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The unimolecular C_2 fragmentation of C_{82}: a computational study

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This article is dedicated to Professor Bill Hase on the occasion of his 60th birthday.

Abstract

The possible fragmentation pathways of three C_2 and three C_s isomers of C_{82} by unimolecular C_2 loss were investigated with semi-empirical (PM3), ab initio (HF/STO-3G) and density functional theory (B3LYP/3-21G) calculations. The C_2 fragmentation energy of the most stable C_2 isomer of C_{82} calculated with the most reliable model chemistry employed here (B3LYP/3-21G) lies in the 9.1–9.4 eV range, which is 0.5–0.9 eV larger than the recently reported experimental values. However, other, less stable, isomers were found to have lower fragmentation energies, closer to the experimental data, which suggests that the presence of other isomers in experiments may affect the measured values of the C_{82} fragmentation energies.

Keywords: C_{82} fullerenes; Binding energy; Fragmentation energy; Molecular modeling; DFT calculations

1. Introduction

Fullerenes, the third major allotropic form of carbon, represent an exciting class of organic molecules which possess many interesting and unusual structural, physical and chemical properties [1–4]. Among these, of particular interest is their high kinetic stability, i.e., their stability with respect to fragmentation. Fragmentation may however occur when fullerene molecules are highly excited by electron impact, laser ablation or after collision with an atom, ion, molecule or surface. The main decay process of a C_n fullerene at high impact energies involves the loss of a neutral C_2 molecule, leading to the formation of a smaller C_{n-2} fullerene [5–7]:

$$C_n \rightarrow C_{n-2} + C_2$$

This reaction is characterized by the dissociation energy $D(C_n)$, also referred to as the C_2 binding energy or the C_2 fragmentation energy, as there is no activation barrier for the reverse association reaction. $D(C_n)$ is simply defined as the energy difference between the products and the reactants:

$$D(C_n) = E(C_{n-2}) + E(C_2) - E(C_n)$$

Despite the apparent simplicity of this dissociation reaction, the actual value of the C_2 fragmentation energy of the most well-known fullerene, C_{60}, was the subject of a long-time controversy between theoreticians and experimentalists [8]. The main reasons for the discrepancy between early experimental and theoretical results are related to the influence of radiative cooling and thermoionic emission on the experimental results (as both processes may partially suppress dissociation) [9], as well as the uncertainty in using different indirect values of the pre-exponential factor A in the Arrhenius decay law [8] or the Klots Gspann factor γ [10,11]. According to recent experimental results [9,12], the C_2 fragmentation energies lie within 9.8–10.2 and 10.5–10.9 eV for C_{60}^+ and C_{60}, respectively, in very good agreement with earlier theoretical predictions based on density-functional theory (DFT) and second-order Møller-Plesset (MP2) perturbation theory

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[13]. We note that the most recent values reported by Głuch et al. (10.7 and 11.2 eV for C_{60}^{+} and C_{60}, respectively) [14] are slightly higher as they were derived under the assumption that the pre-exponential factor *A* does not depend on the number of carbon atoms in the fullerene cage.

Nowadays, higher fullerenes become available in sufficient amounts that their kinetic stabilities is being increasingly investigated by experimentalists [14–16]. However, fragmentation studies of higher fullerenes still pose challenges both theoretically, as quantum chemistry calculations for large molecules are intensive and many isomers have to be considered, and experimentally, as many fullerenes are still not available in pure isomeric form in large quantities. New puzzles also arise, especially when comparing the relative dissociation energies of various size fullerenes with each other [14,15]. For example, $D(C_{80}^{+})$ was found [15] and confirmed independently [14] to be larger than $D(C_{78}^{+})$ and $D(C_{82}^{+})$, pointing out the higher stability of C_{80} in comparison to its neighbors, in disagreement with earlier experimental studies [5], abundance spectra [14] and theoretical considerations based on heats of formation [17]. Further, the main C_{78} and C_{82} isomers were isolated and characterized in 1991 [18] and 1992 [19,20], respectively, shortly after Krätschmer et al. proposed a method of synthesis, separation and purification of fullerenes in large quantities [21], whereas the D_2 isomer of C_{80} was only isolated in 1996 [22], presumably because of its very low concentration in the mixture of isomers formed during arc-discharge fullerene synthesis. In this work, we will concentrate on a theoretical investigation of $D(C_{82})$ by means of semi-empirical and ab initio molecular orbital theory and density-functional theory calculations, and compare our results to the known experimental values of $D(C_{82})$ and $D(C_{80})$.

