

# Quantum Chemical AM1 Study of Growth Mechanisms of Fullerenes: A Facile C<sub>2</sub> Insertion Technique

Ying-Ting Lin, Rama K. Mishra,<sup>†</sup> and Shyi-Long Lee\*

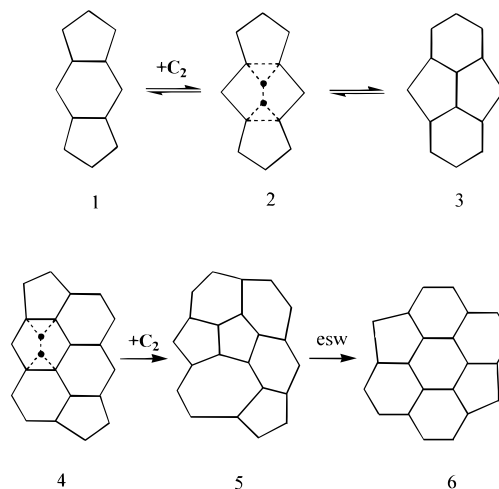
Department of Chemistry, National Chung-Cheng University, Ming-Hsiung, Chia-Yi 62117, Taiwan

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Insertion of a C<sub>2</sub> molecule (fragment) into the cavity of a hexagonal belt containing 10 hexagons generates a honeycomb lattice (C<sub>42</sub>H<sub>16</sub>) and two hydrocarbons containing one and two pairs of {7,5} ring pairs. The vibrational frequency analysis reveals that the hydrocarbon having only one {7,5} ring pair behaves as a transition-state-like structure. The generation of the hydrocarbon containing two {7,5} ring pairs appears to be an innate process compared with the honeycomb lattice when the C<sub>2</sub> fragment is inserted into the vacant space of the hexagonal belt. A very small amount of excitation energy (0.0108 kcal/mol) is required for the annihilation of a {7,5} ring pair to a {6,5} ring pair. Considering two common frames, the motion of the {7,5} and {6,5} ring pairs are studied. The motion of these ring pairs are found to be so natural that there is an insignificant change in the property-like second-order hyperpolarizability ( $\langle\gamma\rangle$ ).

The topological defect consisting of a five- and a seven-membered ring pair in a honeycomb lattice has been proposed in order to study the growth process of stable fullerenes and the crystal growth of the graphene tubules.<sup>1</sup> In the past decade there has been a record number of scientific investigations relating to a family of carbon materials possessing sp<sup>2</sup> covalently bonded carbon atoms such as fullerenes, graphene tubules, and related carbon structures.<sup>2</sup> Kroto et al.<sup>3</sup> and Wakabayashi et al.<sup>4</sup> have suggested that the stable structure of fullerenes consists of 12 pentagonal rings and  $(N - 20)/2$  hexagonal rings, where  $N$  = number of vertexes, which finally form a cage structure. The most important aspect regarding the fullerene formation mechanism has not yet been fully understood. A number of papers report on various experimental and theoretical efforts to penetrate into the subject.<sup>7–17</sup> It has been suggested that the large fullerenes might be obtained by a growth mechanism from a smaller one by absorbing a C<sub>2</sub> molecule (fragment).<sup>1</sup> Also, it is interesting to note that a reverse C<sub>2</sub> elimination mechanism has been proposed by Endo and Kroto<sup>5</sup> (based on the proposition of O' Brien et al.<sup>6</sup>) to account for the degradation mechanism of fullerenes. It is well-known that every fullerene possesses at least three Kekule structures and can be assembled from C<sub>2</sub> fragments only.<sup>18</sup> The experimental study of Wakisaka et al.<sup>19</sup> confirms the formation of C<sub>2</sub> by laser vaporization of graphite. Ōsawa et al.<sup>20</sup> have proposed a mechanism (Scheme 1) to depict the addition of a C<sub>2</sub> fragment (molecule) to a hexagonal ring and termed it a (2 + 2 + 2 + 2) Woodward–Hoffman thermally forbidden reaction. In this insertion mechanism one additional hexagonal ring and a pentalene unit have been produced. Further, they have pointed out that if intermediate **2** is not stabilized, then there is a chance of losing the inserted C<sub>2</sub>. Hence, according to the suggestion of Endo and Kroto,<sup>5</sup> if one of the pentagonal rings in **1** is one 6-ring away, then a C<sub>2</sub> insertion is possible with an intermediate **5** that finally undergoes an extended Stone–Wales<sup>21</sup> rearrangement (eSW) to produce a

