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Prediction of Low-Energy Isomers of Large Fullerenes from C_{132} to C_{160}

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To predict energetically favored isomers, we used a topological scheme as a prescreening tool to select candidate isomers for each fullerene from C_{106} to C_{160}. Comparison with the PM3 and tight-binding (TB) potential calculated results and few published data for the low-energy isomers of C_{106} to C_{130} indicates that the prescreening approach is feasible. For each fullerene from C_{132} up to C_{160}, the selected 1000 candidate isomers were further optimized by PM3 and TB potential. The analysis of the semiempirical PM3 and TB results of C_{106} to C_{160} provides some qualitative features of the large fullerenes. Furthermore, calculations at the B3LYP/6-31G*//B3LYP/3-21G level of theory were carried out on the top ten PM3 and TB low-energy isomers of C_{132} to C_{160} to accurately predict the stable isomers, and the HOMO−LUMO gap, the ionization energy, and electron affinity of the lowest-energy isomers were also investigated at the same level.

Introduction

For the large fullerenes (C_n with n from 76 to 96), over 30 isomers have already been separated and characterized by means of HPLC and NMR techniques.[1−9] The results show that the isolated pentagon rule (IPR)[10,11] can safely be applied to large fullerenes. But for the larger fullerenes, because of their diminishing solubility in common solvents and plenty of IPR isomers, the definitive experimental data on properties of individual isomers of fullerenes beyond C_{96} are seldom so far.

By identifying thermodynamically favorable isomers and allowing assignment of individual structures to NMR spectra, theoretical predictions constantly represent a substantial complementary tool in fullerene research.[12−23] Using the tight-binding molecular dynamics method, Zhang et al.[13,14] predicted the ground-state structures of fullerenes from C_{20} to C_{102}. By DFTB screening of all the IPR isomers of C_{118} and C_{120}, Fowler et al.[22] predicted the stable isomers of C_{118} and C_{120}. Recently, using a molecular mechanics method based on the second generation reactive empirical bond order (REBO) potential[24] as a prescreening tool, we have predicted the energetically favored isomers of fullerenes from C_{90} up to C_{140} at the PM3 semiempirical level.[23] However, although the molecular mechanics method is fast, it is still difficult to use it as a prescreening tool for the fullerenes beyond C_{140} because of the large size and the large number of IPR isomers. For example, the number of the IPR isomers of C_{140} and C_{160} is 121 354 and 836 497, respectively.[25] Therefore, a more efficient prescreening method for predicting the energetically favored isomers of giant fullerenes is necessary. Cioslowski et al.[26] proposed an approximate formula based on counts of 30 distinct structure motifs of IPR fullerenes. Using the formula, they reproduced the calculated values of the standard enthalpies of formation of 115 IPR isomers of fullerenes C_{60-102} and C_{180} at the B3LYP/6-31G* level within 3 kcal/mol. Because only the identification of the structural motifs for the IPR isomers is involved in this scheme, it is very fast and suited for rapid prescreening for the giant fullerenes.

In this work, first Cioslowski et al.'s[26] topological scheme to screen out the energetically favored isomers from the entire sets of IPR isomers of large fullerenes was validated according to the PM3 and tight-binding (TB) potential[27] optimized results and few published low-energy isomers of C_{106} to C_{130}. Second, this prescreening scheme was applied to screen out 1000 candidate isomers for each fullerene from C_{132} up to C_{160}, and these candidate isomers were further optimized by PM3 and TB. Furthermore, according to the PM3 and TB calculated results of C_{106} to C_{160}, some general features of the large fullerenes were discussed. Finally, to obtain more accurate predictions, we further performed calculations at the B3LYP/6-31G*//B3LYP/3-21G level of theory on the top ten PM3 and TB low-energy isomers of C_{132} to C_{160}, respectively. The electronic properties of the lowest-energy isomers were calculated at the same level. The reliability of the B3LYP method for large fullerene molecules has been demonstrated from the good agreement between the B3LYP/6-31G* standard enthalpies of formation and the previously published experimental and theoretical data of C_{70} to C_{90},[26] from the accordance between the predicted and the measured NMR spectra of C_{86},[1] and from the theoretical investigations on relative stabilities of fullerenes C_{94} and C_{96}, which consist quite well with the reported experimental observations.[17,18]

Computational Methods

In this work, all the IPR isomers of fullerenes from C_{106} to C_{160} are generated from CaGe software (http://www.mathematik.uni-bielefeld.de/~senkel/CAGE/contents.html), which is an open source software package used to generate mathematical graphs of different types, often types that relate to interesting chemical molecules.

