization ^g	62.6	57.9	51.8	51.0	48.8	277.1	283.6	284.5	277.0	52.7	± 6.6
			Isodesmic ^h	55.8	53.0	58.2	55.5	56.0					55.7	± 3.7
			Isodesmic ^m	51.6	50.3	51.0	55.0	55.5					53.3	± 5.3
			Homodesmotic ⁱ	55.4	53.6	55.4	54.1	54.8					54.5	± 1.4 ^f
2	C ₃ H ₄	Cyclopropene	Atomization ^g	292.2	286.8	282.2	280.9	279.9	277.1	283.6	284.5	277.0	283.5	± 5.4
			Isodesmic ^j	294.4	282.8	286.4	286.6	284.8					285.1	± 3.0
			Homodesmotic ^k	261.7	272.5	272.7	273.8	271.5					272.6	± 1.7 ^f

^a Reported as derived from non-calorimetric data in ref. [3] referred in the following as LG89.

^b ref. [73].

^c ref. [16].

^d from ref. [76].

^e average μ and two times the standard deviation (2σ for a 95% confidence interval) of the results obtained at the G4, W1BD, SVECV-f12 and jChS levels.

^f best value predicted for the enthalpy of formation.

^g according to reaction (1).

^h according to reactions (2) and (4).

ⁱ according to reactions (2) and (3).

^j according to reactions (2) and (6).

^k according to reactions (2) and (5).

^l ref. [79].

^m according to reaction (7).

given in the Supplementary Information (SI) section.

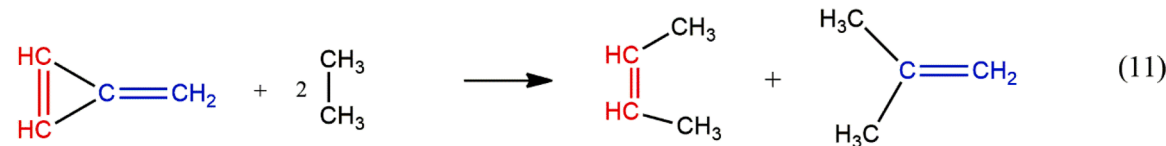
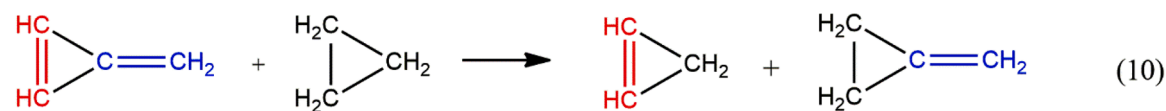
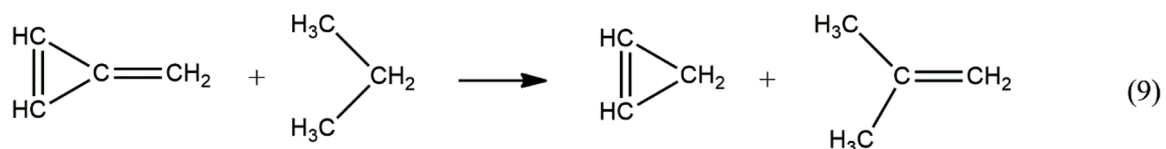
2. Computational methods

2.1. Calculation of the enthalpy of formation

In all cases, standard enthalpies of formation at 298.15 K,

Table 2Strain energy (kJ mol^{-1}) of cyclopropane (1) and cyclopropene (2) using homodesmotic and isodesmic reactions with different computation schemes.

SPECIES				CBS-QB3	G4	W1BD	SVECV -f12	jChS	Other	FINAL ^a	
Nr	Global	Name	Procedure							μ	$\pm 2\sigma$
1	C_3H_6	Cyclopropane	Isodesmic (3)	84.3	81.5	86.7	84.0	84.5	82.8 ^b , 79.1 ^m 110.9 ^b , 115.0 ^m 115.1 ^c , 115.8 ^d , 117.6 ^d 169.9 ^b 222.6 ^b 225.1 ^c , 225.8 ^e , 230.1 ^f , 232.2 ^g , 226.4 ^h , 233.0 ⁱ , 226.4 ^j , 226.4 ^k , 234.3 ^l	84.2	± 2.1
			Isodesmic (7)	114.7	113.4	114.1	116.5	115.7		114.9	± 1.3
			Homodesmotic (4)	118.4	116.6	118.4	117.1	117.8		117.5	± 0.7
			Others								
2	C_3H_4	Cyclopropene	Isodesmic (5)	186.5	174.9	178.5	178.7	176.9	177.2	± 1.5	
			Homodesmotic (6)	211.1	221.9	222.1	223.2	220.9	222.0	± 0.8	
			Others								

^a average (μ) and two times the standard deviation, 2σ (for a 95% significance interval) of the results obtained at the G4, W1BD, SVECV-f12 and jChS levels.^b ref. [35].^c Conventional Ring Strain Energy, as given in ref. [25].^d ref. [80].^e ref. [81].^f ref. [82].^g ref. [83].^h ref. [84].ⁱ ref. [85].^j ref. [86].^k ref. [87].^l ref. [88].^m ref. [89].**Fig. 2.** Isodesmic and homodesmotic reactions used to calculate the enthalpy of formation of methylenecyclopropene.**Table 3**Enthalpies of formation and strain energy of methylenecyclopropene obtained with different composite quantum chemistry methods. Values in kJ mol^{-1} .

Method	Atomization	Isodesmic (9)	Homodesmotic (10)	Homodesmotic (11)	
				Enthalpy of Formation	Strain Energy
CBS-QB3	399.2	372.6	386.6	383.0	241.3
G4	391.2	373.8	387.8	383.8	242.1
W1BD	386.5	372.7	386.7	383.8	242.0
SVECV-f12	386.3	372.4	386.4	386.4	244.6
jChS	384.9	373.3	387.3	382.9	241.2
Bakowies ^a				389.1	
ATcT ^b				388.0	
Derived ^c				423.0	
Ref. [77]				391.6	
$\mu \pm 2\sigma^d$	387.2 ± 4.7	373.1 ± 1.1	387.1 ± 1.1	384.2 ± 2.6	242.2 ± 2.8

^a Reference [16].^b Reference [73].^c Reference [3]3.^d average (μ) and two-times the standard deviation (2σ) of the G4, W1BD, SVECV-f12 and jChS results.

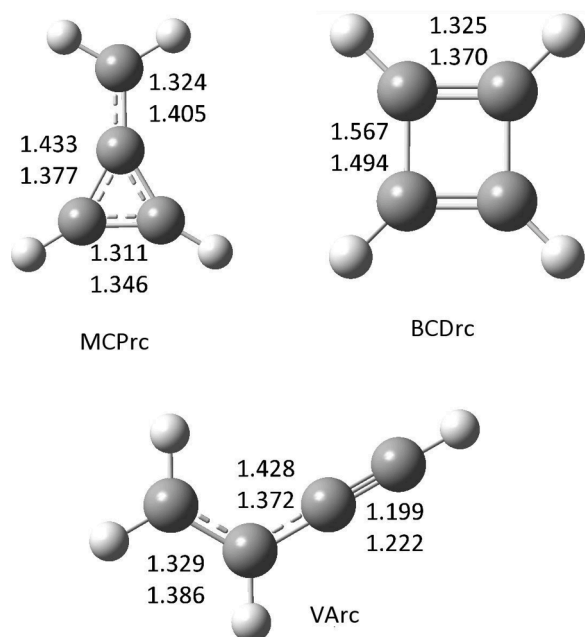


Fig. 3. Structure of the parent species and radical cations of methylcyclopropane, 1,3-cyclobutadiene and vinylacetylene. Carbon-carbon distances (in Å) are shown for the neutral (top entry) and the radical cation (bottom entry) at the M06-2X-D3/aug-cc-pVTZ level of theory.

$\Delta_f H^0(298.15\text{K})$, were derived from the enthalpies of atomization, employing the $\Delta_f H^0(298.15\text{K})$ of the corresponding atoms in their ground states [34] ($\text{H}(^1\text{S}_{1/2})$ $218.00 \pm 0.01 \text{ kJ mol}^{-1}$, $\text{C}(^3\text{P}_0)$ $716.68 \pm 0.45 \text{ kJ mol}^{-1}$) and the formula

$$\Delta_f H^0(A) = \Delta_r^{\text{theor}} H^0_{\text{atomization}} + \sum_a n_a \Delta_f^{\text{exptl}} H^0 \quad (1)$$

where *theor* refers to enthalpies calculated theoretically and *exptl* to experimental values. The subscripts *f* and *r* are abbreviations of formation and reaction respectively, n_a identifies the number of atoms *a* in molecule *A*, and all values are taken at 298.15K. In some cases, the subscript *c* has been used to indicate combustion as opposed to some reaction used to derive the enthalpy of formation.

Moreover, we used homodesmotic reactions [31] for exploring the possibility of failures in the calculation of the enthalpy of formation from other species which experimental $\Delta_f H^0$ are accurately known. Homodesmotic reactions are a special type of isodesmic reactions where the bond types, hybridization of the atoms and number of carbons and hydrogens are equal on both sides of the chemical equation. The general formulation for a reaction $\text{A} + \text{B} + \text{D} \dots \rightarrow \text{X} + \text{Y} + \text{Z} \dots$ would be

$$\Delta_f H^0(A) = -\Delta_r^{\text{theor}} H - \sum_{B,C,D,\dots} \Delta_f^{\text{exptl}} H^0 + \sum_{X,Y,Z,\dots} \Delta_f^{\text{exptl}} H^0 \quad (2)$$

where *A* is the species which enthalpy of formation one wants to obtain and *B*, *C*, ..., *X*, *Y*, ... etc., the other species that participate in the homodesmotic reaction. This procedure is expected to greatly reduce any error in the calculation of the enthalpies of reaction but requires that the experimental (or high-accuracy theoretical) enthalpy of formation of the species *B*, *C*, etc. are known with the desired accuracy.

2.2. Calculation of strain energies

For the calculation of the strain energies, we followed the approach first developed by George et al. [35] which relies in the construction of formal homodesmotic or isodesmic reactions from which the enthalpy of reaction (*i.e.*, the strain energy) is obtained. For instance, in the case of cyclopropane, they proposed the following reactions:



We will present the reactions used in the discussion for each species.