SCHEME 1



stable hexagon-rich structure **6**. Ōsawa et al. have further assumed that though C<sub>2</sub> insertion may be taking place randomly on every hexagonal ring of the clusters, only those cases where eSW rearrangements are possible could survive. This complicated bond-changing mechanism appearing in fullerenes and related structures has been proposed by Saito et al.<sup>1</sup> on a qualitative basis by calling it topological defects in a honeycomb lattice. To study the creation and annihilation of a {7,5} ring pair along with their motion in a honeycomb lattice, a simplified vertex addition–deletion technique has been given.<sup>1</sup> The interchange technique could be represented as

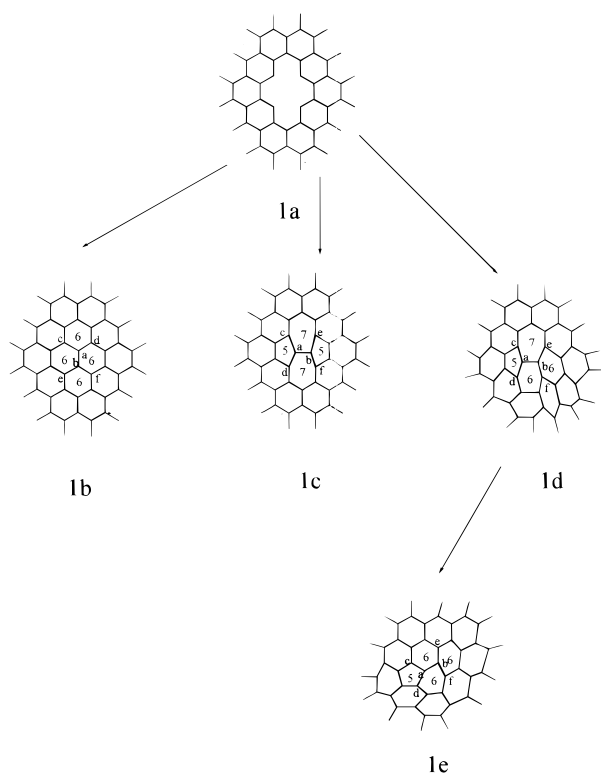
$$\{v_1, v_2, v_3, v_4\} \rightarrow \{v_1 + 1, v_2 - 1, v_3 + 1, v_4 - 1\}$$

where,  $v_1$ ,  $v_2$ ,  $v_3$ , and  $v_4$  are the number of vertexes in each ring.

Here, in this work, we have made a quantum chemical (AM1) study of the creation–annihilation of a {7,5} ring pair along with the motion of this pair in a common framework. Further, the motion of a more realistic {6,5} pair has also been studied.

\* To whom correspondence should be addressed. E-mail: chesll@ccunix.ccu.edu.tw.

<sup>†</sup> On leave from Department of Chemistry, Sambalpur University, Jyoti-Vihar 768 019, India.

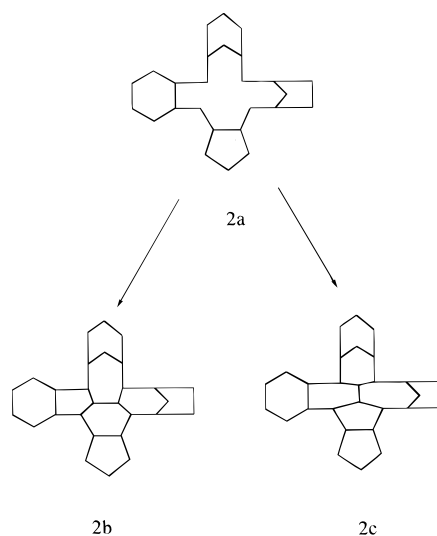


**Figure 1.** **1a** is the hexagonal belt. **1b**, **1c**, and **1d** are the products of C<sub>2</sub> insertion, and **1e** is the annihilation product from **1d**.