It is known that both strain and conjugation strongly affect fullerene stabilities. To give a faithful description of strain and conjugation of IPR fullerenes, Cioslowski et al.[26] proposed a

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simple structural motif approach based upon counts of 30 distinct structural motifs composed of hexagons together with their first and second neighborhoods. An approximate formula was fitted to calculate the predicted standard enthalpies of formation to distinguish the stabilities of different isomers. The approximate formula is shown as follows:[26]

$$\Delta H_f^\circ \approx \sum_I \epsilon_I N_I - 8050.751(N - 30.050)^{-1} \qquad (1)$$

where ϵ_I is the contribution of each structural motif, N_I is the count of the corresponding structural motif, N is the number of carbon atoms, and $8050.751(N - 30.050)^{-1}$ is the global curvature term. The contribution of each structural motif ϵ_I was obtained by fitting the standard enthalpies of formation of 73 IPR isomers of C_{60} to C_{102} and C_{180} at the B3LYP/6-31G* level of theory. Further details about the structural motifs and the fitted values of ϵ_I can be found in ref 26.

For an isomer, the counts of 30 distinct structural motifs can be calculated through the topological connectivity of the isomer. Here, we developed a program to (1) generate the topological connectivity of each IPR isomer for a fullerene based on a top-down divide and conquer approach;[25] (2) calculate the count of each kind of structural motif; and (3) predict standard enthalpies of formation according to the approximate formula. After all the IPR isomers were generated, the candidate isomers could be selected by ranking the predicted standard enthalpies of formation. Because only the geometry is used, the prescreening scheme is very efficient. For example, for C_{160}, it takes about 6.22 h to generate the complete set of 836 497 IPR isomers and screen out the 1000 candidate isomers on the computer with an AMD Athlon(tm) MP 2200 + 1800 MHz CPU.

Using the method described previously, the standard enthalpies of formation for the entire IPR isomer set of each fullerene from C_{106} to C_{160} were predicted and ranked in which the results of C_{106} to C_{130} were used to validate the prescreening scheme. The selected candidate isomers of C_{132} to C_{160} were further calculated at the PM3, TB, and B3LYP/6-31G*//B3LYP/3-21G level of theory to determine the energetically favored isomers. All the PM3 and B3LYP calculations employed the GAUSSIAN 03 suite of programs,[28] and the TB optimizations were performed using a program we developed combining the limited memory quasi-Newton algorithm (L-BFGS)[29] and the TB potential.[27]

Results and Discussion

Validation of the Prescreening Scheme. To investigate the feasibility of the screening method and to estimate a suitable size for the candidate set that can cover the top low-energy isomers, we used the entire sets of IPR isomers of fullerenes C_{106} to C_{130} as the test sets. The standard enthalpies of formation for the entire sets of IPR isomers were calculated purely by the topological approach as eq 1 and ranked by ascending order. Here, the size of the candidate set consisted of the isomers with the lower predicted standard enthalpies of formation ΔH_f° is set to 1000. Moreover, the top 10% low-energy isomers selected from all the IPR ones by REBO potential,[23] were also optimized at the PM3 and TB semiempirical level. Comparing the geometrical and PM3 (TB) calculation results, it would appear that among all the top 10 low-energy isomers, only 6 (0 for TB) out of 130 isomers are missing from the candidate sets, and 90% (98% for TB) of the top 200 low-energy isomers are covered.

To our limited knowledge, for fullerenes from C_{106} to C_{130}, only C_{116}, C_{118}, and C_{120} have been systematically investigated using quantum-chemical methods.[21,22] Through a systematic search and calculation for the complete set of 6063 IPR isomers at the QCFF/PI (quantum-consistent force field/π) semiempirical level, C_{116}:6047, C_{116}:6046, C_{116}:5112, C_{116}:5939, and C_{116}:4761 were suggested as the top five low-energy isomers of C_{116} by Achiba et al,[21] where the integer after the colon is numbered according to the spiral codes.[30,31] The ranking orders of these five low-energy isomers according to the predicted standard enthalpies of formation are 127, 126, 110, 23, and 149, respectively. The stable isomers of C_{118} and C_{120} (C_{118}:7933, C_{118}:7924, and C_{118}:7926 and C_{120}:10253, C_{120}:10243, C_{120}:10268, C_{120}:8143, C_{120}:10262, and C_{120}:4811) were identified by Fowler et al. employing DFTB screening of all the IPR isomers of C_{118} and C_{120}.[22] These isomers also give a very high order of the predicted ΔH_f°, viz. 2, 5, and 3 for three stable isomers of C_{118} and 2, 7, 11, 4, 14, and 3 for the six stable isomers of C_{120}. Clearly, the published low-energy isomers of C_{116}, C_{118}, and C_{120}[21,22] are included in the 1000 candidate isomers selected by the ranking order of ΔH_f°. Additionally, the low-energy isomers for C_{118} and C_{120} identified based on TB optimized results are remarkably consistent with the literature results;[22] the only difference is that a new isomer (C_{120}:10764) is included.