2.3. Calculation of individual energies of the species

The individual values of the enthalpies necessary for using equations (1) and (2) can be calculated using density functional (DFT) methods [36], perturbation theory (second-order Møller-Plesset theory, MP2 [37] for instance) or more refined post-Hartree-Fock methods, such as coupled-cluster theory including single, double and perturbative triple excitations, CCSD(T) [38–40]. Especially in this last case, the use of large and well-balanced basis sets allows to reach what is called the complete basis set (CBS) limit and usually CCSD(T)/CBS is considered large enough to obtain what is called chemical accuracy (*i.e.*, discrepancies with experiment below 4.2 kJ mol^{-1} , *i.e.*, 1 kcal mol^{-1}), also known as “gold standard” [41]. This limit is however quite costly to obtain, and the resources needed increase sharply with the size of the molecular system. Therefore, composite quantum-chemical methods have been developed, of which there are nowadays over 200 different “flavors” [42,43]. The interested reader is referred to those references to find specific details, but basically, they all share the idea that energies can be split into additive contributions, and that some of them can be calculated using less advanced procedures (not so demanding correlated methods or smaller basis sets) without loss of “chemical” accuracy.

In this work we have used two DFT methods, namely the M06-2X [44], and rev-DSDPBEP86 [45] density functionals, with Dunning’s aug-cc-pV(T+d)Z and Truhlar’s jun-cc-pV(T+d)Z [46] basis sets

Table 4

Relative enthalpies of the radical cations (in kJ mol^{-1}), IPs of the parent hydrocarbons and derived enthalpy of formation of 3^+ (in kJ mol^{-1}).

Method	MCPrc ^a		BCDrc ^b		VArC ^c		3^+
	ΔH_{298}^0	IP _a	ΔH_{298}^0	IP _a	ΔH_{298}^0	IP _a	
CBS-QB3	0.0	8.17	32.7	8.05	39.0	9.59	1182.2
G4	0.0	8.13	34.4	8.06	43.6	9.61	1175.4
W1BD	0.0	8.13	32.0	8.02	45.2	9.60	1167.0
SVECV-f12	0.0	8.11	31.7	8.00	44.5	9.57	1176.9
jChS	0.0	8.13	32.1	7.99	44.8	9.55	1173.1
Experimental		8.15 ± 0.01^d		8.24 ± 0.03^e			1177.8 ± 12.5^f

^a Methylcyclopropene radical cation.

^b Cyclobutadiene radical cation.

^c Vinylacetylene radical cation.

^d Staley and Norden [77].

^e Kreile et al. [92].

^f Derived by Staley and Norden [77].

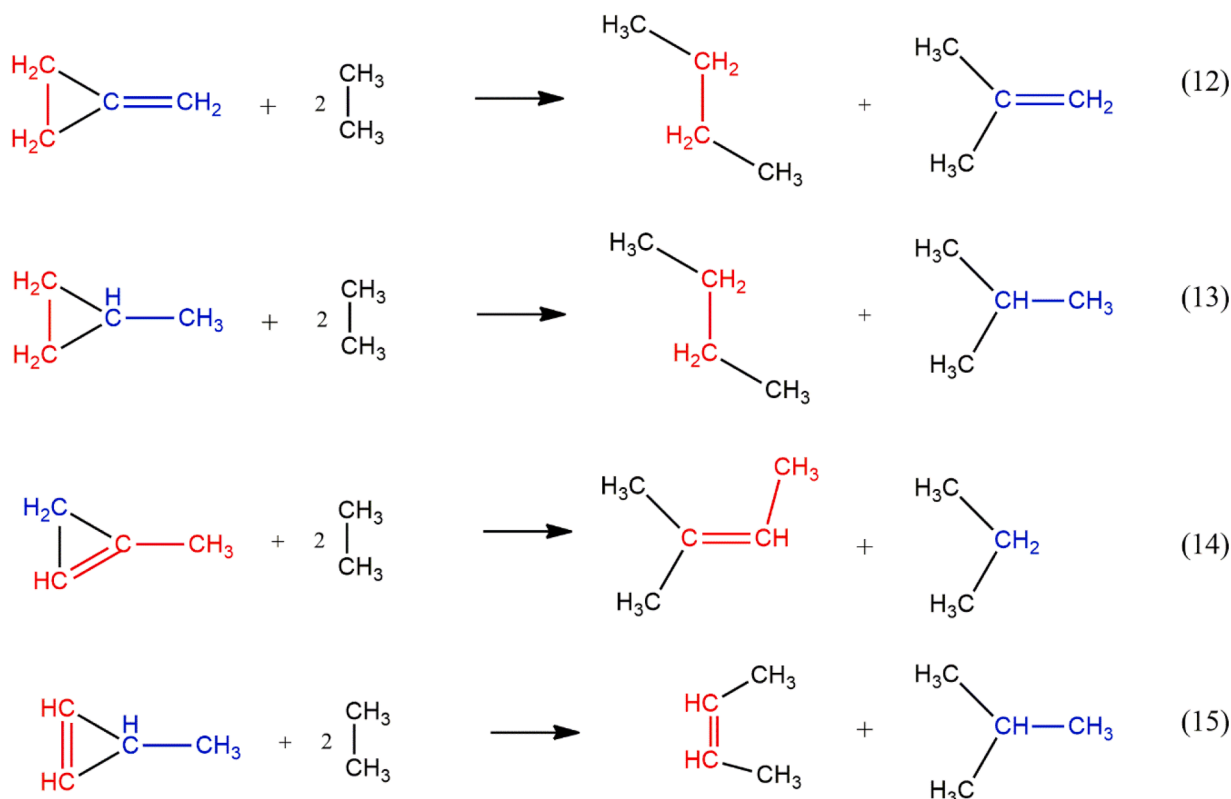


Fig. 4. Homodesmotic reactions used to obtain the enthalpies of formation and strain energy of methylenecyclopropane, methyl cyclopropane and the methyl cyclopropenes.

Table 5

Enthalpies of formation (kJ mol^{-1}) of methylenecyclopropane (28), methyl cyclopropane (29), 1-methyl cyclopropene (30), and 3-methyl cyclopropene (31) using atomization and homodesmotic reactions with different computation schemes.

SPECIES				CBS-QB3	G4	W1BD	SVECV-f12	jChS	Exptl.	FINAL ^a	
Nr	Global	Name	Procedure							μ	$\pm 2\sigma$
28	C ₄ H ₆	Methylene-cyclopropane	Atomization	202.5	196.1	190.7	192.8	188.4		192.0	± 5.6
			Homodesmotic	190.5	191.0	162.2	191.9	189.7	201. $\pm 2.$ ^b	191.2	± 1.9
			Others						200.5 ± 1.8 ^c	194.6 ^e	
29	C ₄ H ₈	Methyl cyclopropane	Atomization	34.0	28.6	20.6	25.1	17.6		23.0	± 8.4
			Homodesmotic	24.8	24.0	24.8	25.8	23.1	24.3 ^c	24.4	± 2.0
			Others							24.6 ^f	
30	C ₄ H ₆	1-Methyl cyclopropene	Atomization	249.9	243.7	237.8	240.2	235.3		239.2	± 6.2
			Homodesmotic	229.2	229.6	230.0	231.3		244. $\pm 1.$ ^b	230.2	± 1.3
			Others								
31	C ₄ H ₆	3-Methyl cyclopropene	Atomization	263.6	257.2	250.8	252.9	247.4		252.1	± 7.1
			Homodesmotic	250.2	250.3	250.7	254.8	249.6	273. $\pm 2.$ ^d	251.4	± 4.1
			Others								

^a Average μ and two times the standard deviation (2σ , for a 95% significance interval) of the results obtained at the G4, W1BD, SVECV-f12, and jChS levels.

^b Wiberg and Fenoglio [93].

^c Kolesov and Kozima [94].

^d Keister et al. [95].

^e Bakowies [16].

^f ATcT tables [73].

respectively, plus several composite methods of progressively larger degree of accuracy (and, of course, increasing demand of computational resources). To account for dispersion interactions, M06-2X and rev-DSDPBEP86 were augmented by Grimme's DFT-D3 semi-empirical dispersion [47,48], which has been applied with considerable success to many different systems, including dimers, large supramolecular complexes and reaction energies/barriers [49–51].

The extensively employed CBS-QB3 [52,53] and G4 [54] composite methods, as well as the more resource intensive and accurate W1BD [55–57] were used in their original implementations, in addition to the

more recent jun-ChS [58,59] and SVECV-f12 [60,61] protocols. The jun-ChS approach employs geometries calculated at the rev-DSDPBEP86-D3(BJ)/jun-cc-pV(T+d)Z level and CCSD (T)/jun-cc-pV(T+d)Z energies corrected for the CBS error and core-correlation effects. These contributions are evaluated by a two-point extrapolation [62] of MP2 [37] energies using the jun-cc-pV(T+d)Z and jun-cc-pV(Q+d)Z basis sets, and as the difference between MP2/cc-pwCVTZ results obtained by correlating all and only valence electrons, respectively. The improvements with respect to the previously mentioned older composite methods lies both in the use of a more