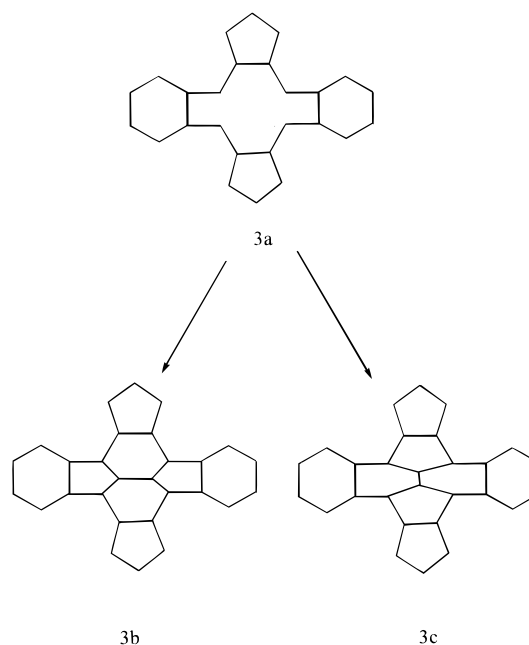
We have also made an attempt to study the static third-order polarizability ( $\gamma$ ) of the systems in which {7,5} and {6,5} ring pairs are changing their positions. It is well-known that  $\langle\gamma\rangle$  does depend on conjugation to a large extent,<sup>22,23</sup> and hence, when the positions of the ring pairs are changed, the conjugation pattern is effected and thereby may influence  $\langle\gamma\rangle$  values.

### Materials and Methods

To study the honeycomb lattice, one and two {7,5} defect pair rings, **1b**, **1c**, and **1d** structures, are chosen and for the annihilation of the {7,5} pair to the {6,5} pair, structure **1e** is taken into consideration (Figure 1). It may be mentioned that a common frame for the study of the creation of one and two {7,5} defect pair rings has been constructed, which happens to be a belt of 10 hexagonal rings (**1a**). In fact, this type of spiral growth in an epitaxial manner for fullerenes has already been suggested earlier.<sup>3,6</sup> Inserting the C<sub>2</sub> fragment in the middle of the belt vertically and horizontally and making appropriate connections with the C<sub>2</sub> molecule, one gets **1b**, **1c**, and **1d** structures. To study the motion of the {7,5} and {6,5} pairs in the lattice, we have considered again common frames for different defective ring pairs. Then, by placing C<sub>2</sub> vertically and making appropriate connections with the carbon frames, we obtained a particular defect pair and its analogous pair depicting the motion can be obtained by placing the C<sub>2</sub> fragment horizontally in the common frames and making the required connections (Figures 2 and 3). While studying this type of interchange mechanism, Saito et al.<sup>1</sup> have considered the local movements of the rings in the lattice. This consideration seems to be logical, since the study of the creation and annihilation of a {7,5} pair needs only two adjacent hexagonal rings centrally located in the honeycomb lattice. But to study the motion of the pair, one needs to consider four adjacent hexagons. The other important aspect of the Saito et al. work is the involvement of the atoms (vertexes) of the inner hexagons of the honeycomb



**Figure 2.** Motion of a {7,5} defect pair in a common frame.



**Figure 3.** Motion of a {6,5} defect pair in a common frame.

lattice. So, to study the motion of the defect pairs we have considered the carbon skeleton of the molecules rather than the true molecules having C–H bonds. It may further be mentioned that in the proposed ad hoc common frames we have kept two five- and six-membered rings. The two five- and six-membered rings are so arranged that after the motion of a {7,5} or a {6,5} pair the changes in the molecules can easily be detected.

### Semiempirical Calculations

All the calculations are performed by using the standard AM1 Hamiltonian implemented within the MOPAC93 program.<sup>25</sup> Molecular geometries are completely optimized by employing BFGS algorithm.<sup>26</sup> In fact, we started our calculation with one initial geometry, considering all the molecules to be having closed-shell singlets and setting the SCF convergence criteria to be 10<sup>−24</sup>. We further mention that while studying the motion of the defect pairs, we have considered only the carbon skeletons without the C–H bonds. Bakowies et al.<sup>27</sup> have correctly pointed out that in such cases the closed-shell SCF calculations often have problems of nonconvergence or convergence with a