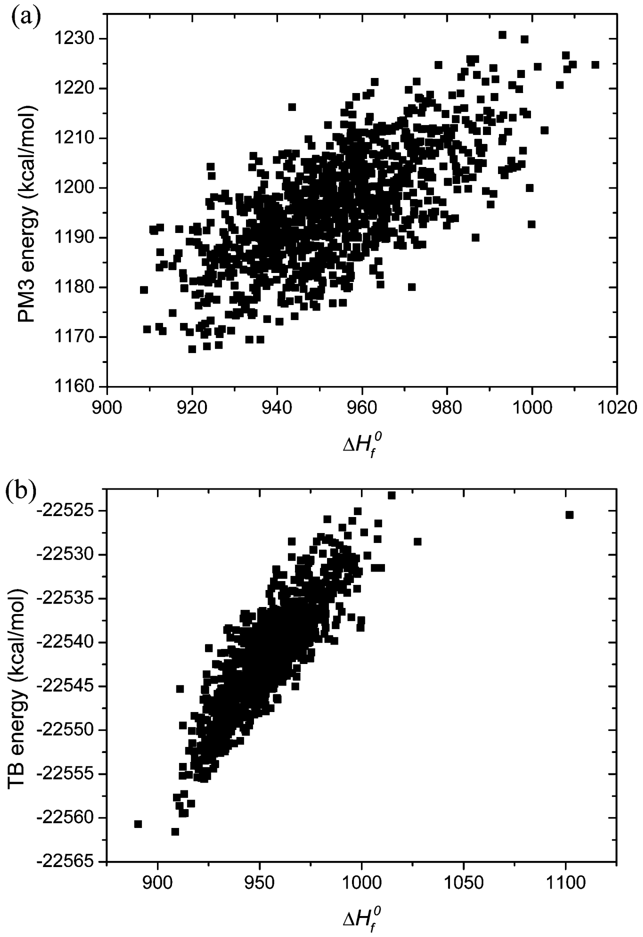

Figure 1. PM3 and TB energy as a function of the predicted standard enthalpies of formation ΔH_f° calculated by eq 1 for C_{120}. (a) PM3 and (b) TB.

All the previous comparisons with the published PM3 and TB calculated results for the fullerenes from C_{106} to C_{130} suggest that this fast topological scheme can be used as a prescreening

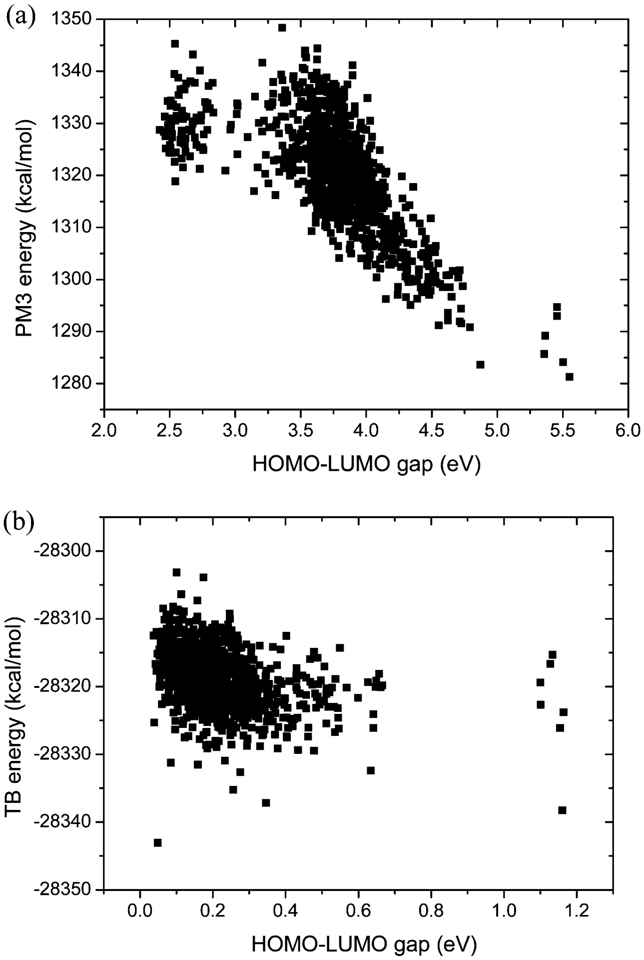

Figure 2. Energy vs HOMO−LUMO gap for C_{150} at the PM3 and TB level. (a) PM3 and (b) TB.

tool to select a small number of candidate isomers for further calculating the energetically favored isomers for the large fullerenes.