A criterion for the stability of different possible fullerene isomers is the absence of adjacent pentagons in their structure, i.e., the so-called isolated-pentagon rule (IPR) [23,24]. In the case of C_{82}, there are nine possible IPR isomers: three of C_2, three of C_s, two of C_{3v} and one of C_{2v} symmetry. All of them are shown in Fig. 1 using the conventional notation of Fowler and Manolopoulos [24]. Experimentally, C_{82} was observed for the first time as a mixture of three major isomers and at least three minor ones [19]. The three major isomers were originally ascribed to C_2, C_{2v} and C_{3v} symmetry on the basis of NMR experimental data, but later theoreti-

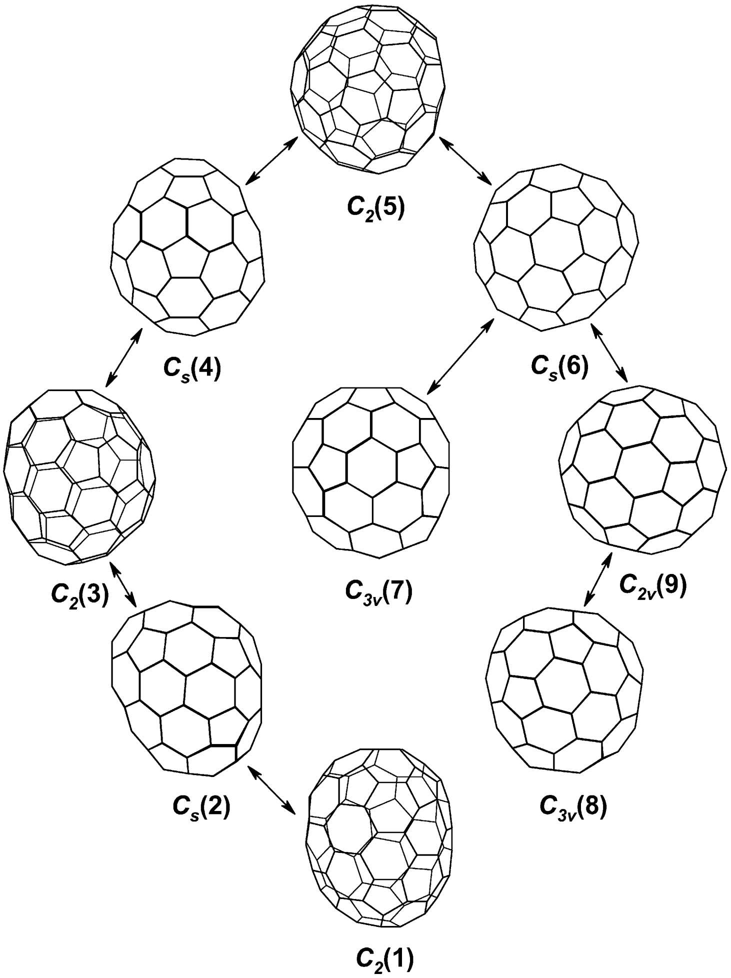


Fig. 1. Stone-Wales family of C_{82} IPR isomers. The isomer labeling follows that of Fowler and Manolopoulos [24].

cal studies [25–28] confirmed the presence of only the C_2 isomer, while the two other isomers were shown [25–29] to have other topological symmetries than the ones originally ascribed. The most reliable calculations reported by Sun et al. [28] predict that the most predominant isomer is $C_2(\mathbf{3})$, and that the $C_s(\mathbf{2})$ and $C_s(\mathbf{4})$ isomers may also be observed. In principle, all three $C_2(\mathbf{1}, \mathbf{3}, \mathbf{5})$ and three $C_s(\mathbf{2}, \mathbf{4}, \mathbf{6})$ isomers may be formed under experimental conditions, since they all have non-zero HOMO–LUMO gaps and they lie close in energy [28]. Therefore, only these isomers were selected in this work for the investigation of C_{82} fragmentation pathways.

The first experimental study of $D(C_{82})$ was carried out in 1995 by Laskin et al. [30], who performed kinetic energy release distributions (KERD) measurements and found a $D(C_{82}{}^{+})$ value of 6.1 ± 0.4 eV, which is 1 eV lower than that of $D(C_{60}{}^{+})$ (7.1 ± 0.5 eV). Taking into account the most reliable $D(C_{60}{}^{+})$ value of 10 eV [9,12], the re-normalized value of $D(C_{82}{}^{+})$ reported by Laskin et al. [30] would be 8.6 ± 0.6 eV. Recent KERD results by Peres et al. [15] and Głuch et al. [14,16] indicate that the value of $D(C_{82}{}^{+})$ should be even smaller, around 8.5 and 8.2 eV, respectively, after re-normalization to the $D(C_{60}{}^{+})$ value of 10 eV. However, Barran et al. [5] reported a $D(C_{82}{}^{+})$ value of about 9.1 eV after re-normalization, from an analysis of metastable fractions observed in a time-of-flight reflectron mass spectrometer. The latter value is not only larger than the previously reported ones, but it also exceeds the re-normalized $D(C_{80}{}^{+})$ value of 8.8 eV [5].