**TABLE 1: Heat of Formation ( $\Delta H_f$  in kcal/mol), Excitation Energy ( $\Delta H_k$  in kcal/mol), HOMO–LUMO Gap ( $\Delta E_g$  in eV), Dipole Moment ( $D$  in debye), and Vibrational Frequencies ( $\nu$ ) in  $\text{cm}^{-1}$  of Structures **1a–e****

structure	$\Delta H_f$	$\Delta H_k$	$\Delta E_g$	$D$	$\nu_{\max}$	$\nu_{\min}$	negative $\nu$
<b>1a</b> ( $\text{C}_{40}\text{H}_{16}$ )	432.0659	2.4592	6.6089	0.1570	3208.74	14.70	−16.50
<b>1b</b> ( $\text{C}_{42}\text{H}_{16}$ )	177.7794	0.9662	5.5620	0.0100	3188.18	42.60	
<b>1c</b> ( $\text{C}_{42}\text{H}_{16}$ )	276.8480	1.5046	5.9228	0.5020	3203.69	40.10	
<b>1d</b> ( $\text{C}_{42}\text{H}_{16}$ )	283.4997	1.5408	5.5763	2.6170	3199.86	40.10	−46.80
<b>1e</b> ( $\text{C}_{38}\text{H}_{14}$ )	253.9240	1.5300	6.0774	4.6330	3187.22	68.60	

reduction in symmetry. The lowering of symmetry does lead to a distortion from the topological symmetry, a deviation in the bond lengths, and HOMO–LUMO (H–L) gaps. But since the systems are considered to be in floppy state during the formation of the defect pairs,<sup>4</sup> one can rationalize the deviations in the bond lengths and the H–L gaps. The Hessian matrix, which happens to be the second derivative of the energy with respect to geometry, has been created, and on diagonalization, this gives the force constants of the relevant molecule. The force matrix, weighted for isotropic masses, has been used for the calculations of the vibrational frequencies. Further, the Hessian is quite sensitive to geometry and is to be evaluated at stationary points. Before the construction of the force matrix, the gradients are evaluated to ensure that the geometry has minimum energy at stationary points. The gradient norms are fixed at the default value, i.e., 1.0. It is well-known that the relationship between the molecular structures and the magnitude of the nonlinear optical (NLO) responses happen to be an interesting area of investigation for the conjugated organic materials. Here, in this work, we have used the time-dependent Hartree–Fock (TDHF) method<sup>28</sup> to calculate the molecular polarizabilities and hyperpolarizabilities. While trying to identify the motion of the {7,5} or {6,5} pair in a common frame, we have noticed that identical geometrical configurations are obtained if a honeycomb lattice framework is considered. Hence, for the motion of a {7,5} pair and a {6,5} pair two carbon frames are proposed and shown in Figures 2a and 3a, respectively. Assuming that the configuration of the system should not change significantly during the motion of the defect pair, calculations of the change in  $\langle\gamma\rangle$  are also performed.

## Results and Discussion

This study consists of two different parts. In the first part, we present the results of the creation and annihilation of the defect pairs from a hexagonal belt, and second, we present the motion of the {7,5} and {6,5} defect pairs in the common frames.

**Creation and Annihilation of the Defect Pairs.** To study the creation–annihilation of the defect pair rings, we have considered frame **1a** (Figure 1), where 10 hexagons are arranged in belt form in order to have a vacant space surrounded by 14 carbon centers. There are only four carbon centers that are connected to two adjacent carbon centers and possess C–H bonds. To create the vacant space, we have neglected these four C–H bonds, and  $\text{C}_2$  is inserted comfortably into the vacant space. Now, placing  $\text{C}_2$  horizontally or vertically and making appropriate connectivities, we have created **1b–d** molecules. Making use of the semiempirical AM1 method, we have calculated the heat of formation ( $\Delta H_f$ ), the HOMO–LUMO gap ( $\Delta E_g$ ), dipole moment ( $D$ ), and vibrational frequencies ( $\nu$ ) of the above molecules. In all the molecules (**1a–d**) 16 C–H bonds are present at the periphery. We further mention that in **1d**, the 16 C–H bonds at the periphery are rearranged so that a {7,5} ring pair can be created. Owing to this kind of rearrangement, two adjacent hexagons have two C–H bonds at the periphery. It is well-known that the isolated atoms and the valence electrons