Semiempirical Calculations for the Candidates of Fullerenes C_{132} to C_{160} and Some General Features of the Large Fullerenes. The topological scheme was first employed to select 1000 candidate isomers for each fullerene of C_{132} to C_{160}, respectively. Then, PM3 and TB semiempirical level calculations were applied to optimize these candidate isomers. The list of 1000 selected candidate isomers for each fullerene along with the corresponding PM3 and TB energy values is available on the website http://chinfo.nankai.edu.cn/chmm/pubmats/CC/structures.html, which can be downloaded free of charge.

On the basis of the PM3 and TB results of fullerenes C_{106} to C_{160}, some factors contributing to the stability of the large fullerenes were qualitatively studied. The PM3 and TB energy as a function of the predicted standard enthalpy of formation ΔH_f° for C_{120} is shown in Figure 1. The employed isomers are selected from the complete IPR set of C_{120} by their REBO energies. The rough linear relation between the semiempirical energy and the predicted standard enthalpy of formation ΔH_f° is observed, and the TB results correlate better than PM3 with ΔH_f°. We note that, for the other fullerenes of C_{106} to C_{160}, the corresponding relation is similar to that for C_{120} (data not shown here). Therefore, it may be concluded that the local topological structures play an important role in the stability of the large fullerenes.

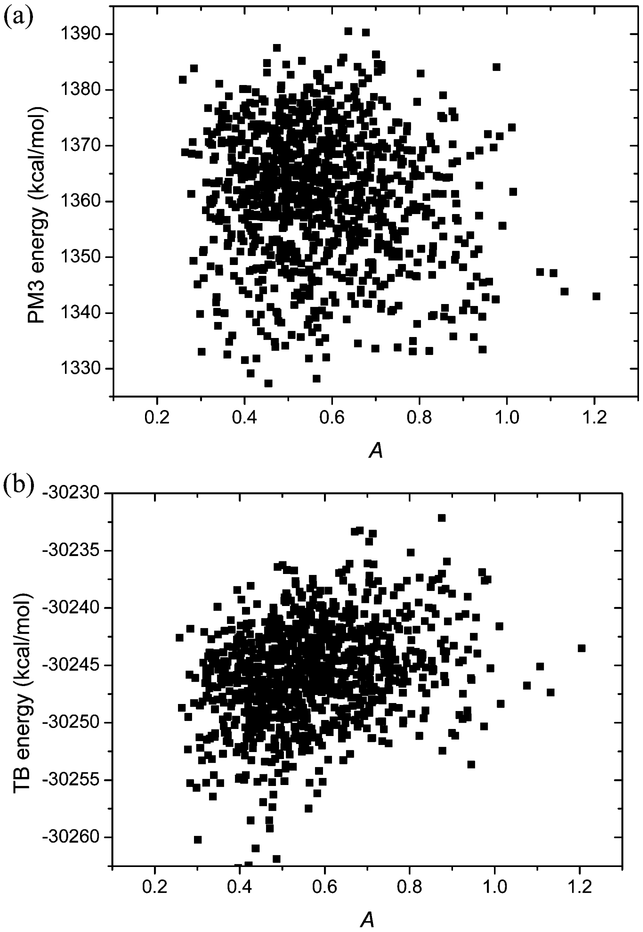

Figure 3. PM3 and TB energy of the selected candidate isomers against the asphericity A in eq 2 for C_{160}. (a) PM3 and (b) TB.

Figure 2 depicts the energy versus the HOMO−LUMO gap for C_{150} at the PM3 and TB level. It can be seen that the PM3 energy correlates to a certain degree with the HOMO−LUMO gap but that the TB energy has almost no correlation with the corresponding gap. As the other fullerenes of C_{106} to C_{160} show similar performances, it can be expected that the HOMO−LUMO gap is not a good criterion for screening.

In ref 22, Fowler et al. suggested that for C_{118} and C_{120}, the stability of the isomers has a poor correlation with their asphericity A

$$A = \sum_i \frac{(r_i - r_0)^2}{r_0^2} \tag{2}$$

where r_i is the radius distance of atom i from the center of mass, and r_0 is the average radius. Here, Figure 3 shows the PM3 and TB energy of the selected candidate isomers against the asphericity A for C_{160}, in which both the PM3 and the TB energy hardly correlate with A. All the other fullerenes of C_{106} to C_{158} exhibit very similar characteristics. The result tends to indicate that, for the selected candidate isomers of the large fullerenes, the stability of the isomers does not correlate with the asphericity A.

