Search for Lowest-Energy Fullerenes: C_{98} to C_{110}

Nan Shao, Yi Gao, Soohaeng Yoo, Wei An, and Xiao Cheng Zeng*

Department of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588

Received: April 19, 2006

By combining the semiempirical density-functional based tight-binding optimization with density-functional theory single-point energy calculation at the PBE1PBE/6-311G* level, we propose an efficient computational approach to determine lowest-energy structures of large-sized carbon fullerenes. Our studies show that C_{92} (D_3: 28) and C_{94} (C_2: 43) are the new leading candidates for the lowest-energy structures of C_{92} and C_{94}. Moreover, for the first time, the lowest-energy structures of $C_{98}-C_{110}$ are identified on the basis of the density-functional theory calculation. The lowest-energy isomers C_{102} (C_1: 603) and C_{108} (D_2: 1771) are readily isolated experimentally because they are much lower in energy than their other low-lying IPR isomers.

I. Introduction

Exploration of the formation mechanism of large-sized multishell fullerenes (e.g., buckyonion $C_{60}@C_{240}$)[1] as well as large-sized endohedral metallofullerenes (e.g., recently isolated $Dy_2@C_{100}$ [2]) calls for a better understanding of the lowest-energy structures of large-sized (empty) fullerenes beyond the size of C_{100}. To date, the largest (empty) fullerene cage isolated and characterized in the laboratory is C_{96}, although some larger fullerenes (e.g., C_{176}) have been detected.[3] On the other hand, previous ab initio theoretical studies have corroborated nearly all the low-lying fullerene structures of C_{80} to C_{96}.[4−12] Additionally, low-lying structures of several larger fullerenes, such as C_{98}, C_{100} and C_{116}, have also been explored on the basis of semiempirical methods.[13−16a] However, few global searches for low-energy fullerenes beyond the size of C_{96} have involved ab initio or density-functional theory (DFT) calculations.[16b]

The theoretical challenge associated with the global search of low-energy structures of large-sized fullerenes stems mainly from the rapid increase of the number of isomers with the fullerene size. For example, the total number of fullerene isomers ranges from 39 718 for C_{82} to 713 319 for C_{110}.[17] In principle, one could determine the lowest-energy isomer by using ab initio electronic structure methods to compute energies of all fullerene isomers.[5−9] However, such an approach becomes increasingly impractical for large-sized fullerenes such as C_{110}. To alleviate this "million-isomer" problem, two theoretical strategies have been commonly adopted: (1) to apply the isolated-pentagon-rule (IPR) as a filter, and (2) to utilize a highly efficient prescreening tool[10−12,16] such as empirical force fields (e.g., Brenner potential) or semiempirical methods (e.g., AM1, PM3 and SAM1) to further reduce the number of candidate isomers for the last-stage ab initio calculation. Indeed, the IPR conjecture can dramatically reduce the number of candidate isomers. For example, the number of IPR isomers of C_{110} is only 2355 as opposed to 713 319 fullerene isomers of C_{110}. However, full geometry optimization of thousands of large-sized fullerene isomers using ab initio methods can still be laborious. It is desirable to further cut down the number of candidate isomers to a few tens for the last-stage ab initio electronic energy calculation. Toward this end, a highly efficient prescreening tool is required. Generally, such a pre-screening tool has to meet three prerequisites: (1) fast geometry optimization, (2) reasonably accurate optimized structures, and (3) modest error bar in the relative energies between isomers. Semiempirical methods, which have been used the most as the prescreening tool to obtain low-lying isomers of $C_{92}-C_{96}$,[10−12] meet the three prerequisites reasonably well. For C_{96}, a complete calculation of the IPR isomer energies by Zhao et al.[12] shows that the error bar in relative energies with the SAM1 method can amount to ∼15 kcal/mol, when compared with the DFT calculation at the B3LYP/6-31G level. As such, at least 10% of total IPR isomers should be subjected to the last-stage ab initio calculation to sort out the energy ranking of low-lying isomers (For C_{110}, this means that more than 200 IPR isomers are subjected to ab initio geometry optimization). In this paper, we demonstrate a highly efficient prescreening tool in conjunction with DFT single-point energy calculation to find out top candidates of the lowest-energy IPR cluster of $C_{98}-C_{110}$.