of all the atoms contribute toward the  $\Delta H_f$  values. Since carbon and hydrogen are two different types of atoms present in the hydrocarbons, it is difficult to have a quantity like  $(\Delta H_f/n)$ , where  $n$  refers to the number of atoms. This quantity gives the stability of the carbon clusters having no C–H bonds. So, to have an analogous term, we have divided the  $\Delta H_f$  by the number of valence electrons ( $k$ ) and call it  $\Delta H_k$ . We have used this quantity to judge the excitation energy of the molecules. Moreover, in the process of creation–annihilation of the different rings, valence electrons are playing a crucial role in bond-making and bond-breaking processes, and hence, a term like  $\Delta H_k$  is necessary in order to judge the mechanism very clearly. Table 1 depicts  $\Delta H_f$ ,  $\Delta H_k$ ,  $\Delta E_g$ ,  $D$ ,  $\nu_{\max}$ , and  $\nu_{\min}$  values of all the molecules (**1a–d**).

When the computed results of **1a–d** are analyzed, it is found that **1a** possesses a maximal  $\Delta H_k$  (2.4592 kcal/mol) and a maximal  $\Delta E_g$ , but interestingly, it possesses only one negative force constant, which refers to a transition state. Hence, **1a** can be viewed as a stable intermediate having a large  $\Delta E_g$ . As expected, the honeycomb lattice (**1b** containing 42 carbon atoms and 16 hydrogen atoms at the periphery) possesses the minimum  $\Delta H_f$  and  $\Delta H_k$  and has all positive vibrational frequencies in the range 42.6–3188.18  $\text{cm}^{-1}$ . However, the difference in the  $\Delta H_k$  between **1a** and **1b** might be more indicative for our purpose. When we compared the  $\Delta H_k$  of **1a–d**, we noticed an interesting feature in the case of the honeycomb and the other hydrocarbons having defect pair rings. The molecule **1d** possessing one {7,5} defect pair ring can be formed from **1a** by an excitation energy equal to 0.9184 kcal/mol (difference in  $\Delta H_k$  values between **1a** and **1d**). Characterizing the vibrational spectrum of **1d**, one obtains again only one negative frequency, suggesting this to be a transition-state-like structure. In fact, Saito et al.<sup>1</sup> have pointed out through their vertex addition–deletion technique the difficulty in the formation of a single {7,5} defect pair, since it requires a global chemical bond transformation in the process. So our quantum chemical study also suggests that **1d** is a transition-state-like structure. The structure **1c** possessing two {7,5} defect pairs appears to be a more easily formed molecule, since it requires only 0.0362 kcal/mol extra energy from the structure possessing one {7,5} defect pair. Further, **1c** possesses all positive vibrational frequencies in the range 40.1–3203.69  $\text{cm}^{-1}$ . Again,  $\Delta E_g$  is also increased from **1d** by an amount of 0.3465 eV. It is interesting to note that  $\Delta E_g$  is highest in **1c**, when one compares **1b–d**. Hence, we can say that **1c** is the more easily formed structure than **1b**. Further, the excitation energy difference between **1a** and **1b** is maximum. Therefore, if a belt of 10 hexagonal rings possessing a cavity is considered and a  $\text{C}_2$  is inserted into the cavity, then the so-called defect appears to be a natural creation (compared with the honeycomb lattice), which eventually helps in the formation of higher fullerenes. While considering the annihilation of a {7,5} pair to a {6,5} pair (**1e**), only a very small amount of excitation energy equal to 0.0108 kcal/mol (difference in the  $\Delta H_k$  values between **1d** and **1e**) is required. Further, **1e** possesses all positive frequencies in the range 68.6–3187.22  $\text{cm}^{-1}$ . The  $\Delta E_g$  value of **1e** is the highest in the series, suggesting a greater stability

**TABLE 2: Geometrical Data of the Structures 1b–e<sup>a</sup>**

structure	a–b	a–c	a–d	b–e	b–f	$T_1$	$T_2$
<b>1b</b>	1.399	1.433	1.431	1.431	1.432	0.0	0.0
<b>1c</b>	1.332	1.471	1.496	1.472	1.466	6.3	6.4
<b>1d</b>	1.382 (1.386 <sup>b</sup> )	1.464 (1.463 <sup>c</sup> )	1.465	1.453	1.443	8.0	24.4
<b>1e</b>	1.376 (1.386 <sup>b</sup> )	1.439 (1.463 <sup>c</sup> )	1.439	1.445	1.444	29.3	29.2

