

Nonplanar Distortions and Strain Energies of Polycyclic Aromatic Hydrocarbons

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Received: August 15, 2005; In Final Form: October 12, 2005

On the basis of HF/6-31G(d) optimized structures, the nonplanar distortions of 135 polycyclic aromatic hydrocarbons (PAHs) have been classified as splitting (S-) and arching (A-) distortions. Three bay structures are proposed as the structural origin of S-distortion. Due to the limitation of sample molecules, a set of universal motifs for molecules containing A-distortions is not available; however, a set of motifs and parameters are developed for the semiquantitative estimation of the nonplanar strain energies of PAHs containing the corannulene structure, and the differences between the E_{np} values from quantum calculations and those from these estimations vary from -5.60 to 5.51 kcal/mol. The above results are fundamentally important for the understanding of nonplanar distortion of PAHs and fullerenes, and this method can also be employed to semiquantitatively estimate strain energies of such molecules containing hundreds of carbon atoms.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have structures similar to fullerenes. For instance, half-buckminsterfullerene (HB) $C_{30}H_{10}$ is a perfect half of C_{60} when the terminating hydrogen atoms are taken away. Hence, the investigation of PAHs is fundamental to the understanding of the stability and formation of fullerenes.^{1,2} It is believed that a predictive capability for the formation and growth of PAHs is highly desirable, to steer PAH chemistry toward the generation of fullerenes and other desirable carbon nanostructures.² One of the unique characteristics of fullerenes is their nonplanar distortions, which introduces remarkable strain energies.^{3–5} For instance, in a previous study of C_{60} , the total strain energy (E_s) was estimated to be approximately 100% of its heat of formation³ and E_s due to nonplanar distortion was estimated to be 78% of the excess energy of the carbon atoms relative to that in graphite.⁵ Moreover, the release of strain energies often relates to some special reactions and the atoms with strong strain energies are the active sites.^{5–7} For example, an unusual behavior has been observed for $C_{30}H_{12}$, whose reaction with $Pt(C_2H_4)(PPh_3)_2$ does not result in simple η^2 coordination of a $Pt(PPh_3)_2$ unit; rather, it accomplishes an insertion of the platinum into one of the C–C bonds on the edge of the hydrocarbon.^{7,8} Such unusual C–C bond breaking has been attributed to the release of the strain energy present in five-membered rings (5-MRs) at the edge of this hydrocarbon.⁷ Hence, the understanding of the strain energy and nonplanar distortions in PAHs is of great importance for insight into the stability, formation, and chemical activity of PAHs and fullerenes.

In the present work, the strain energies of 135 PAHs, including 41 PAHs containing only six-membered rings (6-MRs) and 94 PAHs containing 5-MRs were calculated based on HF/6-31G(d) optimized structures.² Two types of nonplanar distortions, splitting and arching, are proposed and correlated to basic

motifs in these PAHs. A set of motifs and parameters has been developed for the quantitative estimation of the nonplanar strain energies of PAHs containing the corannulene structure with errors limited to only 5.60 kcal/mol.

2. Modeling and Methods

Previously, 135 PAHs were optimized at the level of HF/6-31G(d).² In this work, these molecules were uniquely and sequentially numbered and were also listed in Table 1 as SIX- n or FIVE- n , where n is a number given for each molecule.² For convenience of comparison and expression, the same notation for the PAHs was taken in this work. To check the calculation of the strain energies, C_{60} and C_{70} were also studied as reference molecules in the present work.⁹ To rule out the possibility of calculation errors for several molecules, confirmation of planarity and nonplanarity has been carried out for several molecules using the Gaussian 03 suite of programs.¹⁰

Normally, strain energies are defined relative to some standard structure, such as graphite for carbon structures.^{3,4} When some structural parameters deviate from the standard values, strain energies are introduced, which can be defined based on the types of structural distortions, such as E_{np} and E_{ba} , for strain energies due to nonplanar distortions and bond-angle bending away from the sp^2 ideal, respectively, which have been identified as two major sources of destabilization in a study of large carbon clusters.⁴ Basically, various strain energy terms are calculated based on a force field. For aromatic hydrocarbons, the set of force constants developed by Cyvin et al.¹¹ has been widely and successfully used for fullerenes^{3–5,12} and carbon nanotubes.¹³ Following Cyvin et al.,^{11,12} $E_{np} = \sum 1/2k(D\gamma)^2$, where the sum is over vertexes, k and D are the force constant and the bond length, respectively, and γ denotes the deflection, $\gamma = -3 \sin(\theta_{\sigma\pi} - 1/2\pi)$, with the assumption that the circumstances of equivalent hybrids to each of the three neighboring sites,³ where $\theta_{\sigma\pi}$ is the common angle made by the π -orbital axis vector and the σ -bond based on the theory of the π -orbital axis vector (POAV),¹⁴ which can provide a very logical and natural