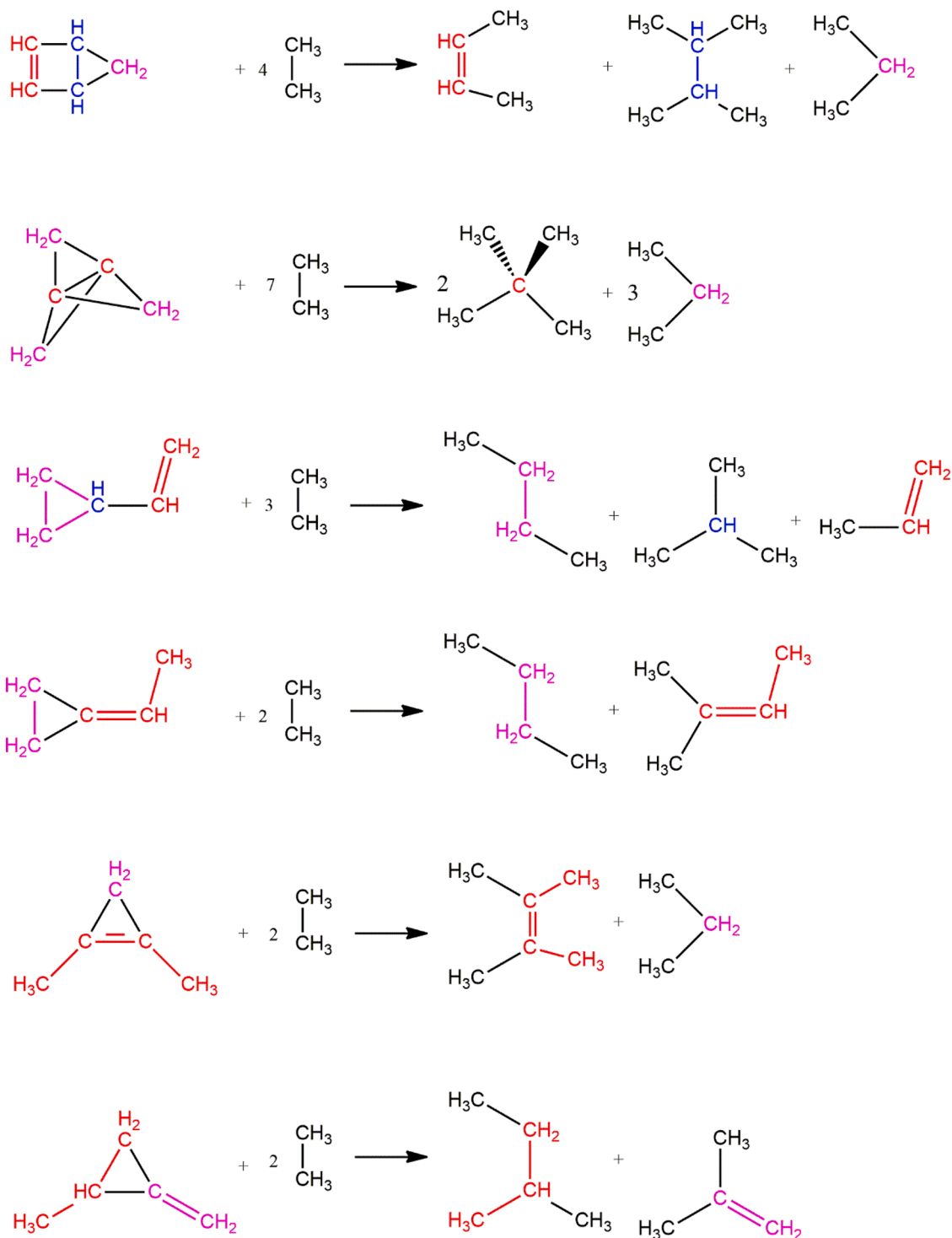


Fig. 5. Homodesmotic reactions employed for the C_5H_8 isomers. Colors on both sides of the equations identify the origin of the fragment.

accurate DFT method for obtaining optimum geometries and frequencies (CBS-QB3, G4 and W1BD use B3LYP [63] for this purpose), and the calculation of the CBS limit and core-valence contributions at the MP2 [37] level, thus providing a reduction of the computational burden.

SVECV-f12 employs M06-2X-D3/aug-cc-pVTZ optimum geometries to perform CCSD(T,fc)-F12b(3C/FIX) [64] complete basis set (CBS) single-point calculations (obtained by extrapolation of cc-pVDZ-F12 and cc-pVTZ-F12 results), augmented by core-valence correlation corrections at the MP2/cc-pwCVTZ level. As such, this method includes

more correlation energy than the jun-ChS method, which starts from the CCSD(T)/jun-cc-pV(T+d)Z energy within the frozen-core approximation and improves the extrapolation to the CBS limit by including the same core-valence correlation corrections at the MP2/cc-pwCVTZ level, but is considerably more resource demanding and, therefore, of a more restricted application. Previous works have shown that both methods are equivalent in several situations [65,66] and give results analogous to W1BD. One could ask then why it is even appropriate to use so many methods. The answer is that, even if small, each one of the methods has a random intrinsic error due to the different

Table 6Enthalpies of formation and strain energies at different levels of theory compared to the experimental values for the C5 species. Units are kJ mol⁻¹.

SPECIES				CBS	G4	W1BD	SVECV	jChS	DRV ^a	Other		FINAL ^f		
Nr	Global	Name	Procedure	-QB3			-f12		LG89	Theor	Exptl	μ	$\pm 2\sigma$	
4	C ₅ H ₆	Bicyclo[2.1.0]pent-2-ene	Atomization	342.1	332.4	326.2	328.5	323.5	334	329.3 ^b	333.5 ^d	326.0	± 4.1	
			Homodesmotic	323.7	323.2	322.9	328.0	324.0					325.0	± 4.4
			Strain energy	279.1	278.6	278.3	283.4	289.4					279.9	± 2.4
5	C ₅ H ₆	[1.1.0]Propellane	Atomization	372.9	363.0	361.3	363.4	358.4	351	365.3 ^c	351.5 ^e	361.0	± 4.1	
			Homodesmotic	359.6	358.2	360.5	365.3	363.8					363.2	± 4.0
			Strain energy	423.5	422.0	424.3	429.1	427.7					425.8	± 6.4
6	C ₅ H ₈	Vinylcyclopropane	Atomization	142.7	134.0	126.7	132.1	123.3	127		127.0 ^e	127.3	± 7.3	
			Homodesmotic	123.6	123.1	124.1	125.0	122.1					123.8	± 2.4
			Strain energy	112.3	111.7	112.8	113.7	110.8					112.6	± 1.7
7	C ₅ H ₈	Ethylidenecyclopropane	Atomization	173.0	165.7	158.1	163.7	155.2	161			159.0	± 7.1	
			Homodesmotic	150.3	150.8	151.8	152.6	149.5					151.3	± 2.6
			Strain energy	150.1	150.6	151.5	152.4	149.2					151.1	± 2.0
8	C ₅ H ₈	1,2-Dimethylcyclopropene	Atomization	209.3	202.6	195.6	201.6	193.0	186			196.8	± 7.2	
			Homodesmotic	197.7	198.5	199.5	198.2	200.3					199.1	± 1.9
			Strain energy	197.5	198.3	199.2	197.9	200.1					198.9	± 1.9
9	C ₅ H ₈	2-Methyl-1-methylene-Cyclopropane	Atomization	174.6	167.2	160.6	165.9	157.2	167			161.2	± 7.2	
			Homodesmotic	163.9	164.9	165.8	165.6	166.5					166.0	± 0.8
			Strain energy	163.6	164.7	165.5	165.3	166.3					164.8	± 1.7

^a LG89 [3].^b Rogers et al. [98].^c Bakowies [16].^d Calculated from $\Delta_{\text{hyd}}H_{298}$ of the bicyclic compounds) relative to $\Delta_{\text{hyd}}H_{298}$ (cyclopentane) [100].^e Roth et al. [97].^f Average and two times the standard deviation (for a 95% significance interval) of the results obtained at the G4, W1BD, SVECV-f12 and jChS levels.

approximations. Using them all gives us the opportunity to obtain a statistical error as a limit of the precision of the theoretical calculations.

Required geometry optimizations at the DFT level were performed with very tight criteria. Analytical frequency calculations were performed using the DFT methods, and the thermochemical properties calculated using the rigid-rotor/harmonic-oscillator approximation. Since no thermal contributions were calculated at the CCSD(T) or CCSD(T)-F12 levels, the individual enthalpies necessary for the calculation of $\Delta_f H^0(298.15K)$ were obtained adding the difference $H_{298} - E_T$ at the corresponding DFT level to the ab initio total energies (E_T is the sum of electronic and fixed nuclei energy). All calculations were performed using the Gaussian 16 [67] and Molpro 20.1 [68–70] computer packages.

2.4. Best available results

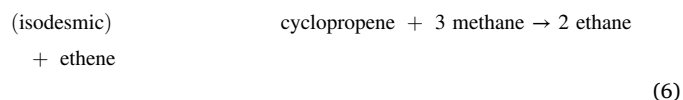
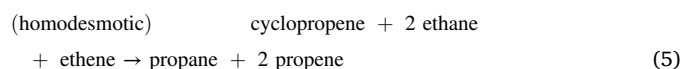
A very important concern in the determination of theoretical enthalpies of formation is the precision and accuracy of the calculations. This implies that a careful examination of previous existing data must be carried out. When trustworthy experimental data is available this is not a problem but causes some trouble when no such data exists. There are several databases which can be used for this purpose, but the larger and most frequently used are those of NIST [34] and the Argonne National Laboratory –known as Active Thermochemical Data Tables (ATcT [71–73]). The ATcT values are currently considered to be the most accurate ones, but one must recall that high-level theoretical calculations are normally mixed in with the experimental determinations. As an example, in the case of methane, about half of the weight in the reported $\Delta_f H^0$ comes from the experimental work of Smith [74], while the rest is considered with very small coefficients from other experimental and theoretical papers, including the seminal work by Klippenstein et al. [75]. As expressed in the original paper, ATcT provides reliable, accurate, and internally consistent thermochemistry by using a thermochemical network (TN) approach. This implies a statistical analysis of thermochemically relevant determinations that define the TN, made possible by redundancies in it, such as competing measurements and alternate network pathways that interrelate the various chemical species. Therefore, the values are correlated and have an internal interdependence. In the case of CH₄, for instance, the most important

correlations (coefficient larger than 80%) are with [CH₃]⁺, CH₃, and [CH₄]⁺, while various smaller correlations appear with respect to several electronic states of the carbon atom. Thus, one must consider that any new modification on some of the correlated values does affect the others.

3. Results and discussion

3.1. Parent compounds

All the species studied in this work exhibit cyclopropane or cyclopropene rings as part of the structure. Therefore, our first goal was to calculate the properties of both parent species, a task we performed using atomization energies, on one side, and homodesmotic and isodesmic reactions on the other, as explained previously. Reactions (3) and (4) were used for cyclopropane, while reactions (5) and (6) were used for cyclopropene.



For purposes that will become clear in the following, we also added a second isodesmic reaction:



The first calculation we performed was that of the auxiliary species for the homodesmotic and isodesmic reactions. Individual values obtained for each method are shown in table S1 in the Supplementary Information (SI), and the presumably more accurate (G4, W1BD, SVECV-f12 and jChS) were averaged. Two times the standard deviation (2σ) is also shown as an indication of the precision (not accuracy) of the predictions at the 95% confidence interval. In general, the discrepancy between the experimental and average values is about 3 kJ mol⁻¹.