II. Computational Details

We employed the semiempirical self-consistent charge density-functional based tight-binding (DFTB) method[18a,b] as the prescreening tool.[18c,d] All the IPR fullerene isomers were fully optimized using the DFTB method. We first used the IPR isomers $C_{82}-C_{96}$ as a testing database to evaluate the typical error bar with the DFTB method in calculating relative energies among the isomers. Guided by the error bar, an energy cutoff criterion is suggested. Next, all isomers that are within the energy cutoff are viewed as top candidates and are subject to the single-point energy calculation using the PBE1PBE hybrid functional[19] with a midsize basis set 6-311G*. Here, we chose the hybrid exchange-correlation functional PBE1PBE, rather than the B3LYP or B3PW91 functional, because we previously showed that the PBE1PBE functional predicts the same energy ranking as that from the high-level coupled-cluster calculation for the top-three lowest-energy isomers of C_{20} (bowl, cage, and ring isomers).[19b] All PBE1PBE/6-311G* single-point energy calculations were performed using GAUSSIAN03 package.[20]

III. Results and Discussions

A. $C_{82}-C_{96}$ as Test Database. Geometries of all 540 IPR isomers of $C_{82}-C_{96}$ were fully optimized using the DFTB

---

* Corresponding author. E-mail: xczeng@phase2.unl.edu. Telephone number: (+1)402-472-9982. Fax: (+1)402-472-9402.

10.1021/jp0624092 CCC: $33.50

TABLE 1: Relative Energies ΔE (kcal/mol) and HOMO−LUMO Gap E_{gap} (eV) of the Low-Lying Isomers of C_{82}−C_{96}[a]

C_N [b]	label[c]	symmetry	PBE1PBE/6-311G*//DFTB		DFTB
			ΔE	E_{gap}	ΔE
C_{82}	**3**	**C_2**	**0.000**	**1.687**	**0.000**
(9)	4	C_s	4.245	1.633	1.977
	5	C_2	9.255	1.333	4.426
	6	C_s	13.628	1.143	6.563
	1	C_2	7.937	1.279	6.966
	2	C_s	6.524	1.687	6.980
	9	C_{2v}	19.871	0.830	9.027
C_{84}	**22**	**D_2**	**0.589**	**2.068**	**0.000**
(24)	**23**	**D_{2d}**	**0.000**	**2.150**	**0.355**
	11	C_2	8.704	1.702	7.935
	16	C_s	8.254	1.959	8.749
	15	C_s	12.090	1.604	9.118
	24	D_{6h}	7.244	2.457	9.140
C_{86}	**17**	**C_2**	**0.000**	**1.578**	**0.000**
(19)	11	C_1	10.959	1.170	6.891
	16	C_s	5.650	1.970	7.430
	18	c3	11.158	1.269	7.648
	12	C_1	10.394	1.242	8.548
C_{88}	**17**	**C_s**	**0.000**	**1.597**	**0.000**
(35)	7	C_2	1.212	1.633	1.313
	33	C_2	2.132	1.796	2.030
	15	C_1	13.065	1.058	8.977
	20	C_2	10.832	1.401	9.109
C_{90}	**45**	**C_2**	**0.000**	**1.736**	**0.000**
(46)	35	C_s	2.877	1.905	3.431
	46	C_{2v}	3.062	1.865	4.736
	30	C_1	6.473	1.807	5.857
	28	C_2	7.734	1.748	6.659
	40	C_2	9.468	1.450	6.910
	18	C_2	10.430	1.524	9.071
C_{92}	**28**	**D_3**	**0.000**	**2.204**	**0.000**
(86)	26	C_2	5.315	1.732	4.567
	84	D_2	4.891	1.984	4.922
	82	D_2	5.760	1.759	5.437
	38	C_1	5.315	1.888	5.505
	71	D_3	11.352	1.440	7.099
	43	C_1	10.175	1.350	7.345
	9	C_2	10.076	1.315	7.736
	81	D_2	9.669	1.614	9.438
C_{94}	**43**	**C_2**	**0.000**	**1.905**	**0.000**
(134)	42	C_s	1.988	1.986	2.130
	133	C_2	7.018	1.660	6.593
	44	C_s	6.032	1.742	6.659
	34	C_1	8.369	1.551	7.322
	37	C_1	8.074	1.712	7.421
	91	C_1	10.676	1.497	7.426
	61	C_2	7.981	1.633	7.475
	15	C_1	10.416	1.438	8.519
C_{96}	**181**	**C_2**	**0.249**	**1.605**	**0.000**
(187)	**183**	**D_2**	**0.000**	**1.714**	**0.616**
	144	C_1	1.660	1.769	2.558
	145	C_1	2.666	1.578	3.238
	182	C_2	3.930	1.551	3.647
	114	C_1	5.544	1.524	3.651
	94	C_1	6.124	1.524	5.624
	146	C_s	4.738	1.751	6.619
	142	C_2	6.572	1.675	6.869
	164	C_1	8.638	1.397	7.143
	130	C_1	7.976	1.605	7.940
	176	C_2	7.291	1.633	7.975
	47	C_1	8.796	1.666	8.084
	180	C_s	7.907	1.299	8.367
	116	C_1	9.130	1.453	8.658
	179	C_2	9.545	1.361	8.794
	90	C_1	9.978	1.310	9.013
	165	C_2	12.674	1.216	9.317