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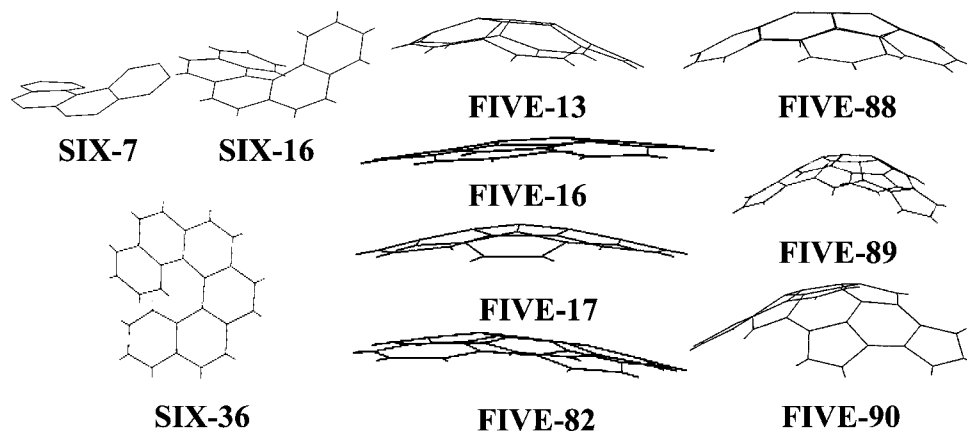


Figure 1. 3-D structures of 10 PAHs. SIX-7, SIX-16, and SIX-36 present splitting distortions, and FIVE-13, FIVE-16, FIVE-17, FIVE-82, FIVE-88, FIVE-89, and FIVE-90 present arching distortions.

bridge between σ - π separability assumed in planar conjugated systems and the realistic condition of π -bonding in nonplanar geometries.¹⁵ For small deflection angles, the expression of E_{np} can be simplified to $E_{np} = 9/2kD^2 \sum (\theta_{\sigma\pi} - 1/2\pi)^2$. In the present work, only the strain energies due to nonplanar distortion are of interest. Following Haddon,⁵ for fullerenes, E_{np} can be further simplified with approximate hybridization conservation as

$$E_{np} = \eta \times \sum \frac{m}{m+1} \quad (1)$$

where $\eta = 100$ kcal/mol, and $m = (2 \sin^2(\theta_{\sigma\pi} - \pi/2))/(1 - 3 \sin^2(\theta_{\sigma\pi} - \pi/2))$ in the POAV1 approximation.^{14,16} The parameter $\theta_{\sigma\pi}$ can be calculated directly from the atomic coordinates. In eq 1, $m/(m+1)$ denotes the fractional hybridization of the atomic π -orbitals ($s^m p$) based on the POAV theory.^{12,14-16} The POAV analysis in the present work was carried out using the POAV package provided by Prof. R. C. Haddon. Although the values of E_{np} for C_{60} and C_{70} calculated from eq 1 are consistent with those from the original force field,⁵ it is cautiously pointed out that, as mentioned above, the absolute value of strain energy is normally not of interest and it is also very difficult to calculate very accurately from a force field or its simplified expression. The goal in the present work was to gain insight into the nonplanar distortion of molecules from the relative values of E_{np} , as illustrated in the following analysis.

3. Results and Discussion

3.1. Nonplanar Distortions and Strain Energies. On the basis of the 3-dimensional (3-D) structures of all the molecules investigated here, it was found that 43 of the molecules (9 SIX-*n* series and 34 FIVE-*n* series) were nonplanar. Figure 1 shows 10 of these nonplanar molecules as examples. From Figure 1, SIX-7, SIX-16, and SIX-36 split from one plane of the starting structure into two planes; while FIVE-13, FIVE-16, FIVE-17, FIVE-82, FIVE-88, FIVE-89, and FIVE-90 exhibit arching distortions, that is, from a plane to a curved surface. The former are referred to as splitting distortions (S-distortions) and the latter as arching distortions (A-distortions). In fact, 19 molecules presented S-distortions and were classified as GROUP I; on the other hand, 24 molecules presented A-distortions and were classified as GROUP II, as listed in Table 1.