For cyclopropane and cyclopropene, the results obtained are shown in Table 1. In the case of cyclopropane, the average values obtained with

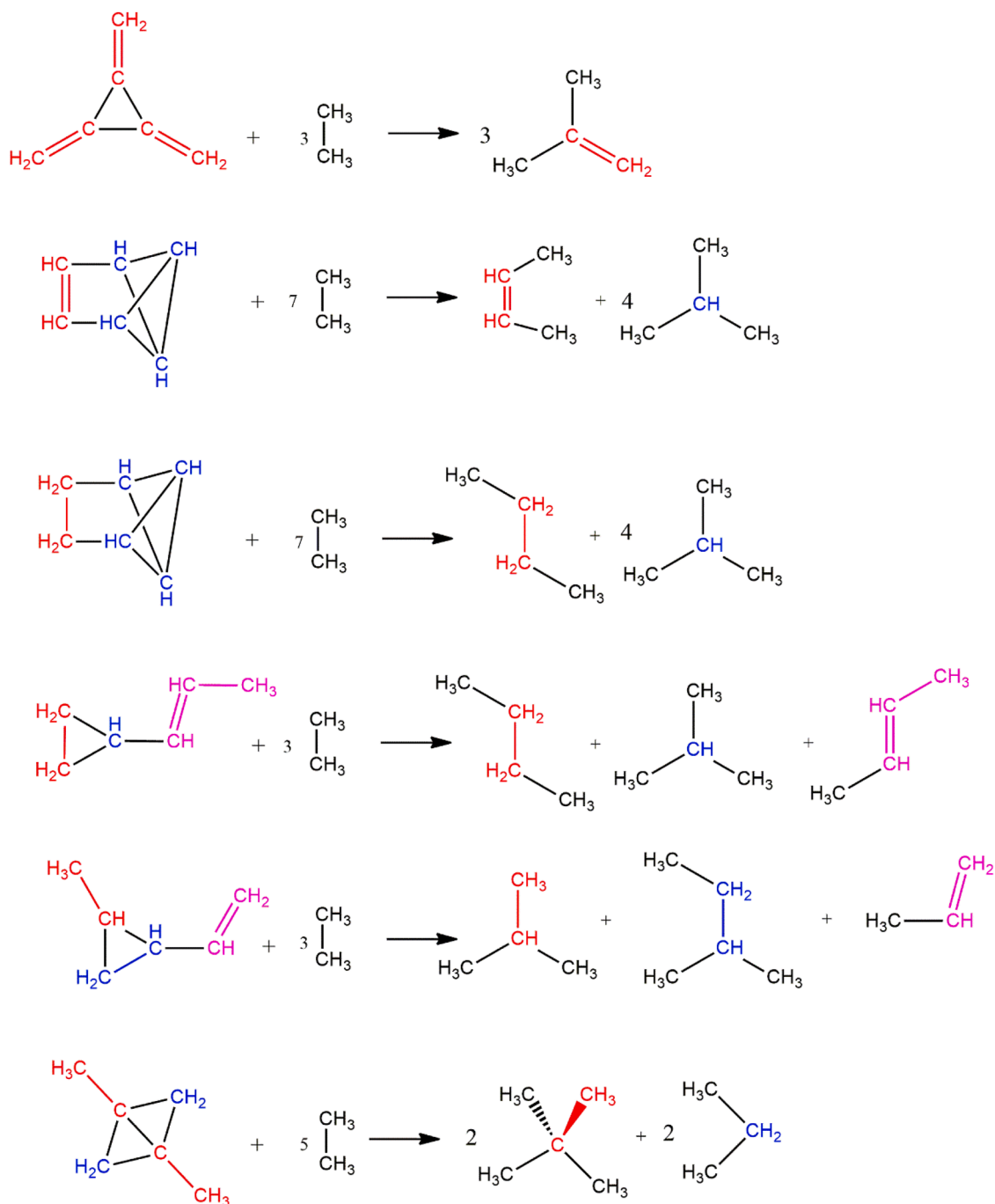


Fig. 6. Homodesmotic reactions employed for the C_6H_n species. Colors on both sides of the equations identify the origin of the fragment.

the atomization, homodesmotic and the two isodesmic reactions are well in agreement, with an error lower than 3 kJ mol^{-1} . It is interesting to notice that the spread among the different methods of calculation decreases in the direction atomization \rightarrow isodesmic \rightarrow homodesmotic reactions, as it should be because of the increasing error compensation between both sides of the equations.

The same holds for cyclopropene. However, in this case the average value obtained using the atomization and isodesmic reactions (283.5 ± 5.4 and $285.1 \pm 3.0 \text{ kJ mol}^{-1}$) are more than 10 kJ mol^{-1} larger than that stemming from the homodesmotic reaction ($272.6 \pm 1.7 \text{ kJ mol}^{-1}$). The values given in the ATcT [73] (which are determined mainly theoretically) and in the very accurate calculations of Bakowies [16] (283.6 ± 0.5 and $284.5 \pm 1.7 \text{ kJ mol}^{-1}$) agree with those determined in this paper using the atomization and isodesmic reactions. The

experimental enthalpy of formation in the thermochemical data compendium of Pedley [76] is $277.0 \pm 2.5 \text{ kJ mol}^{-1}$, nearer to the value determined using the homodesmotic reaction. Since theoretical calculations are state-of-the-art, further experimental studies should be strongly encouraged to resolve the discrepancies.

Table 2 presents our results for the strain energy of both molecules, which have been calculated several times before. The isodesmic reactions (3) and (5) do not yield a good calculation of the strain energy. This is well-known and has been discussed a few times in the literature. The strain energy is too small for both cyclopropane and cyclopropene, 33 and 44 kJ mol^{-1} respectively, judging by the values obtained using the homodesmotic reaction in this work and conventional ring strain energy [35]. This is in fact a defect of the isodesmic reactions used, as can be seen when changing the reaction from (3) to (7) for cyclopropane.

Table 7Enthalpies of formation and strain energies at different levels of theory compared to the experimental values for the C6 species. Units are kJ mol⁻¹.

SPECIES				CBS	G4	W1BD	SVECV	jChS	DRV ^a	Other		FINAL ^e		
Nr	Global	Name	Procedure	-QB3			-f12		LG89	Theor	Exptl	μ	±2σ	
10	C ₆ H ₆	[3]-Radialene	Atomization	454.3	444.7	442.0	445.9	439.7	396	443.9 ^b	396.0 ^c	442.5	± 5.1	
			Homodesmotic	431.4	436.0	438.4	435.5	438.4				414 ^d	437.4	± 2.7
			Strain energy	234.0	238.7	241.1	238.2	241.0					238.6	± 5.8
11	C ₆ H ₆	Benzvalene	Atomization	400.4	389.3	383.5	386.5	380.3	363	388.7 ^b	381 ^d	383.5	± 5.1	
			Homodesmotic	378.0	378.7	380.2	386.3	381.4					382.6	± 5.3
			Strain energy	336.8	337.5	338.9	345.1	340.1					339.6	± 7.6
12	C ₆ H ₈	Tricyclo[3.1.0.0 ^{2,6}]hexane	Atomization	241.0	232.7	223.7	229.4	220.4	228			224.5	± 7.4	
			Homodesmotic	222.7	224.	224.7	228.4	224.7					225.9	± 3.5
			Strain energy	299.4	301.1	301.3	305.1	301.4					301.6	± 4.2
13	C ₆ H ₁₀	[(E)-1-Propenyl] cyclopropane	Atomization	108.9	99.2	89.5	99.0	90.3	96.5			92.9	± 8.5	
			Homodesmotic	74.6	73.8	75.3	78.9	72.1					75.5	± 5.6
			Strain energy	112.9	112.1	113.6	117.2	110.4					113.2	± 5.1
14	C ₆ H ₁₀	cis-1-Methyl-2-vinylcyclopropane	Atomization	113.8	104.1	95.4	104.1	90.9	95.1			96.8	±11.0	
			Homodesmotic	91.4	91.4	92.0	93.1	93.3					92.8	± 1.1
			Strain energy	108.2	108.2	108.8	109.8	110.1					109.0	± 1.8
15	C ₆ H ₁₀	1,3-Dimethylbicyclobutane	Atomization	165.8	157.9	150.7	158.8	146.2	255			166.1 ^f	151.9	±10.4
			Homodesmotic	152.1	152.6	152.6	155.7	155.8					154.7	± 3.0
			Strain energy	278.7	279.2	279.2	282.3	282.4					285.3 ^f	280.4

^a LG89 [3].^b Bakowies [16].^c Bally et al. [102].^d Rosenstock et al. [103].^e Average and two times the standard deviation (for a 95% significance interval) of the results obtained at the G4, W1BD, SVECV-f12 and jChS levels.^f Turner et al. [104].

The calculated strain energy is now in agreement with the results in several previous publications. Notice that the values determined previously for cyclopropene exhibit a rather large range, from 225 to 234 kJ mol⁻¹, while the theoretical calculations carried out here show a much smaller spread and are therefore more precise.

We can also resort to other experimental data to back up our theoretical calculations mentioned before. With the experimental enthalpies of formation present in Pedley's 1994 book [76] we can write the following reactions (SE(C₃H₆) stands for the strain energy of cyclopropane and SE(C₃H₄) for that of cyclopropene):

2 cyclopropane → cyclohexane SE(C₃H₆) = 114.9 ± 1.4 kJ mol⁻¹
 cyclopropene + ethane → (E)-2-pentene SE(C₃H₄) = 220.9 ± 2.7 kJ mol⁻¹
 cyclopropene + ethylene → 1,4-pentadiene SE(C₃H₄) = 223.9 ± 2.8 kJ mol⁻¹

2 cyclopropene → 1,4-cyclohexadiene SE(C₃H₄) = 225.0 ± 3.5 kJ mol⁻¹

Notice also that the sum of the strain energy of cyclopropane and cyclopropene can be obtained from the reaction: cyclopropane + cyclopropene → cyclohexene

SE(C₃H₆) + SE(C₃H₄) = 335.3 ± 2.6 kJ mol⁻¹ in reasonable agreement with the sum of the SE reported before.

A conclusion that can be drawn from this section is that the high-quality methods employed for the determination of both the enthalpy of formation and ring strain energy are sufficient to obtain results within chemical accuracy, and even if each method presents its own particularities, all of them allow for reasonable calculations. However, neither isodesmic nor homodesmotic reactions are sufficient to correct values obtained at the DFT level.

3.2. Methylene cyclopropene

The enthalpy of formation of **3** was not obtained directly, but derived using the following near equality shown in LG89 [3]:

$$\Delta_f H^0(\mathbf{3}) \approx \Delta_f H^0(\mathbf{3}^+) - IP_a(\mathbf{3}) \quad (8)$$

where **3**⁺ is the radical cation of **3**, which enthalpy of formation is known, and IP_a(**3**) is the adiabatic ionization potential (IP) of **3** as determined by Staley and Norden [77]. From these data, LG89 [3]

derived an enthalpy of formation of 423 kJ mol⁻¹. This has been taken as the standard experimental value used for comparison of methylenecyclopropene with theoretical calculations (see, for instance, Bakowies [16]).

In this paper, we have used three different methods to obtain the enthalpy of formation of **3**. On one side, our theoretical values obtained using the atomization energy and the composite methods range from 386.5 to 391.2 kJ mol⁻¹, while Bakowies [16] reports 389.1 kJ mol⁻¹ and a value of 388.0 kJ mol⁻¹ is given in the ATcT [73]. We have used previously this type of high-level calculations to determine accurate enthalpies of formation for some sulfenic acids [78], reporting a significant difference with the only available experimental values, and we are reasonably certain about the accuracy of the theoretical methodology. However, an alternative approach can be considered. As suggested by Staley and Norden [77], one can use a homodesmotic [31] reaction like (10) in this work.