Energetically Favored Isomers of the Large Fullerenes C_{132} to C_{160} Predicted at the B3LYP Level of Theory. Although the lowest-energy isomers for C_{132} to C_{160} are calculated from the 1000 candidate isomers at the PM3 and TB level, previous computational experience has indicated that the

TABLE 1: Top Five Low-Energy Isomers of C_{132} to C_{160} at the B3LYP/6-31G*//B3LYP/3-21G Level

N^{a}	ΔE^{b}	N_{p}^{c}	N_{t}^{c}	N_{s}^{d}	label^{e}:symmetry
132	0.0	1	4	30	17030:D_{3h}
	0.1	3	2	29	49717:T
	1.1	16	1	2	49700:C_2
	1.8	24	3	1	49732:D_2
	3.8	17	5	19	38208:C_2
134	0.0	22	1	7	62358:C_2
	2.6	36	3	3	62195:C_1
	2.9	20	2	4	62153:C_2
	3.3	2	7	23	60365:C_1
	3.8	15	9	27	46125:C_2
136	0.0	3	2	28	79178:D_2
	1.8	28	4	11	55909:C_1
	2.1	38	1	1	79048:C_3
	2.8	23	7	9	55720:C_1
	4.6	33	3	7	79166:C_2
138	0.0	15	2	2	98289:C_2
	0.6	1	3	41	95755:C_1
	1.4	38	1	1	98080:C_2
	2.0	2	8	104	66755:D_2
	3.3	4	7	7	93276:C_1
140	0.0	266	1	1	121354:T
	4.5	54	3	2	120660:D_2
	5.4	53	7	3	118073:C_2
	6.9	193	2	8	120556:C_2
	7.0	1	11	146	120408:C_2
142	0.0	1	2	4	150303:C_{2v}
	4.0	118	1	1	150096:C_2
	9.4	125	3	5	95964:C_1
	9.5	18	5	16	94182:C_1
	9.9	2	24	8	139765:C_s
144	0.0	2	2	10	186610:D_{3d}
	0.6	3	3	2	185774:C_2
	0.9	4	4	9	186609:D_2
	2.1	70	1	1	184524:C_2
	4.2	5	5	17	185191:C_1
146	0.0	172	1	3	222515:C_2
	3.1	1	12	56	129993:C_2
	4.2	2	6	37	223909:D_2
	4.3	33	3	2	222140:C_1
	4.7	24	2	1	222982:C_1
148	0.0	1	3	2	276111:D_2
	3.2	140	1	11	273861:C_2
	4.6	2	6	16	276085:C_1
	4.8	102	2	12	273294:C_1
	5.6	318	4	27	273860:C_1
150	0.0	1	2	2	333052:D_{5h}
	3.0	154	1	1	335569:D_2
	5.8	17	3	4	331494:C_s
	9.9	3	6	3	335566:D_5
	11.6	209	4	5	335564:C_2
152	0.0	822	1	1	404667:T_h
	0.2	137	2	2	404666:D_3
	8.2	1	7	69	400802:C_2
	8.3	3	4	5	400768:C_{2v}
	8.8	7	9	6	400767:C_{2v}
154	0.0	4	2	4	489609:C_2
	0.3	219	1	1	489646:C_2
	0.3	3	3	3	489608:C_{s}
	1.0	14	4	6	484167:C_1
	2.2	1	13	327	93408:C_1
156	0.0	1	1	4	586176:D_2
	2.3	2	2	54	570444:C_1
	2.6	7	3	12	275610:C_1
	2.6	3	5	75	578122:C_2
	5.3	17	7	7	570108:C_2
158	0.0	5	2	15	689318:C_2
	2.1	1	28	5	611414:C_1
	2.4	191	1	9	697600:D_2
	2.6	33	5	10	689332:C_1
	2.8	40	7	11	689333:C_1
160	0.0	1	3	4	819709:C_{s}
	5.5	10	5	13	820406:C_2
	6.5	91	1	1	836497:D_2
	7.1	16	6	2	836211:C_1
	7.2	21	8	35	810630:C_2