To quantitatively describe the nonplanar distortions, strain energies, E_{np} , for 135 PAHs and two reference molecules (C_{60} and C_{70}) were calculated and listed in Table 1. For all molecules with planar 3-D structures, $E_{np} = 0$ kcal/mol, while GROUP I

and GROUP II had values of $E_{np} > 0$ kcal/mol, consistent with their 3-D structures. Moreover, E_{np} varied between 0.03 and 492.58 kcal/mol, indicating that the nonplanar distortion may be attributable to different sources. For GROUP I, the values of E_{np} were very small, ranging from 0.03 kcal/mol to 1.45 kcal/mol. For GROUP II, however, the values of E_{np} covered a wide range, from 1.84 kcal/mol (FIVE-66) to 116.87 kcal/mol (FIVE-92). On the basis of the values of E_{np} , it can be seen that, nonplanar strain energies due to S-distortion were much smaller than those due to A-distortions. Hence, if the types of nonplanar distortion of PAHs are known, then an approximate estimation of E_{np} can be expected. To do this, it is necessary to understand the origin of nonplanar distortion of PAHs and correlate it with their basic geometries.

3.2. Basic Motifs in GROUP I. The planar structures of the GROUP I molecules are shown in Figure 2. All of these molecules contain bay areas consisting of at least four rings, as shown by gray shading. These bay areas were not found in most molecules with $E_{np} = 0$ kcal/mol, indicating that these bay areas are one possible reason for the nonplanar distortions in GROUP I. To confirm this postulation and further understand the small nonplanar distortion, the individual contributions to the strain energies of SIX-7, SIX-16, and SIX-36 were illustrated in Figure 3. These three molecules were selected since they represented three different possible bay structures with 4, 5, and 6 benzenoid rings, respectively. In Figure 3, the contribution to the strain energy due to nonplanar distortions is expressed in units of 10^{-2} kcal/mol for each carbon atom. The leading contributors are especially highlighted as gray atoms, while the white ones indicate hydrogen atoms. The dotted lines denote the symmetry axis. For SIX-7 and SIX-36, there was no nonplanar distortion for carbon atoms on the symmetry axis, suggesting they are a common axis of two planes. In Figure 3, all atoms are drawn in a plane and the saturated atoms are close enough to form chemical bonds. Hence, if there was no nonplanar distortion, there would be strong repulsive forces between the saturated hydrogen and carbon atoms. This condition is universally common to all bay structures if all of the atoms were to remain in the same plane. Since the bay structures have open breaches, splitting distortion easily results from the repulsive forces between these close and saturated atoms. Hence, this is believed to be the main origin of the S-distortions in the GROUP I molecules.

The above hypothesis can be partly confirmed by a special bay structure, which is shown in Figure 4a. As shown in parts b-g of Figure 4, six molecules contain the bay structure shown in Figure 4a, but only FIVE-66 had a nonzero value of E_{np} (0.03