<sup>a</sup> Bond lengths are in angstroms and bond angles are in degrees.<sup>b</sup> Reference 30. <sup>c</sup> Reference 30.

of the structure. On the basis of the examination of the of the excitation energy involved in the series, it is concluded that the creation of a {7,5} pair and the annihilation of it to a lower {6,5} pair is an innate process in the formation of the higher fullerenes. Further, in the proposed mechanism, the annihilation of {7,5} to a {6,5} pair is consistent with the C<sub>2</sub> fragmentation process,<sup>6,29</sup> since two C<sub>2</sub> fragments with two hydrogens are lost during the transformation.

To have a detailed understanding of the systems under consideration, we have made an analysis of the completely optimized geometries of the different molecules. Primarily, we are concerned here with the study of the C<sub>2</sub> insertion mechanism, and hence, only the portion of the geometry where the inserted C<sub>2</sub> is involved has been considered. Let a–b represent the length of the inserted C<sub>2</sub>; a–c and a–d are two incident bonds of the atom a. Similarly b–e and b–f are the two incident bonds of the atom b.  $T_1$  and  $T_2$  are the two torsional angles measured in two different ways involving C<sub>2</sub>. All these data are given in Table 2. It is observed that the a–b bond acquires the bond length of a resonating bond (1.39 Å) in the case of **1b**, while in **1c** it behaves as a double bond (1.34 Å). But interestingly in the case of **1d** and **1e**, it is very close to the  $r_{6-6}$  bond length of C<sub>60</sub> (fullerene) obtained through AM1 calculations.<sup>30</sup> Another important observation is that the a–c and a–d bond lengths of **1d** and **1e** closely resemble the  $r_{5-6}$  bond length of C<sub>60</sub> (fullerene<sup>30</sup>). Analyzing the bond angles around the two terminals of C<sub>2</sub>, one can notice that the planarity decreases from **1b** to **1e**. The two torsion angles ( $T_1$  and  $T_2$ ) reveal the strain accumulated in the structures in a qualitative way. In the case of **1d** the  $T_1$  and  $T_2$  differ to a great extent, and this is due to the involvement of different kinds of rings in the measurement of  $T_1$  and  $T_2$ . Further, when we try to compare the strain in C<sub>60</sub> by selecting a portion containing {6,6,6,5} rings, we obtained the torsion angle to be 37.5°. The torsion angle of **1e** is found to be 29.3° and could be thought to approach that of C<sub>60</sub> (fullerene) when the growth process would be complete.

**Motion of {7,5} and {6,5} Ring Pairs.** Saito et al.<sup>1</sup> have considered only the core hexagons of the honeycomb lattice (C<sub>42</sub>H<sub>16</sub>) for the motion of the {7,5} and {6,5} ring pairs. Further, they have mentioned that in the vertex addition–deletion technique only the carbon–carbon bonds are considered without any dangling bond. So, here in this work, we have also considered the carbon skeleton without hydrogen atoms (hy-