We have recently carried out a computational study of the possible fragmentation pathways of C_{80} [31] and found a value of the C_2 fragmentation energy (8.7–9.0 eV) in agreement with experimental data [5,14–16]. Now turning to the fragmentation of higher fullerenes, we report an analogous investigation to characterize the C_2 fragmentation energy of C_{82} from a theoretical point of view and compare it to experimental results, and to assess whether the same theoretical tools will predict a $D(C_{82}{}^{+})$ value larger or smaller than that for $D(C_{80}{}^{+})$.

2. Computational details

All input Cartesian coordinates of the IPR isomers of C_{82} have been generated using the CaGe program [32]. These structures, together with the products of C_2 elimination from the three C_2 and three C_s IPR isomers of C_{82}, were first minimized using the MM+ forcefield [33] implemented in the Hyperchem program package [34]. The resulting structures

Table 1
Relative energies (ΔE, kcal/mol) and bond length distributions ($r_{\min}$, $r_{\max}$ in Å) of C_{82} IPR isomers

Isomer	$C_2(\mathbf{1})$	$C_s(\mathbf{2})$	$C_2(\mathbf{3})$	$C_s(\mathbf{4})$	$C_2(\mathbf{5})$	$C_s(\mathbf{6})$	$C_{3v}(\mathbf{7})$[a]	$C_{3v}(\mathbf{8})$[a]	$C_{2v}(\mathbf{9})$[a]
MM+									
$r_{\min}$	1.384	1.380	1.382	1.381	1.381	1.381	1.377	1.382	1.384
$r_{\max}$	1.417	1.415	1.417	1.418	1.418	1.418	1.418	1.418	1.417
ΔE	4.7	7.1	0.0	−2.9	−6.8	−10.9	1.1	−13.1	−15.0
AM1[b]									
ΔE	4.0	6.0	0.0	6.5	12.0	16.5[c]	31.0	35.6[c]	21.8
PM3									
$r_{\min}$	1.358	1.358	1.360	1.355	1.355	1.354	1.356	1.352	1.354
$r_{\max}$	1.468	1.469	1.468	1.476	1.476	1.477	1.478	1.477	1.477
ΔE	4.1	5.2	0.0	6.4	11.8	16.6	29.3	35.2	22.1
HF/STO-3G									
$r_{\min}$	1.344	1.344	1.347	1.341	1.340	1.340	1.342	1.336	1.338
$r_{\max}$	1.487	1.487	1.485	1.491	1.495	1.496	1.498	1.499	1.497
ΔE	7.8	6.3	0.0	10.1	19.3	28.2	42.8	59.8	38.6
B3LYP/STO-3G[d]									
ΔE	7.8	6.7	0.0	5.3	10.4	15.4	–	38.6	23.4
B3LYP/3-21G[e]									
$r_{\min}$	1.361	1.358	1.366	1.363	1.361	1.362	1.355	1.357	1.360
$r_{\max}$	1.475	1.475	1.474	1.476	1.476	1.477	1.477	1.478	1.479
ΔE	6.1	5.4	0.0	5.3	11.0	16.3	27.7	33.9	21.6
B3LYP/6-31G*[d]									
$r_{\min}$	1.365	1.363	1.371	1.369	1.366	1.367	–	–	–
$r_{\max}$	1.470	1.472	1.470	1.472	1.471	1.473	–	–	–
ΔE	7.7	6.6	0.0	3.9	8.1	12.2	–	30.7	18.3

[a] The $C_{3v}(\mathbf{7})$, $C_{3v}(\mathbf{8})$ and $C_{2v}(\mathbf{9})$ isomers distort from their topological symmetries during optimization into C_s, C_s and C_1 structures, respectively, because of Jahn-Teller distortion.

[b] Ref. [51].

[c] Ref. [27].

[d] Ref. [28].

[e] Almost identical values were reported in Ref. [28].

were further optimized without symmetry constraints at the semi-empirical (PM3 [35,36]), ab initio (HF/STO-3G [37]) and DFT (B3LYP/3-21G [38,39]) levels of theory. The combination of the Becke three-parameter (B3) hybrid functional [38] with the Lee–Yang–Parr (LYP) correlation functional [39], together with the 3-21G basis set [40] was shown to yield reliable results for fullerenes [13,17,28,41]. Further, extension of the basis set from 3–21G to 6–31G* was shown not to significantly affect the resulting $D(C_{60})$ [13] and $D(C_{80})$ [31] values. A vibrational analysis was performed for all structures to ensure that they were indeed minima on the potential energy surface. These calculations were carried out using the Gaussian 98 program [42]. Finally, $D(C_{82})$ was calculated as the difference between the sum of the product energies and the energy of the starting C_{82} isomer.