TABLE 1: Calculated Values of E_{np} for 135 PAHs, in Units of kcal/mol^a

no.	E_{np}	no.	E_{np}	no.	E_{np}	no.	E_{np}	no.	E_{np}
SIX-1	0.00	SIX-29 ^{lb}	0.93	FIVE-16 ^{IIb}	1.95	FIVE-44	0.00	FIVE-72	0.00
SIX-2	0.00	SIX-30	0.00	FIVE-17 ^{II}	8.07	FIVE-45	0.00	FIVE-73 ^I	0.34
SIX-3	0.00	SIX-31	0.00	FIVE-18	0.00	FIVE-46	0.00	FIVE-74 ^I	0.55
SIX-4	0.00	SIX-32	0.00	FIVE-19	0.00	FIVE-47	0.00	FIVE-75 ^{II}	71.83
SIX-5	0.00	SIX-33	0.00	FIVE-20	0.00	FIVE-48	0.00	FIVE-76 ^{II}	70.74
SIX-6	0.00	SIX-34 ^I	0.43	FIVE-21	0.00	FIVE-49	0.00	FIVE-77	0.00
SIX-7 ^I	0.75	SIX-35	0.00	FIVE-22	0.00	FIVE-50	0.00	FIVE-78	0.00
SIX-8	0.00	SIX-36 ^I	1.44	FIVE-23	0.00	FIVE-51	0.00	FIVE-79 ^{II}	40.36
SIX-9	0.00	SIX-37	0.00	FIVE-24	0.00	FIVE-52 ^{II}	57.08	FIVE-80 ^{II}	84.12
SIX-10	0.00	SIX-38	0.00	FIVE-25 ^I	0.52	FIVE-53 ^{II}	57.69	FIVE-81 ^{II}	47.21
SIX-11	0.00	SIX-39	0.00	FIVE-26 ^I	0.72	FIVE-54	0.00	FIVE-82 ^{II}	1.84
SIX-12	0.00	SIX-40	0.00	FIVE-27	0.00	FIVE-55	0.00	FIVE-83 ^{II}	115.49
SIX-13	0.00	SIX-41 ^I	1.45	FIVE-28 ^I	0.25	FIVE-56	0.00	FIVE-84 ^{II}	105.13
SIX-14	0.00	FIVE-1	0.00	FIVE-29	0.00	FIVE-57	0.00	FIVE-85 ^{II}	95.98
SIX-15	0.00	FIVE-2	0.00	FIVE-30	0.00	FIVE-58	0.00	FIVE-86 ^{II}	106.91
SIX-16 ^I	1.39	FIVE-3	0.00	FIVE-31	0.00	FIVE-59	0.00	FIVE-87 ^{II}	67.93
SIX-17	0.00	FIVE-4	0.00	FIVE-32	0.00	FIVE-60	0.00	FIVE-88 ^{II}	69.10
SIX-18 ^I	0.97	FIVE-5	0.00	FIVE-33	0.00	FIVE-61 ^I	0.91	FIVE-89 ^{II}	45.38
SIX-19 ^I	0.77	FIVE-6	0.00	FIVE-34	0.00	FIVE-62	0.00	FIVE-90 ^{II}	31.19
SIX-20 ^I	0.82	FIVE-7	0.00	FIVE-35	0.00	FIVE-63	0.00	FIVE-91 ^{II}	57.44
SIX-21	0.00	FIVE-8	0.00	FIVE-36	0.00	FIVE-64	0.00	FIVE-92 ^{II}	116.87
SIX-22	0.00	FIVE-9	0.00	FIVE-37	0.00	FIVE-65	0.00	FIVE-93 ^{II}	61.62
SIX-23	0.00	FIVE-10	0.00	FIVE-38 ^{II}	41.908	FIVE-66 ^I	0.03	FIVE-94 ^{II}	79.04
SIX-24	0.00	FIVE-11	0.00	FIVE-39	0.00	FIVE-67	0.00	C ₆₀	483.91
SIX-25	0.00	FIVE-12	0.00	FIVE-40	0.00	FIVE-68 ^I	1.41	C ₇₀	492.58
SIX-26	0.00	FIVE-13 ^{II}	24.23	FIVE-41	0.00	FIVE-69 ^I	0.54		
SIX-27	0.00	FIVE-14	0.00	FIVE-42	0.00	FIVE-70	0.00		
SIX-28	0.00	FIVE-15	0.00	FIVE-43	0.00	FIVE-71 ^I	0.25		

^aC₆₀ and C₇₀ are also listed as reference molecules. ^bNote: Superscripts of I and II indicate that the molecule belongs to GROUP I or II as illustrated in text.

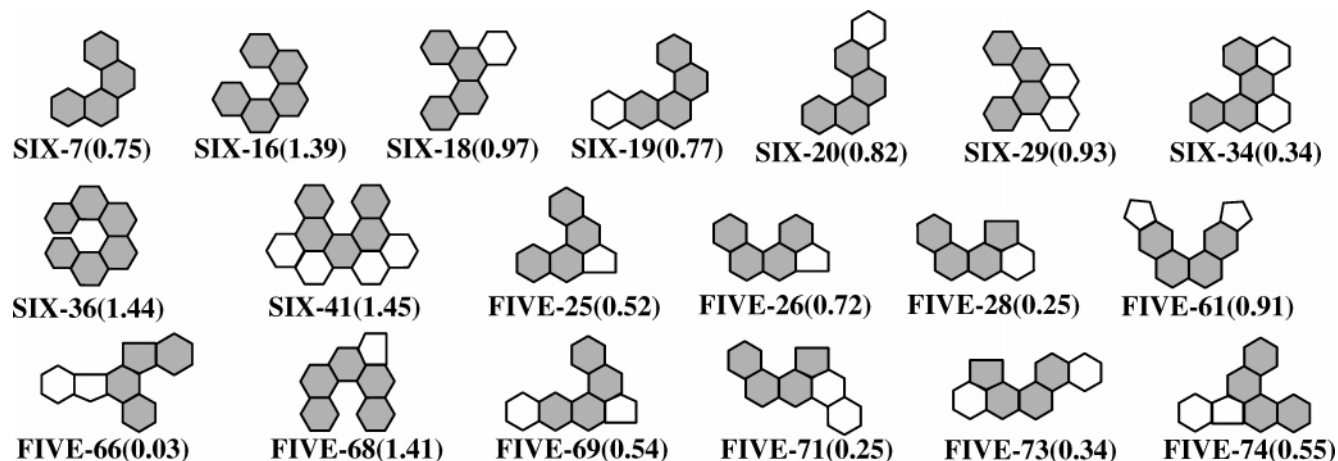


Figure 2. Planar structures of group I. The shaded rings are the basic bay structures. The number in parentheses indicates the value of E_{np} in the units of kcal/mol.