[a] Number of carbon atoms. [b] ΔE is the relative energy compared to the corresponding lowest-energy isomer in units of kcal/mol at the B3LYP/6-31G*//B3LYP/3-21G level. [c] N_{p} and N_{t} are the PM3 and TB energy rank over 1000 candidate isomers, respectively. [d] The candidates were screened out by ranking the predicted standard enthalpies of formation calculated by eq 1. N_{s} is the corresponding ranking order over the whole IPR isomer. [e] Numbering according to the spiral code.[30,31]

semiempirical optimizations went to a wrong direction on some larger fullerenes. Therefore, higher-level quantum-chemical methods for further optimizing to determine the ground-state structures are still necessary. The top ten PM3 and top ten TB low-energy isomers of C_{132} to C_{160} were further optimized by the B3LYP/3-21G method and then calculated by B3LYP with the 6-31G* basis set. The results of the final top five isomers ranked by the B3LYP/6-31G* energy are given in Table 1. Comparing the energy rank of the PM3 and TB methods, N_{p} and N_{t}, with that of B3LYP, it is found that TB has an obvious better performance of prescreening than PM3. As shown in Table 1, all the most favorite isomers of C_{132} to C_{160} by B3LYP are covered in the top ten TB isomer set, and the top five low-energy isomers also have a rather small TB energy rank N_{t}, whereas some isomers have a very large PM3 energy rank N_{p}. The small value of N_{s}, the prior rank order of the predicted enthalpy of formation, also indicates that this measurement can be applied in the prescreening scheme. The lowest-energy isomers of C_{132} to C_{160} are shown in Figure 4. All the structures of the low-energy isomers listed in Table 1 are available on the website http://chinfo.nankai.edu.cn/chmm/pubmats/CC/structures.

For fullerenes C_{132} to C_{160}, the average B3LYP/6-31G* energy per atom of the lowest-energy isomers as a function of the cluster size N is plotted in Figure 5. It can be seen that, by and large, the average B3LYP/6-31G* energy decreases monotonically as the cluster size increases from 132 to 160. C_{150} and C_{152} possess a relatively low energy among these fullerenes.

In Table 1, many fullerenes have one or several isomers with their relative energies to the corresponding lowest-energy isomer below 3 kcal/mol, especially for C_{154} and C_{158}. Thus, it can be expected that the coexistence of more than one isomer is common for the large fullerenes. The symmetry in Table 1 shows that the 75 energetically favored isomers (five for each) possess 13 kinds of symmetry (C_1 (22), C_2 (26), C_3 (1), C_s (4), C_{2v} (3), D_2 (11), D_3 (1), D_5 (1), D_{3h} (1), D_{3d} (1), D_{5h} (1), T (2), and T_{h} (1)), where the C_1, C_2, and D_2 low-symmetry isomers are predominant in number. And for the lowest-energy isomers, there are nine kinds of symmetry (C_2 (5), C_s (1), C_{2v} (1), D_2 (3), D_{3h} (1), D_{5h} (1), D_{3d} (1), T (1), and T_{h} (1)), where the low symmetries are still leading. It indicates that for the large fullerenes, the energetically favored isomers prefer low symmetries, which is in agreement with the general conclusion in ref 14.