3. Results and discussion

3.1. *Structure and stability of C_{82} IPR isomers*

The distinctive feature of the nine C_{82} IPR isomers is that they all belong to the same Stone-Wales (SW) family [43], i.e., each isomer can be converted to any of the others by one or several SW transformations (cf. Fig. 1). Table 1 summarizes the main geometrical and energetic parameters of the minimized C_{82} IPR isomers. Inspection of Table 1 reveals that the MM+ force field cannot predict either the pentagon–hexagon bond lengths (r_{max}) values, which should be larger than 1.45 Å, or the relative stability of the C_{82} IPR isomers. This is not a surprising result, since MM+ employs simple empirical potentials for aromatic carbon with benzene-like bond length of 1.392 Å [34]. The average bond lengths calculated with MM+ are about 1.40 Å, whereas quantum chemistry methods give more reasonable values of 1.43–1.44 Å, comparable to that measured from gas-phase electron diffraction for C_{60} (1.439 Å) [44]. The reliability of the bond length values obtained with different methods seems to increase in the order MM+ < HF/STO-3G < PM3 < B3LYP/3-21G < B3LYP/6-31G*, consistent with improved geometries upon increase of the basis set size and inclusion of electron correlation. Further, all quantum chemical methods predict that C_2(**3**) is the most stable isomer, with the lowest range of bond lengths as a result of lower strain. The relative energies of the other C_2 and C_s IPR isomers of C_{82} are slightly larger in comparison to C_2(**3**), which suggests that their possible formation under conditions of arc discharge or laser ablation fullerene syntheses should not be ruled out.

3.2. *Fragmentation of the C_2 and C_s IPR isomers of C_{82}*

It is commonly accepted that fullerenes undergo C_2 dissociation reactions by two main possible mechanisms (cf. Fig. 2). One of them assumes an initial SW transformation of the pyracylene fragment, followed by C_2 elimination from the pentagon–pentagon edge (cf. Fig. 2, top panel) [45]. The second possible mechanism involves C_2 excision from the pentagon-hexagon bond, with the formation of a seven-membered-ring C_{n-2} fullerene isomer (cf. Fig. 2, bottom panel) [46]. Both of these mechanisms were investigated for the fragmentation of the C_2(**3**) isomer of C_{82} in the present study.

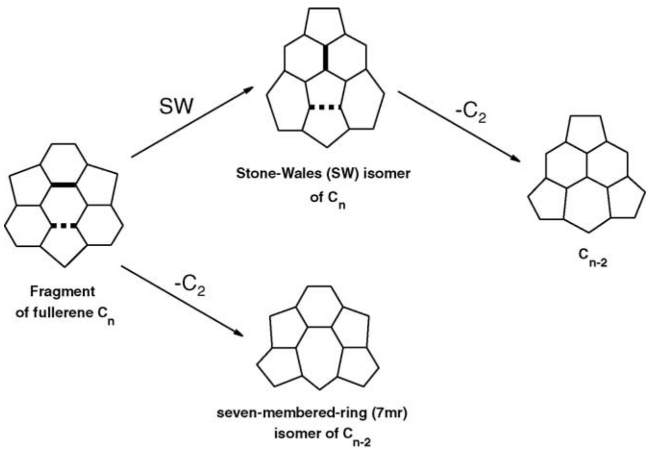


Fig. 2. Two main C_2 loss mechanisms of fullerene C_n fragmentation. The bonds from which C_2 elimination may occur are shown in dashed lines; while the Stone-Wales (SW) bond is shown in bold.

3.2.1. *Fragmentation of the most stable C_2(**3**) isomer*

As shown in Fig. 3, the C_2(**3**) isomer has seven distinct Stone-Wales bonds (labeled as SWa – SWg) and 30 distinct pentagon–hexagon ones (labeled as 1–30), from which the C_2 fragment may be extracted to form the corresponding seven-

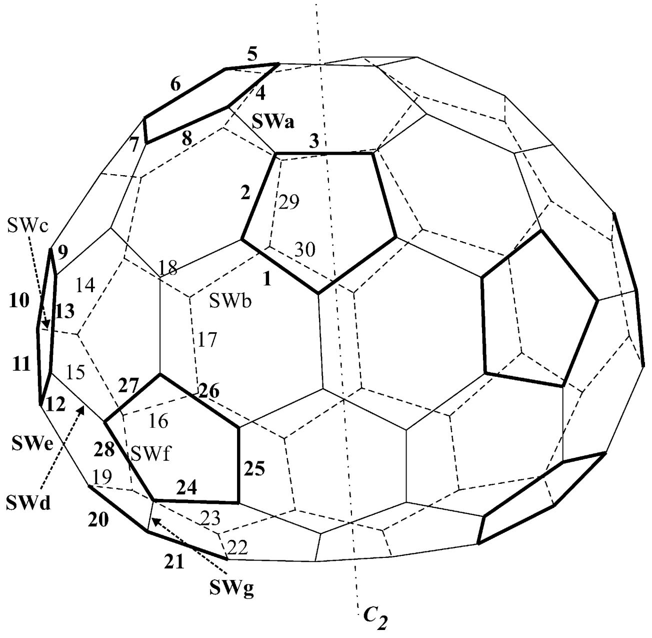


Fig. 3. Location of the distinct Stone-Wales bonds (labeled as SWa – SWg) and the pentagon-hexagon bonds (labeled as 1–30) in the C_2(**3**) isomer of C_{82}. The C_2 symmetry axis is shown as a dotted line.