kcal/mol). The planarity of the former five ones was confirmed by a complete optimization without any limitation of symmetry at the level of B3LYP/6-31G(d) even using nonplanar structures as the starting configurations. The same optimization of FIVE-66 was also carried out, and a nonplanar strain energy of $E_{np} = 0.04$ kcal/mol was obtained, which was very small with respect to the strain energies of other molecules in Figure 2. Compared to the bay structure with four rings in Figure 2, there is a 5-MR, but the 5-MR is not at an edge of the bay structure, like that in FIVE-28. Compared with their planar structures, it is found that a 5-MR in the middle of a bay structure can increase the distance between those saturated atoms at the edge. Although FIVE-66 also showed nonplanar distortion, its value of E_{np} was much smaller than those of the other molecules in GROUP I. Similarly, it is noticed that, in GROUP I, FIVE-28, FIVE-71, and FIVE-73 contain bay structures with a 5-MR, and their nonplanar strain energies were much smaller than those of the

other molecules without a 5-MR in the bay structure, suggesting that the 5-MR in this bay structure reduces the nonplanar strain energies due to S-distortions.

3.3. Arching Distortion in GROUP II. For GROUP II, there was no bay structure, and so, no repulsive force between saturated atoms, as suggested for GROUP I. Therefore, there are two logical questions to ask (i) why is there nonplanar distortion, and (ii) how can the nonplanar strain energies be correlated to the molecular geometries? For PAHs, the molecular configuration is basically affected by two factors, strain energy and resonance energy. The strain energies are very difficult to compute and analyze separately, because of the complexity in separating the strain energy from the loss of aromaticity and other effects. Hence, the above questions can only be partially answered from the viewpoint of the strain energies. It is noticed that, among the 24 molecules of GROUP II, 18 contained the corannulene structure, as shown in Figure 5. As illustrated

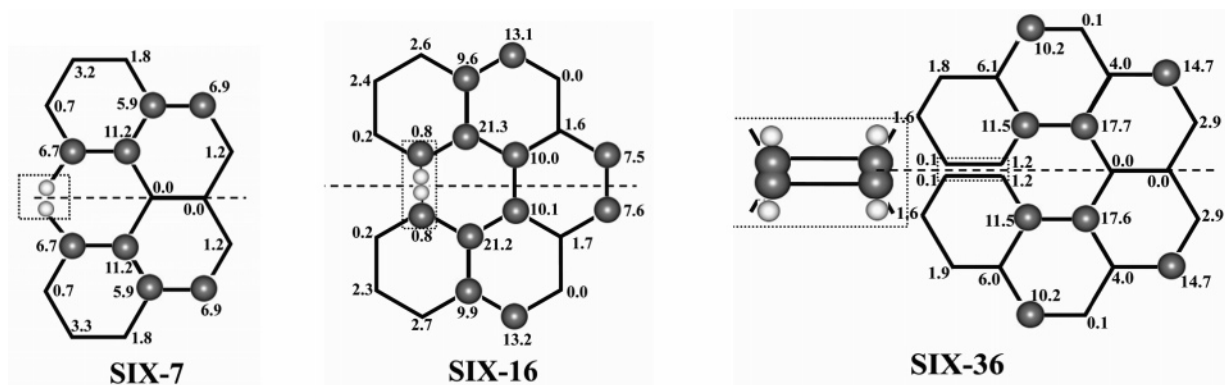


Figure 3. Distribution of nonplanar strain energies. For a better legibility, strain energies are shown in units of 10^{-2} kcal/mol. The gray and white are carbon and hydrogen atoms, respectively.

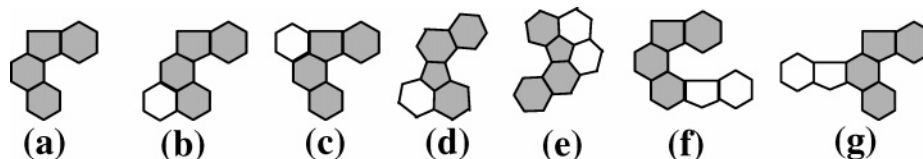


Figure 4. (a) Special bay structure; (b–g) planar structures of FIVE-24, FIVE-34, FIVE-36, FIVE-49, FIVE-63, and FIVE-66. The bay structure is shaded.