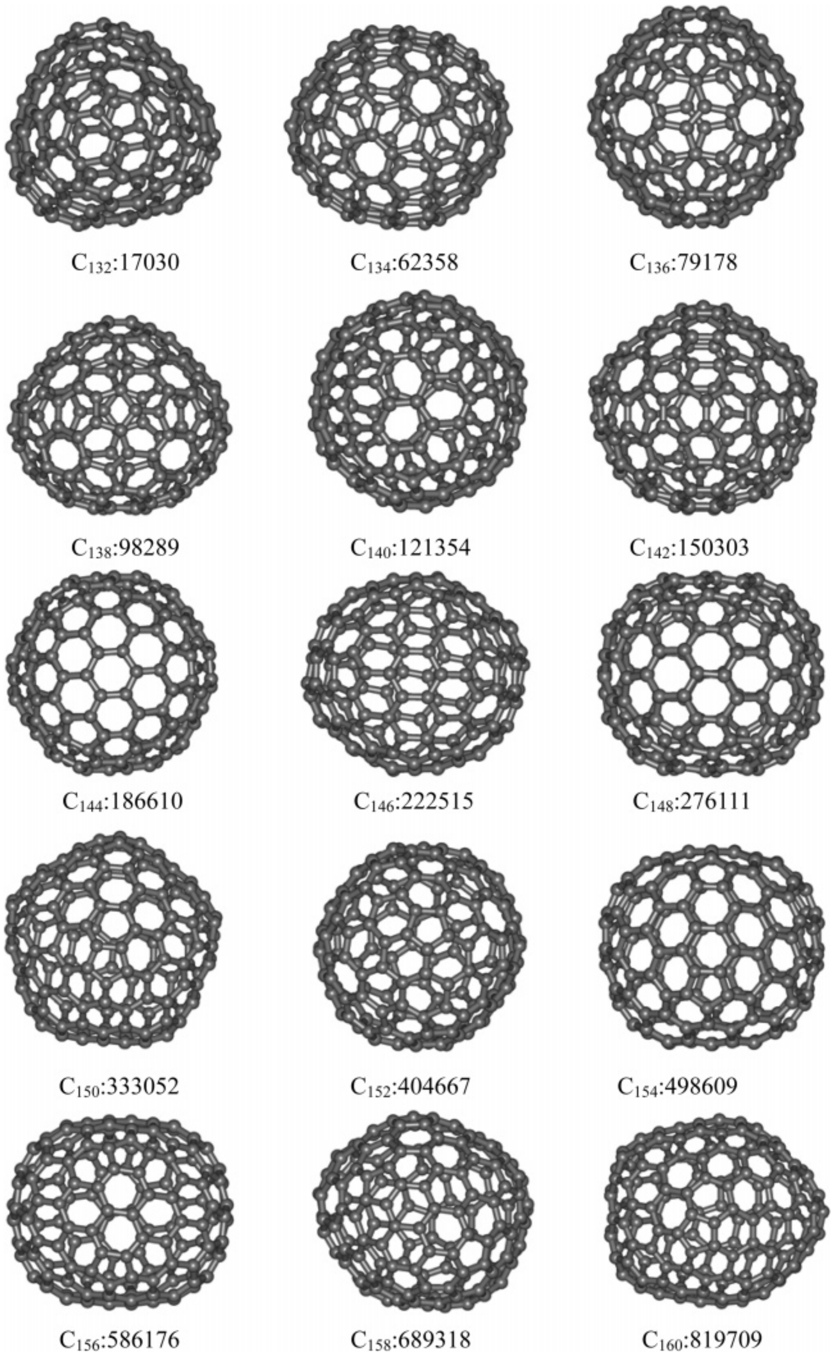

Figure 4. Lowest-energy isomers of fullerenes from C_{132} to C_{160} at the B3LYP/6-31G*//B3LYP/3-21G level. The isomers are identified using C_{xxx}:*yyy*, with *xxx* the number of carbon atoms. *yyy* is numbering according to the spiral codes.[30,31]

Electronic Property Calculations of the Lowest-Energy Isomers of C_{132} to C_{160} at the B3LYP Level of Theory. Both the ionization energy (IE) and the electron affinity (EA) of the lowest-energy isomers of C_{132} to C_{160} were calculated at the same DFT level, B3LYP/6-31G*//B3LYP/3-21G. IE refers to the energy difference between the cation and the neutral molecule, and EA corresponds to the energy difference between the neutral molecule and the anion. Here, the optimized geometry of the cation and anion is used, resulting in the adiabatic IE and EA, respectively. The results along with the HOMO−LUMO gaps at the same level are listed in Table 2. Figure 6 depicts the IE, EA, and HOMO−LUMO gap versus the cluster size *N*. In refs 32 and 33, the IE of C_{20} to C_{180} was found to decrease with increasing size for fullerenes, while the EA of C_{32} to C_{106} increased. But, in this study, this overall tendency has not been clearly observed in the small range from C_{132} to C_{160}, and Figure 6 shows no drastic dependence on the size of fullerenes, also for the HOMO−LUMO gap. Only the slight variation of the IEs for C_{132} to C_{160} is basically in agreement with the smooth trend in Figure 1 of ref 32 from C_{120} to C_{180} (in fact, there are no data for fullerenes ranging from C_{122} to C_{178}). Similarly, no drastic change of EA occurs in the C_{132} to C_{160} range.

The correlation between IE−EA and the corresponding B3LYP/6-31G* HOMO−LUMO gap is shown in Figure 7. Obviously, IE−EA has a good linear relationship with the HOMO−LUMO gap. Thus, it can be used as a measure for the HOMO−LUMO gap.[33] As shown in Figure 6, among the fullerenes ranging from C_{132} to C_{160}, a relatively high IE and low EA of C_{150} and C_{132} result in large HOMO−LUMO gaps,

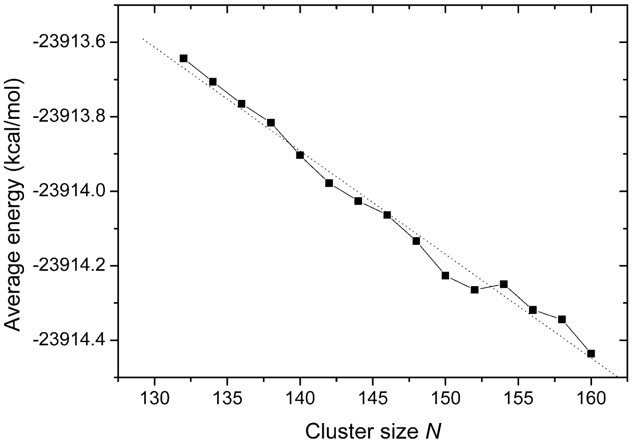

Figure 5. Average B3LYP/6-31G* energy per atom of the lowest-energy isomers of C_{132} to C_{160} as a function of the cluster size *N*.