We have considered in the following an isodesmic (9) and two homodesmotic reactions (10) and (11), which are shown in Fig. 2. Reaction (10) is the same as reaction (1) in Staley and Norden [77]. The values for the enthalpy of formation of **3**, calculated at different theoretical levels, are displayed in Table 3.

Considering all these high-level theoretical determinations, a result of 384.2 ± 2.6 kJ mol⁻¹ appears as the most accurate theoretical value for Δ_fH⁰(**3**), about 39 kJ mol⁻¹ less than that reported in LG89 [3]. It is noticeable that both homodesmotic reactions and the atomization energies gave quite similar values, while the result obtained from the isodesmic reaction (9) is misaligned with the rest. As we explained before, the homodesmotic reactions exhibit the largest cancellation of errors and should therefore be preferred.

An interesting fact can be derived also from the use of reaction (10) with different reported values of the experimental enthalpy of reaction of cyclopropane. If we use the value of 39.3 kJ mol⁻¹ for the enthalpy of formation of cyclopropane from Lacher et al. [90], Δ_fH⁰(**3**) comes out as 372.8 ± 6.1 kJ mol⁻¹. If one uses instead the generally accepted value of Knowlton and Rossini [91] for the enthalpy of formation of cyclopropane, 53.3 ± 0.6 kJ mol⁻¹, then the average Δ_fH⁰(**3**) is 386.8 ± 6.1 kJ mol⁻¹. This value overlaps the result obtained using the other methods thus suggesting that the enthalpy of formation of cyclopropane from Knowlton and Rossini [91] be accepted while the value from Lacher

Table 8Enthalpies of formation and strain energies at different levels of theory compared to the experimental values for the C7 to C11 species. Units are kJ mol⁻¹.

SPECIES				CBS	G4	W1BD	SVECV	jChS	DRV ^a	Other		FINAL ^g		
Nr	Global	Name	Procedure	-QB3			-f12		LG89	Theor	Exptl	μ	±2σ	
16	C ₇ H ₆	Benzocyclopropene	Atomization	391.0	384.2	377.3	382.4	376.1	367	382.8 ^b	366.5 ^c	380.0	± 6.8	
			Homodesmotic	376.7	377.8	378.4	382.5	381.3					380.0	± 3.9
			Strain energy	295.0	296.0	296.6	300.7	299.5					284.5 ^d	297.6
17	C ₇ H ₈	Quadricyclane	Atomization	349.8	338.4	329.1	334.7	326.1	339.1	336.8 ^b	333.0 ^d	332.1	± 9.6	
			Homodesmotic ^h	315.2	318.0	315.3	315.8	315.4					316.1	± 2.2
			Homodesmotic ⁱ	322.8	324.8	324.2	330.2	325.0					326.1	± 4.8
			Strain energy	202.2	204.2	203.6	209.6	204.4					204.8	± 5.6
18	C ₇ H ₈	Norcaradiene	Atomization	226.3	214.9	206.1	213.8	203.3	202.0	211.7 ^b	207.5 ^e	209.6	± 9.9	
			Homodesmotic	203.0	204.4	204.8	210.7	209.3					207.3	± 5.5
			Strain energy	276.0	277.4	277.8	283.7	282.3					280.3	± 6.3
19	C ₇ H ₁₀	5,5-Dimethyl bicyclo[2.1.0]pent-2-ene	Atomization	280.4	268.7	261.0	269.9	255.5	267.0			263.8	± 11.8	
			Homodesmotic	258.5	258.7	258.1	263.7	259.7					260.0	± 4.4
			Strain energy	355.0	354.5	357.9	361.9	359.7					358.5	± 6.3
20	C ₇ H ₁₀	Tricyclo[4.1.1.0 ^{2,7}]heptane	Atomization	211.0	200.3	190.4	199.3	185.8	185.8			193.9	± 12.2	
			Homodesmotic	189.1	190.3	187.5	192.6	190.0					190.1	± 3.7
			Strain energy	207.8	209.0	206.2	211.3	208.7					208.8	± 4.2
21	C ₇ H ₁₂	5,5-Dimethyl bicyclo[2.1.0]pentane	Atomization	109.3	100.2	89.4	101.0	83.8	92			93.6	± 14.5	
			Homodesmotic	91.6	92.5	90.8	93.9	91.3					92.0	± 2.7
			Strain energy	228.1	229.1	227.4	230.5	227.9					228.7	± 2.8
22	C ₈ H ₈	Semibullvalene	Atomization	321.3	308.1	300.0	307.9	296.8	308	314.2 ^j	307.9 ^f	303.2	± 9.9	
			Homodesmotic	289.8	292.9	293.1	301.4	295.0					295.6	± 6.9
			Strain energy	165.6	168.7	168.9	177.2	170.8					171.4	± 7.9
			Atomization	238.7	224.0		227.0		258				225.5	± 3.0
23	C ₉ H ₁₂	Bicyclo[6.1.0]nona-2,4-diene	Homodesmotic ^h	200.1	201.4		203.4	199.8				201.5	± 2.9	
			Homodesmotic ⁱ	217.3	218.1		227.7	218.6					221.5	± 13.6
			Strain energy	128.7	129.5		139.1	130.0					132.9	± 10.8
			Atomization	239.1	224.1		227.0		269				225.5	± 2.9
24	C ₉ H ₁₂	Bicyclo[6.1.0]nona-3,5-diene	Homodesmotic ^h	200.2	200.9		212.1	202.8				205.3	± 12.0	
			Homodesmotic ⁱ	217.3	217.5		236.3	218.6					224.1	± 21.1
			Strain energy	128.7	129.0		147.7	130.0					133.8	± 18.6
			Atomization	370.2	354.6	346.3	359.3	340.2	322				350.1	± 14.7
25	C ₁₀ H ₁₂	[IrH ₂ tH ₂ 3cH ₂ 5cH ₂ 6 ^{tt} ,7cH]-Tetracyclo[5.2.1.0 ^{2,6} .0 ^{3,5}]dec-8-ene	Homodesmotic	334.8	337.7	340.6	347.4	344.1				342.4	± 7.3	
			Strain energy	338.9	341.8	344.7	351.5	348.2					346.5	± 8.4
			Atomization	457.3	444.9	—	448.0	435.5	435				442.8	± 10.6
26	C ₁₁ H ₈	Naphtho[b]cyclopropene	Homodesmotic	409.2	415.0	—	419.3	419.7				418.0	± 4.3	
			Strain energy	159.4	165.2	—	169.5	169.9					168.2	± 5.3
			Atomization	329.8	321.0	—	—	313.6	338				317.3	± 7.3
27	C ₁₁ H ₁₀	[4.4.1]Propellatetraene	Homodesmotic ^h	272.8	287.6	—	—	289.4				288.5	± 1.8	
			Homodesmotic ⁱ	287.4	301.1	—	—	308.7					304.9	± 10.6
			Strain energy	5.5	19.2	—	—	26.8					23.0	± 10.6

^a LG89 [3].^b Bakowies [16].^c Billups et al. [109].^d Turner et al. [104].^e Roth et al. [110].^f Martin et al. [111].^g Average and two times the standard deviation (for a 95% significance interval) of the results obtained at the G4, W1BD, SVECV-f12 and jChS levels.^h Homodesmotic reaction using *trans,trans* hexa-2,4-diene as reference.ⁱ Homodesmotic reaction using *cis* 2-butene instead of *trans,trans* hexa-2,4-diene as reference.^j Shyamala et al. [112]

et al. [90] is continued to be ignored. We will therefore use the value of 53.3 ± 0.6 kJ mol⁻¹ for the enthalpy of formation of cyclopropane in our current study, a practice seemingly employed by LG89 [3] and others studying strained ring species, and cyclopropanes in particular.

Since the logic of the work of LG89 [3], i.e., equation (8), is sound, the difference must be in the accuracy of the data and/or the actual species participating in this reaction. Notice that Staley and Norden [77] discussed the possibility that the C₄H₄⁺ radical cation is the species derived from either vinylacetylene (the H₂C=CH-C≡CH⁺ radical cation) or 1,3-cyclobutadiene. In their work they ruled out the non-cyclic structure and concluded also that C₄H₄⁺ must be 3⁺ instead of the 1,3-cyclobutadiene radical cation. With these assumptions, they derived a value of 391.6 kJ mol⁻¹ for the enthalpy of formation of methylenecyclopropene (quite near to our own result) and 1177.8 ± 12.6 kJ mol⁻¹ for the enthalpy of formation of 3⁺, using the measured value of IP = 8.15 eV.

Computational chemistry allows us to calculate those structures with

the accurate methods employed in this paper. The geometrical structures calculated using the DFT methods are shown in Fig. 3 for the three possible radical cations (i.e., those of methylenecyclopropane, vinylacetylene and 1,3-cyclobutadiene), and the C-C bond distances compared to those of the parent species. The values for the ionization potential, calculated at different levels of theory, can be seen in Table 4. Clearly, the radical cation obtained cannot be that of vinylacetylene since the calculated IP is more than 1 eV larger than those observed experimentally. However, the difference between the IP of the methylenecyclopropane radical cation and that of the cyclobutadiene radical cation is less than 0.1 eV (with the former being the largest one) and it is not completely clear which one (or perhaps both?) is present in the experiment. As can be seen in Table 4, however, computational chemistry sheds some light on this problem, since both the vinylacetylene and cyclobutadiene radical cations are much higher in energy than the methylenecyclopropane radical cation. Nonetheless, a discrepancy remains between experiment and theory with respect to the ordering of