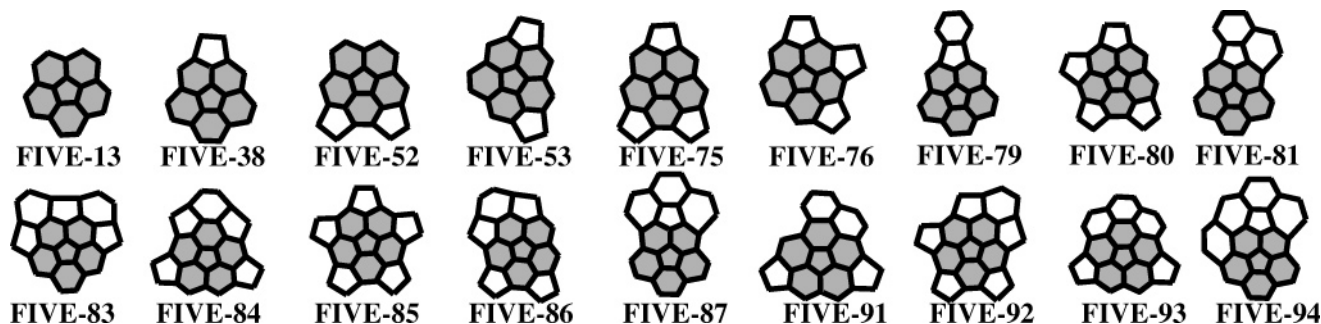


Figure 5. Sketches of the planar structures of molecules containing the corannulene structure, which is shown by the shaded.

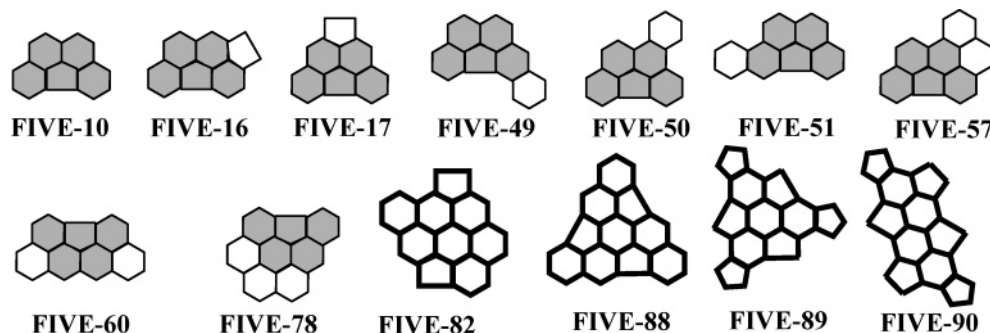


Figure 6. Sketches of the planar structures of molecules containing the corannulene structure, which is shown by the shaded.

above, strain energy results when the structural parameters, such as bond lengths and bond angles, deviate from ideal values. Normally, for carbon clusters and hydrocarbons, the ideal C–C bond length and bond angles of C–C–C or C–C–H take the values of 1.42 Å and $2\pi/3$, using graphite as the relative structure. For the corannulene structure, the central 5-MR is surrounded by five 6-MRs; hence, without substantial deviations in bond length or bond angle, it is impossible to maintain the local atomic surface as in GROUP I. Therefore, arching distortions occur in GROUP II.

Although all of the molecules in GROUP II exhibited arching distortions, the distortions seemed to be induced by different motifs, as can be seen in their structural sketches. For molecules

containing the corannulene structure as shown in Figure 5, there is a remarkable nonplanar distortion, as indicated by E_{np} . For the other ones (FIVE-16, FIVE-17, FIVE-82, FIVE-88, FIVE-89, and FIVE-90, as shown in Figure 6), no basic motif could be recognized due to the limited number of sample molecules. However, some clues for further design of sample molecules were still obtainable. First, except those containing the corannulene structure, all of the other molecules in the group contained at least two 5-MRs. Second, FIVE-16, FIVE-17, FIVE-10, FIVE-49, FIVE-50, FIVE-51, FIVE-57, FIVE-60, and FIVE-78 all contained the structure of benzo[ghi]fluoranthene (FIVE-10), as shown in Figure 6; however, only FIVE-16 and FIVE-17 showed nonplanar distortions. It seems that nonplanar

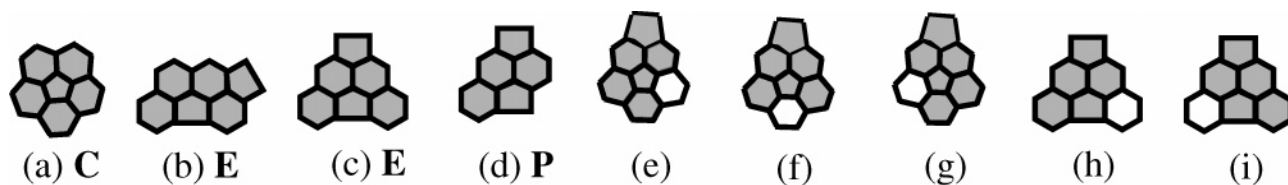


Figure 7. (a–d) are basic fragments, C, E, and P defined and used in the estimation of E_{np} for the molecules in Figure 5. (e–g) are E-structures derived from a C-structure and shown by shading; (h) and (i) are P-structures derived from the E-structures of (b) and (c), respectively, and shown by shading.