TABLE 2: IE, EA, and HOMO−LUMO Gap of the Lowest-Energy Isomers of C_{132} to C_{160} at the B3LYP/6-31G*//B3LYP/3-21G Level

N	IE (eV)	EA (eV)	gap (eV)
132	6.41	2.50	2.24
134	6.13	3.22	1.23
136	6.12	2.95	1.50
138	6.06	3.14	1.22
140[a]			0.59
142	6.19	3.05	1.51
144	6.38	2.93	1.81
146	5.86	3.27	0.97
148	6.13	2.78	1.73
150	6.40	2.54	2.25
152	5.64	3.19	0.78
154	6.13	3.23	1.31
156	6.26	3.23	1.43
158	6.05	3.11	1.37
160	6.22	3.10	1.56

[a] Geometry optimization for the cation and anion of C_{140} not converged.

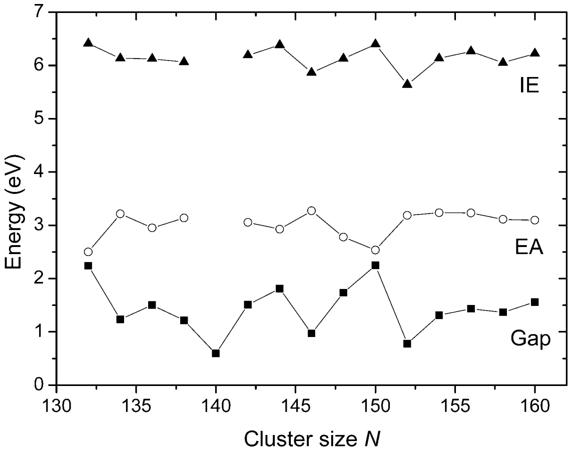

Figure 6. IE, EA, and HOMO−LUMO gap of the lowest-energy isomers of C_{132} to C_{160} at the B3LYP/6-31G*//B3LYP/3-21G level vs the cluster size *N*.

indicating that they may be more abundant than the others in the experimental extract.

Conclusion

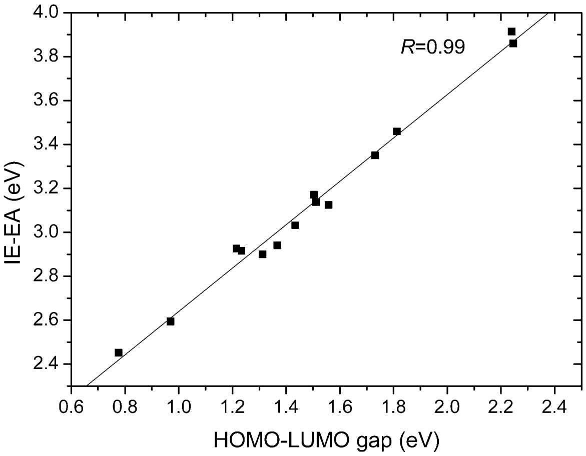

Figure 7. IE−EA at the B3LYP/6-31G*//B3LYP/3-21G level as a function of the corresponding HOMO−LUMO gap at the same level for the lowest-energy isomers of C_{132} to C_{160}. The correlation coefficient for the linear regression is $R = 0.99$.

Our study has shown that a topological scheme can be used to select candidates from large amounts of isomers for the large fullerenes, which are potential low-energy isomers. Using the prescreening scheme, 1000 candidate isomers for each fullerene from C_{132} up to C_{160} were selected, from which the low-energy isomers at the PM3 and TB semiempirical level were calculated. Furthermore, the B3LYP/6-31G*//B3LYP/3-21G calculations were carried out on the top ten PM3 and TB low-energy isomers to predict the energetically favored isomers. However, we cannot guarantee that the B3LYP/6-31G* result should be preferred. For the sophisticated prediction of the most stable isomers for large fullerenes, more candidate isomers, hierarchical screening, and further higher-level quantum-chemical methods, for example, MP2/6-31G*, are probably necessary. Thorough analysis of the PM3 and TB calculated results of C_{106} to C_{160} suggests that the local topological structures formed by hexagons together with their first and second neighbors play an important role in the stability, and the contribution of the HOMO−LUMO gap to the energy rank of isomers is not obvious, whereas the asphericity of the isomers does not seem to correlate with the stability. The electronic property calculations show that for fullerenes C_{132} to C_{160}, their IE and EA values slightly fluctuate near 6.14 and 3.02 eV, respectively, and the difference of IE−EA can be used as a measure for the HOMO−LUMO gap.

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