drogen-suppressed molecules<sup>24</sup>). To study the movement of a {7,5} or a {6,5} pair, we need to consider four adjacent rings. If a honeycomb lattice is considered, then the motion of the ring pairs is not properly judged owing to the identical situation observed after the motion of the relevant ring pairs. Further, the calculation of a property like  $\langle\gamma\rangle$  has become difficult to evaluate for the honeycomb lattice because of computational limitations. Hence, to judge the movement of the defect pair, we have considered a common frame consisting of two hexagons and two pentagons at the periphery and having a vacant space in the middle surrounded by 14 carbon centers. Figures 2 and 3 depict the common frames in which the movements of the {7,5} and {6,5} pairs are judged. When a particular ring pair changes its position, then both of the relevant rings of the pair find different adjacent rings attached to them. The change in the energy is then computed to estimate the effect caused by the motion of that ring pair. Further, we mention that intentionally we have considered two hexagons and two pentagons at the periphery of the frames, and after the motion of the said pair one of the structures (**2c** and **3c**) possesses adjacent pentagons (pentalene unit). It is well-known that the presence of a pentalene unit creates many problems in the fullerene formation and violates the IPR rule,<sup>31</sup> though there are reports on anti-IPR concepts in the literature of fullerene formation.<sup>32–34</sup> Here, our sole aim is to show the motion of the ring pair and what it could cause to the system, but not to broach on IPR rule. To judge the effect of the motion more accurately, we have tried to create a pentalene unit that is known to be strained<sup>35</sup> and antiaromatic<sup>36</sup> and to have a negative second-order hyperpolarizability in the anion radical state.<sup>37</sup> After the motion of the defect pairs, the pentagon of the defective pair finds another pentagon at the periphery and results in the formation of a pentalene unit (**2c** and **3c** of Figures 2 and 3, respectively). If the motions of these pairs are not natural, then at least we hope to have a dramatic change in the energy and other properties due to the presence of the pentalene unit. Table 3 depicts the point group,  $\Delta H_f$ ,  $\Delta H_f/n$ ,  $\Delta E_g$ ,  $D$ ,  $\nu_{\max}$ ,  $\nu_{\min}$ , and  $\langle\gamma\rangle$  values for all the above systems. In an analysis of Table 3, it is observed that when a C<sub>2</sub> fragment is placed suitably and when proper connections are made, then the two structures depicting the motion of the pair are obtained and the stability of these two structures is increased compared with the stability of the common frames. It is interesting that only 0.3707 kcal/mol of energy per carbon center is required for the movement of a {7,5} pair and 0.1561 kcal/mol amount of energy per carbon center is necessary for the motion of a {6,5} pair. Hence, the motion of a {7,5} or a {6,5} pair is an innate process in fullerenes. Moreover, when we try to judge the change of a more involved property like  $\langle\gamma\rangle$ , there is a slight difference in **2b** and **2c**, and in **3b** and **3c** it is almost negligible. Hence, even if, the pentalene moiety is present in **2c** and **3c**, the motion is so natural that the changes in the properties are very close to each other. The vibrational frequency analysis suggests that all these hydrogen-

**TABLE 3: Data Obtained for 2a–c and 3a–c Structures through AM1 and TDHF Calculations**

structure	point group <sup>a</sup>	$\Delta H_f$	$\Delta H_f/n$	$\Delta E_g$	$D$	$\nu_{\max}$	$\nu_{\min}$	$\langle\gamma\rangle$
<b>2a</b>	C <sub>1</sub> /C <sub>1</sub>	1350.1983	51.93	5.577	0.441	2059.48	50.12	61.336
<b>2b</b>	C <sub>1</sub> /C <sub>1</sub>	1379.1675	49.26	5.880	3.573	1988.72	69.03	76.702
<b>2c</b>	C <sub>1</sub> /C <sub>1</sub>	1389.5499	49.63	5.996	3.512	2079.10	41.30	71.686
<b>3a</b>	C <sub>1</sub> /C <sub>1</sub>	1319.4569	50.75	6.500	0.071	2241.34	45.10	60.892
<b>3b</b>	C <sub>2v</sub> /C <sub>2h</sub>	1186.2134	42.36	7.132	0.013	1996.20	50.01	57.381
<b>3c</b>	C <sub>2v</sub> /C <sub>s</sub>	1218.5831	42.53	6.224	1.216	2050.86	32.90	59.346

<sup>a</sup> The first entry refers to the topological point group, and the other one is found in the geometry optimization.  $\Delta H_f$  and  $\Delta H_f/n$  are in kcal/mol,  $\Delta E_g$  is in eV,  $D$  is in debye,  $\nu(\max, \min)$  are in cm<sup>−1</sup>, and  $\langle\gamma\rangle$  is in 10<sup>−36</sup> esu.



depleted molecules have positive frequencies, and hence,  $\Delta H_f$  values are acceptable. Further, during the course of the geometry optimization the symmetries are not lowered, and hence, the topologies are not distorted.

## Conclusions

1. Considering a hexagonal belt having 10 hexagons, a honeycomb lattice and two other hydrocarbons consisting of one and two {7,5} ring pairs are generated by inserting a C<sub>2</sub> fragment into the cavity of the hexagonal belt. It is observed that the hydrocarbons possessing {7,5} and {6,5} ring pairs are generated more easily than the honeycomb lattice itself.

2. The motion of the so-called defect pair rings observed in the formation of the higher fullerene appears to be an innate process inside the carbon cages.

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