Table 2
Relative energies (kcal/mol) of the $C_2(\mathbf{3})$ isomer of C_{82} and its SW isomers with adjacent pentagons

Isomer	Number of adjacent pentagon pairs	MM+	PM3	HF/STO-3G	B3LYP/3-21G
$C_2(\mathbf{3})$	0	−7.7	−20.7	−27.0	−20.3
SWc	1	0.0	0.0	0.0	0.0
SWd	1	8.1	8.5	10.0	6.8
SWe	2	17.9	35.4	44.4	30.4
SWf	1	2.4	19.8	28.6	16.4
SWg	1	3.5	23.7	32.8	19.4

membered-ring isomers. Among the possible SW transformations, only five of them lead to isomers with adjacent pentagons in their cages, while the other two lead to $C_s(\mathbf{2}, \mathbf{4})$ IPR isomers (cf. Fig. 1). The relative energies of the five SW isomers that lead to isomers with adjacent pentagons are listed in Table 2. The SWc isomer was found to be the most stable amongst all isomers, and, not surprisingly, all methods predict that the SWe isomer is the least stable one because of a structure with two pairs of adjacent pentagons. C_2 elimination from the SWc – SWg isomers leads to only two C_{80} isomers, A and B, whose energetic parameters, together with the corresponding C_2 fragmentation energies of C_{82}, are given in Table 3. Both C_{80} A and B isomers possess a structure with only one pair of adjacent pentagons, and their energies differ by only a few kcal/mol, which is reflected by the close $D(C_{82})$ values of 10.6 and 10.7 eV calculated with B3LYP/3-21G.

The relative energies of the seven-membered-ring (7mr) isomers arising from C_2 fragmentation of $C_2(\mathbf{3})$, along with the corresponding $D(C_{82})$ values, are shown in Fig. 4. All methods except for MM+ reveal that isomer #26 is the lowest-energy structure, yielding the lowest value of the fragmentation energy of C_{82} (10.9 eV). Interestingly, HF/STO-3G predicts this structure to be almost isoenergetic with the C_{80} B isomer which results from C_2 elimination from C_{82} SW isomers, with resulting $D(C_{82})$ values of 13.21 versus 13.19 eV, respectively, while PM3 and DFT methods slightly favor the fragmentation pathway via SW transformation, similar to the trends that were also observed for D_2 C_{80} fragmentation [31]. According to our B3LYP/3-21G calculations, the fragmentation pathway of C_{82} via SW transformation is found to be approximately 0.3 eV more favorable than that via 7mr isomer formation. This value is in agreement with the difference in $D(C_{80})$ values found for the C_2 fragmentation of C_{80} via SW and 7mr pathways with the same model chemistry [31], and slightly exceeds the corresponding differences found for $D(C_{60})$ with BPW91/6-311G*//BPW91/6-31G* and B3LYP6-311G*//B3LYP/6-31G* (0.17 and 0.10 eV, respectively) [13]. Therefore, only the fragmentation of the less stable C_2 and C_s IPR isomers of C_{82} via SW transformation has been considered in the following.