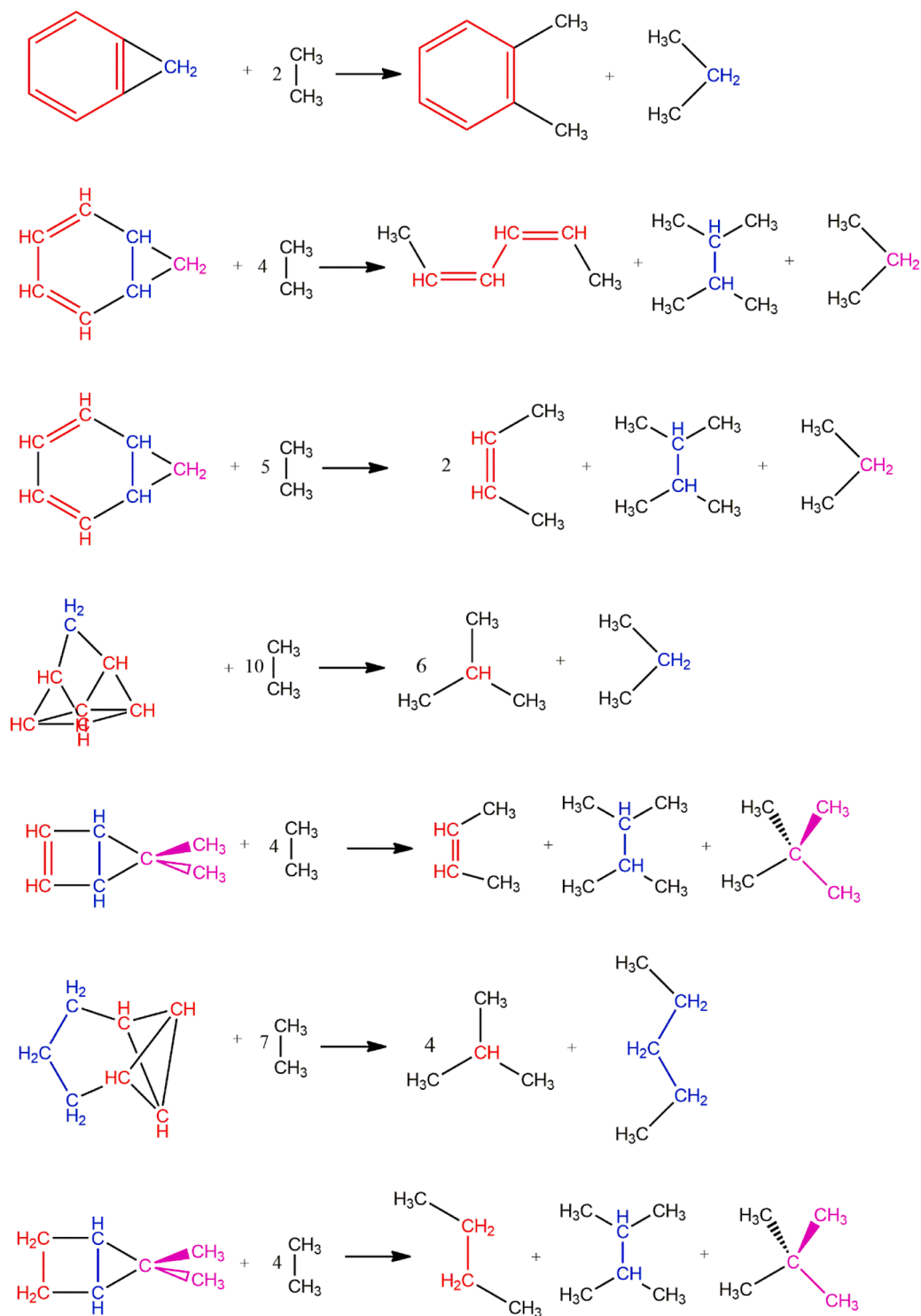


Fig. 7. Homodesmotic species for the molecules with global formula C_7H_6 to C_7H_{12} . Colors on both sides of the equations identify the origin of the fragment.

the IPs of methylenecyclopropane and cyclobutadiene. While the experimental IP of the former is smaller than that of the latter, the theoretical values show just the opposite order. More experimental and theoretical research is needed to reconcile these results.

To have a better perspective of the simplest substituted C3 carbocycles, we also investigated methylene- and methylcyclopropane, as well as 1-methyl- and 3-methylcyclopropane. These molecules will help us later to get a more precise description of the dependence of strain energy on the substituents in the carbocycle. Atomization energies are used as before, and the homodesmotic reactions (12)-(15) are also

employed to obtain both the enthalpies of formation and strain energies (see Fig. 4). The relevant results are collected in Table 5.

A general comment on this data is that the results at both the atomization and homodesmotic levels are very similar (the largest difference is 9 kJ mol^{-1}) but that the spread among the methods is much lower when the latter are used. This fact supports the notion of the error cancellation that occurs in these circumstances.

A second comment is that there is an excellent agreement between the experimental data and the theoretical ones for methylcyclopropane, which is the only of the four molecules which is also present in the ATCT

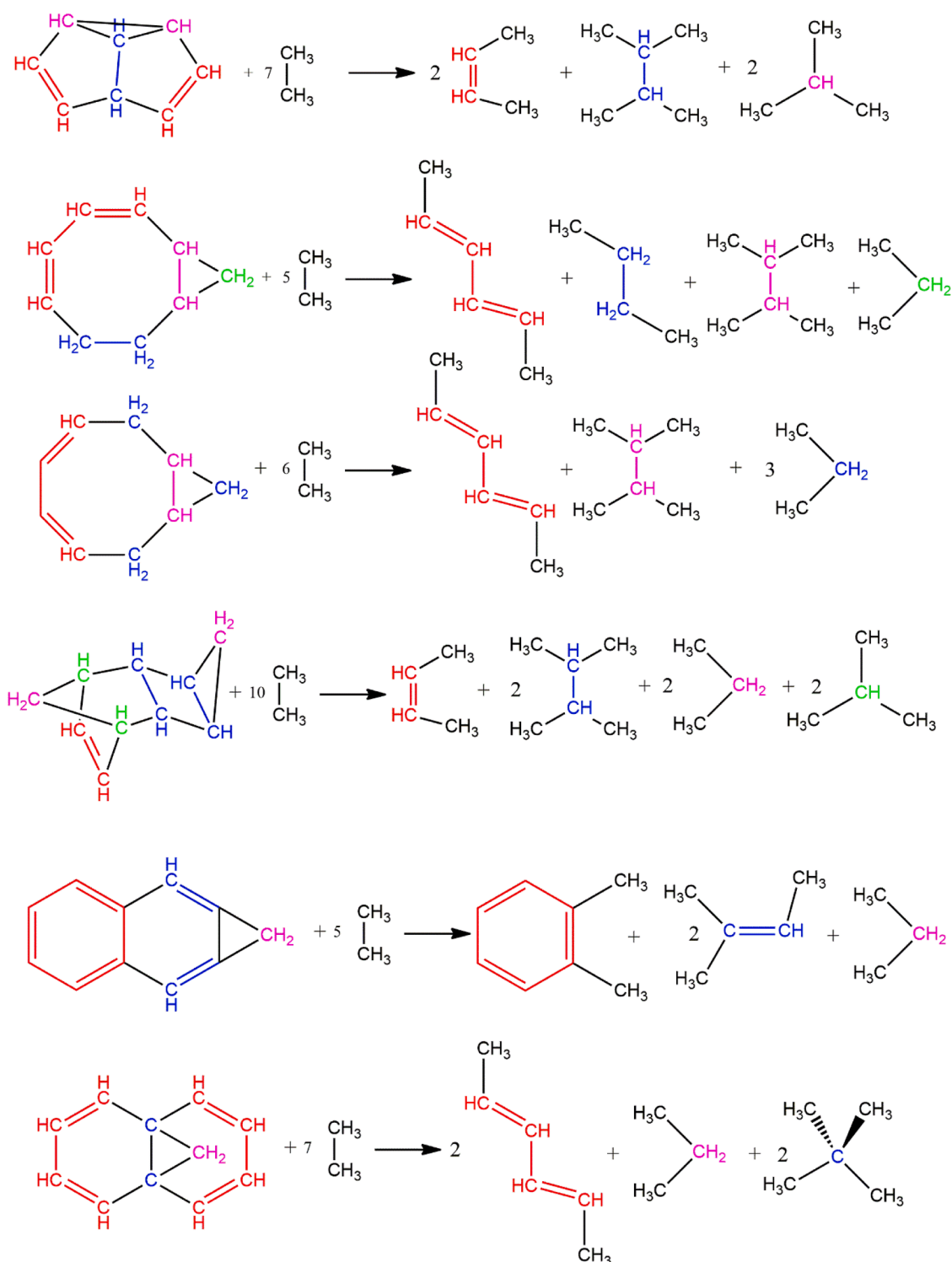


Fig. 8. Homodesmotic equations for the molecules with global formula C_7H_6 to $C_{11}H_{10}$. Colors on both sides of the equations identify the origin of the fragment.

tables, with a result also in agreement. For the other three molecules, the differences between theory and experiment range from 10 to 22 kJ mol^{-1} , a discrepancy which is difficult to explain and unlikely to be due to the theoretical calculations, given the degree of precision and the accuracy with which they represent methylcyclopropane. Hence, we suggest then that the theoretical data be considered the most accurate ones, until new experimental determinations are performed.

3.3. C_5 carbocycles

Six species containing five-carbon skeletons were examined in LG89 [3]. Bicyclo[2.1.0]pent-2-ene (4) and [1.1.1]propellane (5) were studied theoretically also by Bakowies [16] and experimental data was produced by Wiberg et al. [96], Roth et al. [97] and Rogers and McLafferty [98]. On the contrary, no theoretical or experimental information is available for the C_5H_8 isomers. In this work, we calculated the enthalpies of formation via the atomization reactions, as explained