TABLE 2: Structures of Molecules in Figure 5 Are Expressed in C, E, P, CC, and CE

no.	structures	E_{np}^{est}	E_{np}^{err}	no.	structures	E_{np}^{est}	E_{np}^{err}
FIVE-13	1C	28.00	3.77	FIVE-83	1C+12E+4P-10CE	113.90	-1.59
FIVE-38	1C+3E-3CE	42.19	0.21	FIVE-84	1C+12E+4P-12CE	106.16	1.03
FIVE-52	1C+6E-6CE	56.38	-0.70	FIVE-85	1C+15E-15CE	98.95	2.97
FIVE-53	1C+6E-6CE	56.38	-1.31	FIVE-86	1C+12E+4P-12CE	106.16	-0.75
FIVE-75	1C+9E-9CE	70.57	-1.26	FIVE-87	2C+6E-6CE-CC	73.44	5.51
FIVE-76	1C+9E-9CE	70.57	-0.17	FIVE-91	1C+6E-6CE	56.38	-1.06
FIVE-79	1C+3E-3CE	42.19	1.83	FIVE-92	1C+12E+4P-9CE	117.77	0.90
FIVE-80	1C+12E-12CE	84.76	0.64	FIVE-93	1C+6E-6CE	56.38	-5.24
FIVE-81	1C+4E-4CE	46.92	-0.29	FIVE-94	2C+6E-6CE-CC	73.44	-5.60

E_{np}^{est} is the estimated value of E_{np} , and $E_{np}^{err} = E_{np}^{est} - E_{np}^{cal}$, in units of kcal/mol.

distortion can occur only when there is at least one 5-MR attached to the FIVE-10 structure. It is cautiously pointed out that the above suggestion is rough and needs to be verified using additional molecules.

3.4. Quantitative Estimation of E_{np} . Theoretically, if all possible sources of nonplanar distortion are considered, an accurate estimate of E_{np} can be expected based on simple motifs contained in the molecules. However, in the present work, the available data for E_{np} from high-level quantum calculations were limited. For instance, the nonplanar distortions in FIVE-82 were thought to be due to different motifs from those in FIVE-88 and FIVE-89. With limited data to fit, it was difficult to get a set of universal parameters for the prediction of E_{np} for all PAHs. In the present work, 20 PAHs containing the corannulene structure are quantitatively analyzed since this structure is the basic motif in fullerenes. It was noticed that the nonplanar strain energies for these molecules, shown in Figure 5, vary remarkably from 24.23 kcal/mol for FIVE-13 to 116.87 kcal/mol for FIVE-92. For FIVE-38, there is only one additional 5-MR around FIVE-13, while additional nonplanar strain energy of 17.75 kcal/mol was obtained. This result suggested that the added 5-MR may have formed new basic motifs which led to a much greater nonplanar distortion. Hence, the corannulene structure alone was not enough for the quantitative estimation of arching distortions for these molecules. Arbitrarily, three basic fragments are proposed in Figure 7, based on the reasoning suggested above. Figure 7a is the corannulene structure and is defined as motif C. Parts b and c of Figure 6 are two possible configurations for a 5-MR with five 6-MRs as nearest neighbors and one 5-MR as a second nearest neighbor. These configurations are shown as FIVE-16 and FIVE-17 in Figure 6, respectively, and b and c are labeled as motif E. Figure 6d presents a motif containing one 5-MR surrounded by three 6-MRs with another 5-MR as its second nearest neighbor; this structure was defined as motif P. In addition to these individual motifs, there are some compounds of different motifs. For instance, when there is one 5-MR around a corannulene structure, three E-motifs can be implied. As shown in parts e–g of Figure 7, when the white benzene ring is taken away, the remaining is simply motif E, as shown in parts b and c of Figure 7. In a similar manner, two P-motifs can also be derived from one E-motif, as shown in parts h and i of Figure 7. From the

limited sample molecules, motifs C, E, and P may induce nonplanar distortion. If all the contributions of C, E, and P motifs are simply summed, some parts may be considered twice or more since the motifs of C, E, and P have overlapping fragments. For instance, for FIVE-87 as shown in Figure 5, if it is counted as two C-motifs, two 6-MRs between two 5-MRs would be counted twice. Essentially, this conflict can occur between any motifs of C, E, and P; therefore, the overlaps must be subtracted. Here, such a concurrent fragment is written as the combination of the two motifs, such as CC, CE, and CP. But if all these were to be taken into account, many more parameters would be needed and the structural description of the PAHs and the estimation of E_{np} would be very complex. In the present study, only CC and CE were taken into account since using more terms did not improve the quality of fit in our tentative fitting. Hence, the molecules shown in Figure 5 are described by C, E, P, CC, and CE, as listed in Table 2.