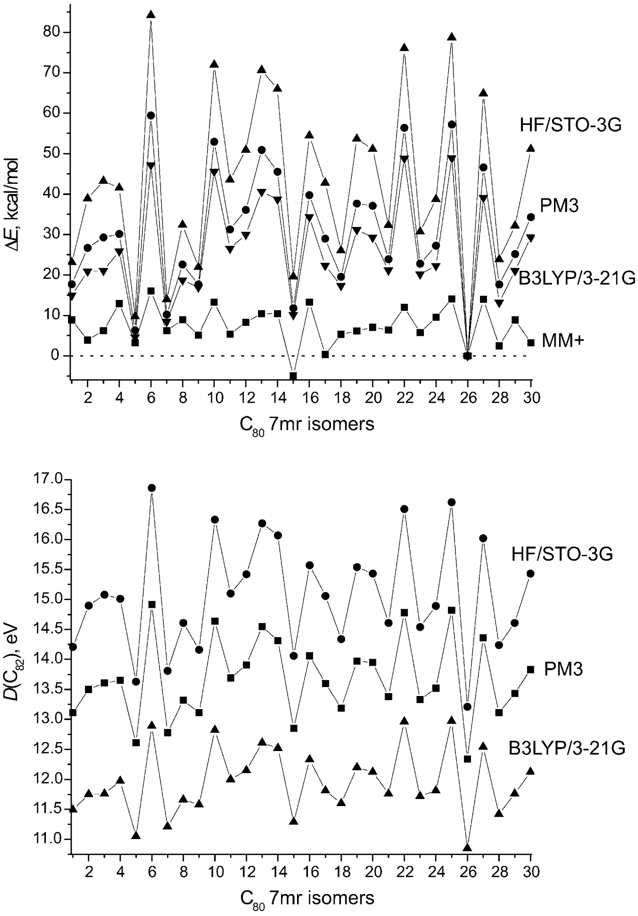


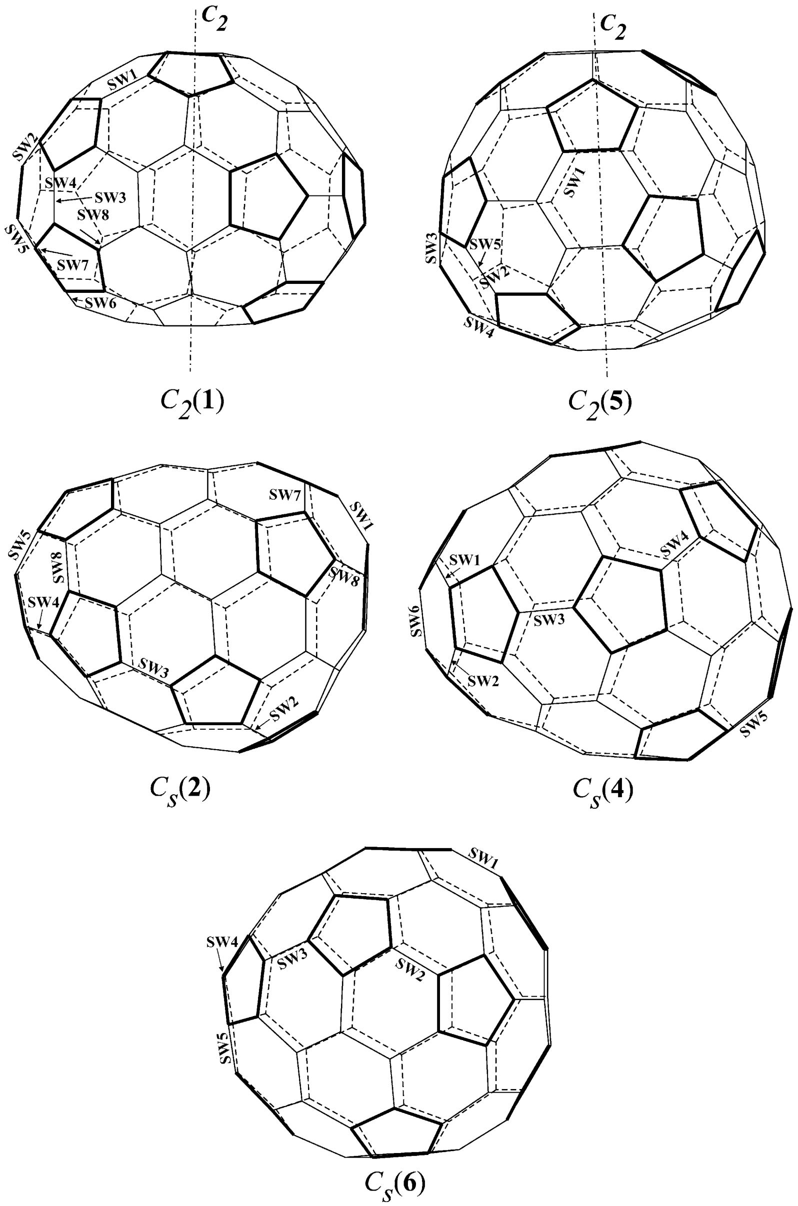
Fig. 4. Relative energies (ΔE) of the C_{80} seven-membered-ring isomers (top panel) and corresponding C_2 fragmentation energies [$D(C_{82})$] of C_{82} (bottom panel).

3.2.2. *Fragmentation of other C_2 and C_s isomers via the SW pathway*

Fig. 5 summarizes all possible locations of the SW bonds in the $C_2(\mathbf{1})$, $C_2(\mathbf{5})$ and C_s IPR isomers of C_{82}, whereas the relative energies of the resulting C_{80} isomers and the corresponding $D(C_{82})$ values are collected in Table 4. The number of SW bonds for these isomers varies from five to eight, depending on how far pentagons are separated from each other in the symmetrical fragment of a given IPR isomer, and it di-

Table 3
Relative energies (kcal/mol) of the A and B isomers of C_{80} formed by C_2 elimination from the SW isomers (SWc – SWe) of $C_2(\mathbf{3})$ C_{82}, and corresponding C_2 fragmentation energies [$D(C_{82})$, eV] of C_{82}

Isomer	ΔE (kcal/mol)				$D(C_{82})$ (eV)		
	MM+	PM3	HF/STO-3G	B3LYP/3-21G	PM3	HF/STO-3G	B3LYP/3-21G
A	−5.4	1.5	4.5	1.9	12.25	13.38	10.69
B	0.0	0.0	0.0	0.0	12.19	13.19	10.60



$C_2(\mathbf{1})$ $C_2(\mathbf{5})$ $C_s(\mathbf{2})$ $C_s(\mathbf{4})$ $C_s(\mathbf{6})$

Fig. 5. Stone-Wales bond locations in the C_2(**1**), C_2(**5**) and C_s IPR isomers of C_{82}. The isomer labeling follows that of Fowler and Manolopoulos [24].