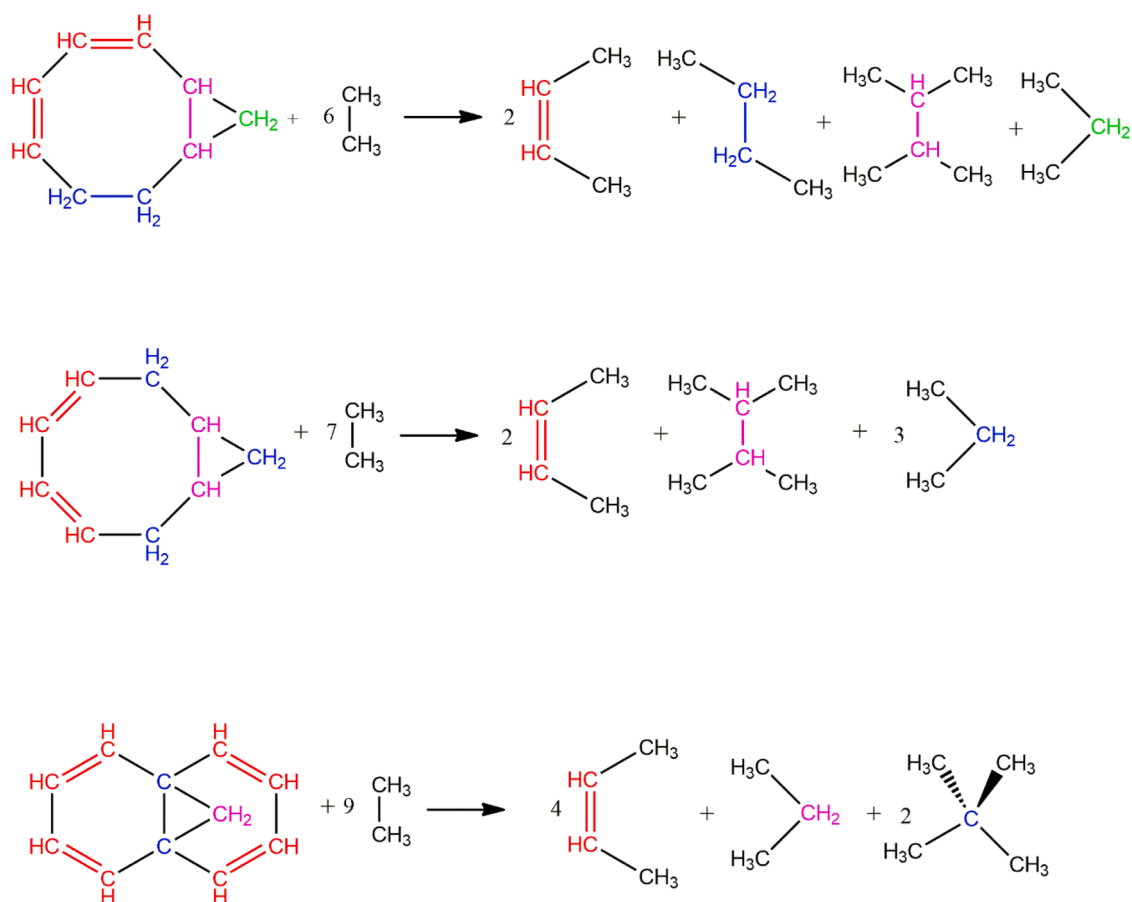


Fig. 9. Alternative homodesmotic reactions for bicyclo[6.1.0]nona-2,4-diene, bicyclo[6.1.0]nona-3,5-diene, and [4.4.1]propellatetraene. Colors on both sides of the equations identify the origin of the fragment.

before, and using homodesmotic reactions, which are also useful for calculating the strain energy. Such homodesmotic reactions are collected in Fig. 5 and the values obtained for the enthalpies of formation and the strain energy collected in Table 6.

As expected, the homodesmotic reactions yield values of the enthalpies of formation with smaller spread than those obtained using the atomization reactions (2.2 kJ mol^{-1} in the first case and 6.2 kJ mol^{-1} in the second). However, the largest spread observed using atomization reactions is 3.6 kJ mol^{-1} (remember that in the table we report 2σ values) which implies that the values obtained are within chemical accuracy.

In those three cases for which there is experimental data (4-6) the theoretical results agree reasonably well with experiment. In the case of bicyclo[2.1.0]pent-2-ene, the value of 333 kJ mol^{-1} reported by LG89 [3] on the basis of its hydrogenation reaction to form cyclopentane agreed very well with that reported shortly after by Roth et al. [97] Theoretically, Rogers et al. [98] calculated it as $341.0 \text{ kJ mol}^{-1}$ at the G2 (MP2) level and Bakowies [16] found a value of $330.5 \pm 2.5 \text{ kJ mol}^{-1}$. Using the atomization energies, in the same way as Bakowies [16], we got $326.0 \pm 4.0 \text{ kJ mol}^{-1}$ which overlaps with his value when the errors are considered and is identical to the value that we got using the homodesmotic reaction.

The situation is a bit different for [1.1.1]propellane. The experimental determination reported by LG89 [3] of $351.5 \pm 4.1 \text{ kJ mol}^{-1}$ was obtained through indirect ring-opening, solution-phase acetolysis experiments by Wiberg et al. [96]. Bakowies [16] obtained $365.3 \pm 2.9 \text{ kJ mol}^{-1}$, which does not overlap the experimental range but agrees with our values of $361.0 \pm 4.1 \text{ kJ mol}^{-1}$, when using atomization energies, and $364.5 \pm 1.4 \text{ kJ mol}^{-1}$, when using the homodesmotic reactions. It appears then that the experimental value should be revised upwards.

Since no internal rotators (which may complicate the accuracy of the harmonic oscillator approximation) are present, we tend to believe that the experimental value is $10\text{-}15 \text{ kJ mol}^{-1}$ too low, something that may be caused, for instance in Wiberg et al. study [96], because of using 3-methylenecyclobutyl acetate, the sole suggested acetolysis product, for which the enthalpy of formation was estimated using the enthalpy of formation of methylenecyclobutane from Good et al. [99] Notice however that the value for the gaseous species reported in this paper differs ca. 16 kJ mol^{-1} from the value given by Roth et al. [97] If this last one is used in Wiberg's procedure then our calculation and the so-modified experimental value of Wiberg are almost identical.

Vinyl cyclopropane is the one relevant C_5H_8 isomer for which some experimental data exists. LG89 [3] report the value of $127.3 \pm 1.3 \text{ kJ mol}^{-1}$ determined by Roth et al. [97,100] but also a slightly larger value of $131.2 \pm 1.4 \text{ kJ mol}^{-1}$ was produced by Lebedeva et al. [101] No other theoretical determination was found in the literature and our determination using the atomization energies, $127.3 \pm 7.3 \text{ kJ mol}^{-1}$, exhibits a considerable spread. Using the homodesmotic equation however, the spread is much less and the value slightly but not significantly smaller, $123.8 \pm 2.4 \text{ kJ mol}^{-1}$.

None of the other three C_5H_8 isomers has been studied theoretically (or experimentally) after the report by LG89 [3]. In the three cases, the spread of the theoretical values obtained at different levels from the atomization reactions are larger than those obtained from the homodesmotic reactions, which should be considered as the more accurate ones. LG89 [3] made an interesting discussion of these three results, which they obtained combining energies of hydrogenation with enthalpies of formation of the products. They reported a certain pessimism about the results, which however appear to be confirmed by the calculations. If anything, the theoretical results even increase the gap among

Table 9Summary of enthalpies of formation and strain energies, in kJ mol^{-1} , for all the species studied in this work.

Species	Heat of formation		Strain energy	
	Suggested value ^a	Expected accuracy ^b	Suggested value ^a	Expected accuracy ^b
Cyclopropane	54.5	± 1.4	117.5	± 0.5
Methylcyclopropane	24.4	± 2.0	116.9	± 2.2
Methylenecyclopropane	191.2	± 1.9	167.3	± 2.2
Cyclopropene	272.6	± 1.7	222.0	± 0.7
Methylenecyclopropene	384.2	± 2.6	237.7	± 2.8
1-Methylcyclopropene	230.2	± 1.3	209.0	± 1.5
3-Methylcyclopropene	251.4	± 4.1	225.9	± 4.7
Bicyclo[2.1.0]pent-2-ene	325.0	± 4.4	279.9	± 2.4
[1.1.0]Propellane	363.2	± 4.0	425.8	± 6.4
Vinylcyclopropane	123.8	± 3.4	112.6	± 1.7
Ethylidenecyclopropane	151.3	± 2.6	151.1	± 2.0
1,2-Dimethylcyclopropene	199.1	± 1.9	198.9	± 1.9
2-Methyl-1-methylenecyclopropane	166.0	± 0.8	164.8	± 1.7
[3]-Radialene	437.4	± 2.7	238.6	± 5.8
Benzvalene	382.6	± 5.3	339.6	± 7.6
Tricyclo[3.1.0.0 ^{2,6}]hexane	225.9	± 3.5	301.6	± 4.2
[(E)-1-Propenyl]cyclopropane	75.5	± 5.6	113.2	± 5.1
cis-1-Methyl-2-vinylcyclopropane	92.8	± 1.1	109.0	± 1.8
1,3-Dimethylbicyclobutane	154.7	± 3.0	280.4	± 3.6
Benzocyclopropene	380.0	± 3.9	297.6	± 4.9
Quadricyclane	326.1	± 4.8	204.8	± 5.6
Norcaradiene	207.3	± 5.5	280.3	± 6.3
5,5-Dimethyl bicyclo[2.1.0]pent-2-ene	260.0	± 4.4	358.5	± 6.3
Tricyclo[4.1.1.0 ^{2,7}]heptane	190.1	± 3.7	208.8	± 4.2
5,5-Dimethyl bicyclo[2.1.0]pentane	92.0	± 2.7	228.7	± 2.8
Semibullvalene	295.6	± 6.9	171.4	± 7.9
Bicyclo[6.1.0]nona-2,4-diene	201.5	± 2.9	132.9	± 10.8
Bicyclo[6.1.0]nona-3,5-diene	205.3	± 12.0	133.8	± 18.6
(1 <i>H</i> ,2 <i>H</i> ,3 <i>CH</i> ,5 <i>CH</i> ,6 <i>tH</i> ,7 <i>CH</i>) -Tetracyclo[5.2.1.0 ^{2,6} .0 ^{3,5}] dec-8-ene	342.4	± 7.3	346.5	± 8.4
[4.4.1]Propellatetraene	304.9	± 10.6	23.0	± 10.6

^a Average of the G4, W1BD, SVECV-f12 and jChS values when available.^b Two times the standard deviation (2σ) of the average value.

the enthalpy of formation of the three isomers. We will discuss in detail the effect of substituents on the strain energy of cyclopropane and cyclopropene in another section of the paper.

3.4. C6 carbocycles

Six species of the formula C_6H_n containing three-membered rings, and for almost all of which there is not direct experimental data, were considered in this paper. The homodesmotic reactions adopted are shown in Fig. 6. [3]-radialene is one species for which an enthalpy of formation was derived experimentally (Table 7) by Bally et al. in 1978 [102] as $396.0 \pm 12.0 \text{ kJ mol}^{-1}$. This value differs markedly from the most accurate one calculated by Bakowies [16] as $443.9 \pm 3.3 \text{ kJ mol}^{-1}$ using atomization reactions, also in agreement with our own one employing atomization energies, $442.5 \pm 5.1 \text{ kJ mol}^{-1}$. The use of the homodesmotic reaction yields a slightly smaller number, $437.4 \pm 2.7 \text{ kJ mol}^{-1}$, but also very far from the experimental value, which should be discarded in favor of the theoretical one. As was properly assessed by LG89 [3], this error is probably connected to the wrong identification of the process leading to the butatriene radical cation.

Notice that Rosenstock et al. [103] also reported experimental values for two of the molecules we considered here, one of them being [3]-radialene. For this species, their value is a bit larger than that of Bally et al. [102] and more in agreement with our theoretically determined one. For benzvalene they reported a value of 381 kJ mol^{-1} which is in very good agreement with those found theoretically, but about 18 kJ mol^{-1} larger than that estimated in LG89 [3]. Based on this agreement for benzvalene and the better agreement in the case of [3]-radialene, we may conclude that Rosenstock et al. [103] values are better than those of Bally et al. [102]. Admittedly, the suggested strain energy, 239 kJ mol^{-1} , is surprisingly small given that there are three trigonal planar carbon atoms. Then again, the three double bonds are conjugated and there may be some 6π benzene-like stabilization in [3]-radialene,

both of which contribute to a seemingly anomalous small strain energy.