On the basis of the above analysis, the nonplanar strain energy was estimated in terms of the contribution from five terms

$$E_{np}^{est} = xE_{np}^C + yE_{np}^E + zE_{np}^P - uE_{np}^{CC} - vE_{np}^{CE} \quad (2)$$

E_{np}^i ($i = C, E, P, CC, CE$) denotes the contributions from motifs C, E, P, CC, and CE; the coefficients of $x, y, z, u,$ and v represent the numbers of those motifs. On the basis of the least-squares theory, the values of E_{np} of the molecules shown in Figure 5 were fitted using eq 2, which resulted in a set of parameters of 28.00, 8.60, 5.35, 3.87, and 10.94 kcal/mol for $E_{np}^C, E_{np}^E, E_{np}^P, E_{np}^{CC},$ and E_{np}^{CE} , respectively. The comparison of E_{np} obtained from quantum calculations (as shown in Table 1) to the above estimates obtained as above is summarized in Table 2 and Figure 8. The developed parameters work very well for estimating E_{np} with errors varying from -5.60 to 5.51 kcal/mol, suggesting that the semiquantitative estimation of strain energies based on these motifs is quite valid and effective. This finding is very important, since in fullerenes, basic structural fragments are very simple (12 5-MRs and a lot of 6-MRs for prominent fullerenes, for instance) and possible basic motifs for nonplanar distortions are limited. In fact, the success of the semiquantitative estimation of standard heats of formation of fullerenes¹⁷ has vividly illustrated the possibility that quantitative estimations of the nonplanar distortions in fullerenes also can

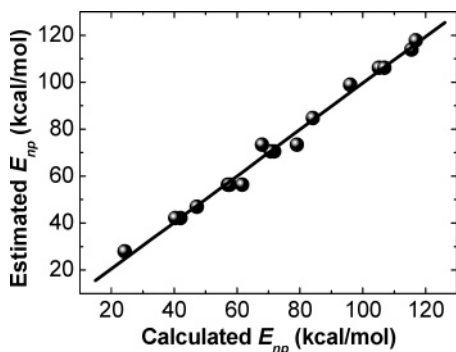


Figure 8. Estimated E_{np} vs calculated E_{np} for the 18 PAHs shown in Figure 5.

be expected if basic motifs are correctly selected, as will be reported elsewhere.

4. Conclusion

In the present work, the nonplanar strain energies E_{np} were calculated for 135 PAHs. On the basis of their nonplanar distortion, we have classified nonplanar PAHs investigated here into two groups: GROUP I and GROUP II with splitting and arching distortions, respectively. Through the analysis of the distribution of E_{np} in GROUP I, it was concluded that S-distortion may be induced by the strong repulsive forces between saturated hydrogen and carbon atoms in molecules containing a basic bay structure. For GROUP II, nonplanar distortions were related to several possible motifs. Moreover, the values of E_{np} for 18 PAHs containing the corannulene structure were reproduced based on three basic motifs. The differences between the E_{np} values from quantum calculations and those from these estimations vary from -5.60 to 5.51 kcal/mol; hence, the selected motifs successfully described the nonplanar distortion of the selected molecules. This result suggests that nonplanar distortions in PAHs and fullerenes are attributable to some basic motifs. This insight is fundamentally important for the understanding of nonplanar distortion of PAHs and fullerenes since this technique can be employed to semiquantitatively estimate strain energies of such molecules containing hundreds of carbon atoms for which optimizations and quantum calculations are very expensive.

Acknowledgment. We thank Miss D. Yao, Miss Y. T. Liu, Miss Y. N. Chen, Mr. J. Gao, and Mr. W. S. Xia for helpful discussions and the Center of Computational Molecular Science, UQ, for the CPU time. The authors are grateful to Prof. W. H.

Green, Jr. and Prof. J. Cioslowski for kindly offering the coordinates of the PAHs used here and to Prof. R. C. Haddon for helpful discussion and kindly offering the POAV package. The financial support from the Chinese Academy of Sciences' Shenyang Research Centre for Interfacial Materials and the ARC Centre for Functional Nanomaterials, Australia to this work are acknowledged. This work was also supported by the National Science Foundation of China (No. 50328204, 90406012) and the State Major Fundamental Research Project of MOST (G2000026403).

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