Table 4
Relative energies (ΔE, kcal/mol) of C_{80} isomers formed by C_2 elimination from SW isomers with adjacent pentagons, for the C_2(**1**), C_2(**5**) and C_s IPR isomers of C_{82}, and corresponding C_2 fragmentation energies [$D(C_{82})$, eV]

C_{82} IPR isomer	SW isomers	C_{80} SW isomer	ΔE (kcal/mol)				$D(C_{82})$ (eV)		
			MM+	PM3	HF/STO-3G	B3LYP/3-21G	PM3	HF/STO-3G	B3LYP/3-21G
C_2(**1**)	SW2-SW8	A	6.2	26.6	38.9	20.1	12.56	13.91	10.77
		B	9.4	9.6	9.9	6.0	11.83	12.65	10.16
		C	21.0	38.9	48.1	33.1	13.10	14.31	11.33
C_2(**5**)	SW3-SW5	A	−8.9	7.9	14.9	3.9	11.42	12.37	9.85
C_s(**2**)	SW1, SW4-SW8	A	5.1	15.5	20.3	10.8	12.03	13.17	10.39
		B	23.9	42.8	50.8	35.7	13.22	14.49	11.47
		C	16.7	17.0	17.1	14.6	12.10	13.03	10.56
C_s(**4**)	SW1, SW2, SW5, SW6	A	1.9	22.4	29.8	18.1	12.28	13.42	10.71
		B	0.0	0.0	0.0	0.0	11.31	12.12	9.93
C_s(**6**)	SW4, SW5	A	−17.6	18.2	31.8	10.6	11.66	12.72	9.91

Table 5
Comparison of the corrected B3LYP/3-21G values of $D(C_{82})$ with known experimental values.

Pathway	$D^{\text{corrected}}_{\text{B3LYP/3-21G}}(C_{82})$ (eV)	$D_{\text{exp}}(C_{82}{}^{+})$ (eV)[a]			
		Laskin et al. [30]	Barran et al. [5]	Peres et al. [15]	Głuch et al. [16]
C_2(**1**) – SW	8.7	8.6 ± 0.6	9.1	8.5 ± 0.4	8.2 ± 0.5
C_2(**3**) – SW	9.1				
C_2(**3**) – 7mr	9.4				
C_2(**5**) – SW	8.4				
C_s(**2**) – SW	8.9				
C_s(**4**) – SW	8.4				
C_s(**6**) – SW	8.4				

[a] These values were re-normalized to the $D(C_{60}{}^{+})$ value of 10 eV [9,12].

rectly influences the number of distinct C_{80} isomers arising from C_2 elimination from the SW C_{82} isomers. The calculated $D(C_{82})$ values for these IPR isomers are found to be lower than those obtained for fragmentation of the C_2(**3**) isomer of C_{82}. The B3LYP/3-21G value of $D(C_{82})$ closest to that of C_2(**3**) is obtained for the C_s(**2**) isomer and is 0.2 eV lower than that of C_2(**3**). The C_2 fragmentation energies for the other isomers range from 9.9 to 10.2 eV, according to the most reliable B3LYP/3-21G, and are 0.4 to 0.7 eV lower than the value obtained for the fragmentation of the C_2(**3**) IPR isomer of C_{82}.

4. Comparison with experimental data

Comparison of calculated electronic fragmentation energies for neutral fullerenes, with experimentally measured fragmentation energies for fullerene cations, should be possible if one takes into account: (1) the difference in the ionization energies of the C_n and C_{n-2} fullerenes; (2) the zero-point vibrational energy correction to fragmentation energies; and (3) the necessity of including an empirical energy correction to compensate for the poor description of the C_2 fragment.