The four other species exhibit mixed situations. There is a good agreement between theory and LG89 [3] in the case of tricyclo[3.1.0.0^{2,6}]hexane and in that of cis-1-methyl-2-vinylcyclopropane, for which there is no experimental data. In the case of [(E)-1-propenyl] cyclopropane it seems to be a reasonable agreement when the atomization energies are employed, but the better calculations using the homodesmotic reactions show that the true value is much lower and LG89 [3] is too high by about 21 kJ mol^{-1} .

The case of 1,3-dimethylbicyclo[1.1.0]butane is a bit disconcerting at first. The value quoted in LG89 [3] is much too high according to the theoretical calculations, but this is plausibly a typographical error in the publication. The experimental value from hydrogenation measurements derived by Turner et al. [104] is much nearer to the theoretical value, although still a bit higher. However, the strain energy is in very good agreement with what we obtained theoretically.

We note that the difference in the strain energies of benzvalene and tricyclo[3.1.0.0^{2,6}]hexane is $[339.6 \pm 7.6] - [301.6 \pm 4.2] = 38.0 \pm 8.7 \text{ kJ mol}^{-1}$. It was surprising that this difference is so large. The fact that the (vertical) IP of benzvalene is $8.54 \pm 0.1 \text{ eV}$ [105], while that of the related 1-ring species 3-methylcyclopentene is $8.98 \pm 0.02 \text{ eV}$ [106], suggests that there is some destabilization of benzvalene that is ameliorated by the loss of an electron. Indeed, loss of two electrons from benzvalene, or more properly its hexamethyl derivative, results in a highly stable, indeed isolable, dication [107,108], a finding again suggesting some destabilization in benzvalene itself.

3.5. C7 – C11 carbocycles

The remaining species studied in this work, containing from seven to eleven carbon atoms, are reported in Table 8, while the homodesmotic reactions used in this case are collected in Figs. 7 and 8. Very few experimental or theoretical thermochemically relevant data exist for

these molecules. In the case of benzocyclopropane, Bakowies [16] derived the enthalpy of formation from the atomization reaction as $382.8 \pm 3.8 \text{ kJ mol}^{-1}$, in agreement with our best value of $380.0 \pm 3.8 \text{ kJ mol}^{-1}$ obtained from the homodesmotic reaction (which in this case agrees very well with the value obtained from the atomization reactions and has smaller standard deviation). The experimental value quoted by Billups et al.¹⁰⁵ is about 14 kJ mol^{-1} lower. Notice that the same difference as in the enthalpy of formation exists between our theoretically calculated strain energy and that reported by Billups et al. [109]. We note that many assumptions and additional measurements were made in this paper, from which the enthalpy of formation of benzocyclopropane was derived.

We wonder if some error did not accordingly arise. The authors derived the enthalpy of formation of benzyl methyl ether, the product of the reaction used in ref. [109] as part of their investigation. The enthalpy of formation of this ether remains unmeasured but the enthalpy of vaporization is now available. The original paper used an estimated value of 39 kJ mol^{-1} , but a more recent measurement [113] gave the very discrepant value of $51.4 \pm 0.3 \text{ kJ mol}^{-1}$. Using this revised value increases the enthalpy of formation of gaseous benzocyclopropane by ca. 12 kJ mol^{-1} . Accordingly, the derived strain energy of benzocyclopropane should be likewise increased, thus reconciling theory with experiment.

In the case of quadricyclane, the value obtained by Bakowies¹⁶ and us using the atomization reaction are well in agreement with the experimental result in Bradley et al.⁷⁴ The value obtained from the homodesmotic reaction is however much lower. This might be due to our use of (*E,E*)-hexa-2,4-diene as reference in the r.h.s. of the chemical equation for this homodesmotic reaction, as well as others.

The reference value was taken from the work by Fang and Rogers [114], namely $44.4 \pm 1.7 \text{ kJ mol}^{-1}$, who also derived the enthalpy of formation of (*Z,Z*)-hexa-2,4-diene as $52.3 \pm 1.7 \text{ kJ mol}^{-1}$ and (*E,Z*)-hexa-2,4-diene as $48.1 \pm 1.7 \text{ kJ mol}^{-1}$, showing a monotonic increase among the isomers (*E,E*) < (*E,Z*) < (*Z,Z*). These enthalpies of reaction, however, were not directly measured by classical combustion calorimetry, but derived from generally reliable hydrogenation reactions. Therefore, we also used another isodesmic reaction, in which the (*E,E*)-hexa-2,4-diene was substituted by a pair of *cis* 2-butene molecules (see Fig. 9). This procedure may solve one of the problems, but it also introduces another issue: we don't consider the delocalization of the double bonds in quadricyclane. The results are shown in Table 8. When *cis* 2-butene is used instead of (*E,E*)-hexa-2,4-diene, the value of the enthalpy of formation increases and is now in agreement with that obtained using the atomization reaction, if the error margins are considered. We then preferred to use this second homodesmotic reaction to obtain the strain energy that is reported in the table. Nonetheless, we don't consider this problem to be solved. In fact, besides the result by Turner et al. [104] mentioned before, Kozina et al. [115] determined a value of $253.3 \pm 1.1 \text{ kJ mol}^{-1}$ (presumably erroneous) and Kabakoff et al. [116] found $325.1 \pm 4.2 \text{ kJ mol}^{-1}$, while later Steele [117] reported even a lower value, $302.1 \pm 2.2 \text{ kJ mol}^{-1}$, using a static combustion bomb calorimeter. To make any decision even more complex, Rogers et al. [118] determined the enthalpy of formation of quadricyclane in solution and from these experiments casted doubts about the latest findings in gas phase, again favoring Turner's data [104]. There is then clearly room enough for more careful research on this subject, both experimental and theoretical, before a firm conclusion can be reached.

Finally, norcaradiene is a case in which, considering the error bars, all the theoretical calculations are well in agreement with the experimental derived value by Roth et al. [110]. Consequently, we believe that the strain energy would also be similarly well reproduced.

3.6. Analysis of strain energies

From the enthalpies of reaction for the homodesmotic reactions

studied in this work, we can make useful deductions about the strain energy of the cyclopropane ring with different substituents. As shown in Table 9, the theoretically derived strain energy of cyclopropane is $117.5 \pm 0.7 \text{ kJ mol}^{-1}$ and that of cyclopropene is $222.0 \pm 0.7 \text{ kJ mol}^{-1}$, in both cases in agreement with other experimentally and theoretically derived values. This means that the double bond adds about 100 kJ mol^{-1} to the strain energy of cyclopropane.

Now we can ask questions about the effect of simple (i.e., containing only carbon and hydrogen) substituents in both species. The effect of a methyl group on the strain energy of the ring can be assessed through the values for methylcyclopropane ($116.9 \pm 2.3 \text{ kJ mol}^{-1}$, see Table SI2) which coincides with that of cyclopropane itself, given before, within the error margins. Thus, it can be said that a substituent methyl group has basically no influence on the strain energy of cyclopropane. But, what about cyclopropene? In this case, the strain energy of 3-methylcyclopropene is $209.0 \pm 1.5 \text{ kJ mol}^{-1}$, i.e., it decreases by the not insignificant amount of 13 kJ mol^{-1} . What happens if, alternatively, we introduce the methyl substituent directly on the double bond? Then we would have 1-methylcyclopropene, with a strain energy (see Table SI1) of $225.9 \pm 4.7 \text{ kJ mol}^{-1}$ which is essentially identical to that of cyclopropene itself, within the error margins. Thus, we conclude that substitution of one of the alkene hydrogens by a methyl group does not affect the strain energy of cyclopropene, while it does lower it if the methyl group substitutes a hydrogen on the CH_2 group.

Let's consider now what happens if the double bond is introduced in the substituent, instead of in the ring. For that we can use the value of the strain energy of methylenecyclopropane (see Table SI2), which is $167.3 \pm 2.2 \text{ kJ mol}^{-1}$, midway the strain energy of cyclopropane and cyclopropene. Thus, the double bond inside the ring adds about 100 kJ mol^{-1} to the strain energy of cyclopropane ($\text{SE}(\text{cyclopropene}) - \text{SE}(\text{cyclopropane}) \approx 104 \text{ kJ mol}^{-1}$, $\text{SE}(1\text{-methylcyclopropene}) - \text{SE}(\text{methylcyclopropane}) \approx 109 \text{ kJ mol}^{-1}$) while the double bond in the methylene substituent adds only about three quarters of that strain energy ($\text{SE}(\text{methylenecyclopropane}) - \text{SE}(\text{methylcyclopropane}) \approx 75 \text{ kJ mol}^{-1}$).

4. Conclusions

Density functional theory and composite quantum-chemical methods have been used to determine the enthalpy of formation and, concomitantly, the strain energy of species containing three-membered carbocycles which experimental data was not known directly but were derived from indirect methods [3]. A summary of the theoretical findings in this work is provided in Table 9.

In general, the theoretically calculated values with different methods are in fair agreement when the atomization energies are used, covering a range typically below 12 kJ mol^{-1} . This spread is strongly reduced when homodesmotic reactions are used, and in this case the error is typically below 4.5 kJ mol^{-1} . In general, the results from the atomization and homodesmotic reactions overlap when the spread of the methods is taken as the standard deviation, and only in a few cases this trend is not followed. Some of these can be related to the use of references (like (*E,E*)-hexa-2,4-diene) that introduce some extra errors, and we have shown that using smaller molecules, which enthalpies of formation are well-known experimentally, considerably eases this error.

The methods used in this paper have distinctive advantages. On one side, being all of them approximations to the best possible theoretical energies, it is to be expected that they are accurate. Moreover, since the specific approximations are different within each method, and their degree of accuracy vary, it is to be expected that the more coincident they are, the more accurate the answer is. This is a case in which precision supports accuracy. Moreover, the use of homodesmotic reactions, balancing potential errors in the description of geometric and electronic structure, increases even more the robustness of the enthalpies of formation and strain energies obtained theoretically.

Considering those advantages, we are of the opinion that the values provided in this work should be adopted as the best available estimates

of the enthalpy of formation and strain energy of the investigated species, pending more accurate experimental determinations for comparison.

Declaration of Competing Interest

The authors declare that they have no conflict of interests regarding the present study.

Data availability

Data will be made available on request.

Acknowledgments

O.N.V. thanks Pedeciba, CSIC, and ANII (Uruguay) for the continuous support to his research. N.T. and Z.S. thank the Avogadro data-center for providing high-performance computing facilities and the financial support by Scuola Normale Superiore (SNS22_A_FE_TASINATO).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.ctta.2023.100121](https://doi.org/10.1016/j.ctta.2023.100121).

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