In contrast to C_{60}, higher fullerenes are known to have very similar ionization energies, and thus, the differences in ionization energy between different size fullerenes is negligible [47]. In the particular case of C_{82} and C_{80}, the difference in ionization energy is only -0.05 ± 0.03 eV [47], and one can directly compare experimental $D(C_{82}{}^{+})$ and calculated $D(C_{82})$ values without correction for ionization energies. The zero-point energy correction to the fragmentation energy is also insignificant, since the zero-point energy difference between reactants and products typically lies within 0.1–0.2 eV. However, it was shown earlier [31,41] that the poor description of the C_2 wavefunction by single-reference methods such as PM3, HF and DFT, because of its multi-reference character [48], dictates the inclusion of an empirical correction to compensate for the inaccurate C_2 fragment energy. The latter empirical correction, taken as the difference between theoretical and experimental C_2 atomization energies, is -1.5 eV for the best method of choice employed here, B3LYP/3-21G [31].

The choice of the 3-21G basis set, which was employed with B3LYP hybrid density-functional theory (DFT) in the present work, may deserve some justification, in light of the commonly admitted view that large basis sets with many polarization functions are necessary to obtain quantitatively correct structures and energetics with methods that include electron correlation [49,50]. We note however that DFT calculations are generally considered to be less sensitive to basis sets than wavefunction-based methods [49,50]. As a matter of fact, as mentioned earlier in Section 2, extension of the basis set from 3-21G (738 basis functions for C_{82}) to 6-31G* (1230 basis functions for C_{82}) leads to marginal changes in the resulting fragmentation energies but significantly affects the computational cost of the calculations. For instance, the difference between the B3LYP/3-21G and B3LYP/6-31G* fragmentation energies of the C_2(**3**) isomer of C_{82} via the SW pathways is only about 0.02–0.04 eV, which is insignificant–especially in comparison to the 1.5 eV empirical correction to the fragmentation energies, while the computational time increases by a factor of at least 6.[1] We note that, even though the B3LYP/3-21G and B3LYP/6-31G* relative energies of C_{82} isomers may differ by as much as 4 kcal/mol (cf. Table 1), C_{82} fragmentation energies are much less sensitive to the choice of basis set, most likely due to a cancellation of similar errors for C_{82} and C_{80} species. Therefore, the choice of the 3-21G basis set is well justified as a compromise between accuracy and efficiency for the present calculations.

The corrected values of $D(C_{82})$, together with known experimental values of $D(C_{82}{}^{+})$, which have been re-normalized to the most reliable experimental $D(C_{60}{}^{+})$ value of 10 eV [9,12], are collected in Table 5. Inspection of the data in Table 5 reveals that the $D(C_{82}{}^{+})$ value of Barran et al. [5] is in exact agreement with the calculated value of the fragmentation energy of the most stable C_2(**3**) isomer via SW transformation, while other experimental values are signifi-

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[1] Based on calculations of the energy and gradient of a given C_{82} structure on an Intel Pentium IV 2.0 GHz computer (the B3LYP/3-21G calculation takes 4 h, and the B3LYP/6-31G* over 24 h).

cantly lower. This may suggest that the other isomers, which have lower fragmentation energies closer to experimental values, are present in sufficient amounts in experimental samples and, as a result, bring down the measured fragmentation energies. We note that the re-normalized $D(C_{80}^{+})$ value reported in the same work by Barran et al. [5] (8.8 eV) also agrees very well with the results of our previous calculations for the fragmentation energy of C_{80} (8.7–9.0 eV) [31].

5. Conclusions

We have performed semi-empirical, ab initio and DFT calculations for the possible fragmentation pathways of the most stable C_2(**3**) isomer of C_{82} via Stone-Wales transformation and via the formation of seven-membered-ring isomers, together with those for the other C_2 and C_s IPR isomers of C_{82} via SW transformation. With our most reliable B3LYP/3-21G model chemistry, the calculated fragmentation energy values were found to be higher by more than 1.5 eV than the experimentally obtained ones. Inclusion of an empirical correction, to compensate for the poor description of the C_2 fragment by single-reference methods leads to values of 9.1 and 9.4 eV for the fragmentation of the most stable C_2(**3**) isomer of C_{82} via Stone-Wales transformation and with the seven-membered-ring isomer formation, respectively. The fragmentation pathway via Stone-Wales rearrangement is thus more favorable than that via seven-membered-ring isomer formation by 0.3 eV. However, the corrected fragmentation energies of the C_2(**3**) isomer are still almost 1 eV larger than the recent experimental $D(C_{82}^{+})$ values (8.2–8.6 eV) [5,14–16,30], even though they agree perfectly with the earlier experimental result of Barran et al. (9.1 eV) [5]. Other, less stable, C_{82} IPR isomers were found to have lower corrected fragmentation energies (8.4–8.9 eV), which are much closer to the recent experimental values [14–16]. This suggests that the experimentally determined $D(C_{82})$ may correspond to other IPR isomers than the lowest-energy C_2(**3**) isomer, with lower fragmentation energies. Our calculations of $D(C_{80})$ and $D(C_{82})$ are not only in perfect agreement with the experimental results of Barran et al. [5], but also support their finding that $D(C_{82})$ value is larger than $D(C_{80})$, suggesting that C_{80} is not more stable than its fullerene neighbors.

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