[a] An arbitrary energy cut-off value of 0.015 au (9.4 kcal/mol) was adopted to collect all the leading candidates for the lowest-energy isomers. The boldface marks the top candidates for the lowest-energy isomer. [b] The number of IPR isomers is given in parentheses. [c] The labels are according to Fowler and Manolopoulos.[21]

TABLE 2: Total Electronic Energies E (au), Relative Energies ΔE (kcal/mol) and HOMO−LUMO Gap E_{gap} (eV) of the Lowest-Energy Structures of C_{92} (D_3: 28) and C_{94} (C_2: 43) (in Boldface), Compared with Those of C_{92} (D_2: 84)[10] and C_{94} (C_2: 133)[11,16a] [a]

C_N	label	symmetry	PBE1PBE/6-311G*			B3LYP/6-311G*		
			E	ΔE	E_{gap}	E	ΔE	E_{gap}
C_{92}	**28**	**D_3**	**−3502.572737**	**0.000**	**2.204**	**−3506.403673**	**0.000**	**2.007**
	84	D_2	−3502.564828	4.963	2.106	−3506.396750	4.344	1.872
C_{94}	**43**	**C_2**	**−3578.733040**	**0.000**	**1.948**	**−3582.648302**	**0.000**	**1.755**
	133	C_2	−3578.722665	6.511	1.793	−3582.637759	6.616	1.578

[a] Two hybrid density functionals are used for geometry optimization and energy calculation.

method. Relative energies of low-lying isomers (those with energy within 0.015 au or 9.4 kcal/mol from the lowest-lying DFTB isomer) are listed in the Table 1, together with the PBE1PBE/6-311G* relative energies and HOMO−LUMO gaps. All isomers are labeled according to the Flower and Manolopoulos scheme,[21] along with their point-group symmetries. First, we found that the lowest-energy isomers (based on the PBE1PBE/6-311G* calculation) are mostly consistent with the literature results (see below for C_{92} and C_{94}).[5−12] Second, many lowest-lying DFTB isomers are also the lowest-energy isomers according to the PBE1PBE/6-311G* calculation. Third, with exception of two isomers of C_{82}, the error bar in relative energies using the DFTB method is less than 4.9 kcal/mol, compared with the PBE1PBE/6-311G* calculation. We therefore adopted 0.01 au (6.3 kcal/mol) as an energy cutoff criterion. Namely, those isomers within 0.01 au from the lowest-lying DFTB isomer are considered to be a candidate for the true lowest-energy isomer. A noteworthy byproduct from this preliminary test is that new lowest-energy IPR isomers of C_{92} (D_3: 28) and C_{94} (C_2: 43) are identified. To further ensure that both isomers are true global minima, we performed full geometry optimization of the two isomers using two hybrid DFT functionals, PBE1PBE/6-311G* and B3LYP/6-311G*. As shown in Table 2, the two newly identified lowest-energy isomers are about 4−7 kcal/mol lower in energy than those previously reported lowest-energy isomers,[10,11,16a] indicating that our newly proposed energy-ranking determination scheme is quite robust.

In Table 1, we also list the HOMO−LUMO gaps for all the leading IPR isomers, which were calculated at the PBE1PBE/6-311G* level of theory. It can be seen that the HOMO−LUMO gaps span a large range from 0.83 to 2.46 eV. Except for C_{82} and C_{92}, all lowest energy isomers of C_{82}−C_{96} do not possess the largest HOMO−LUMO gap. Although the HOMO−LUMO gaps of the low-lying isomers do not show special correlation with the relative energies, the HOMO−LUMO gaps of all the

TABLE 3: Relative Electronic Energies Δ*E* (kcal/mol) and HOMO−LUMO Gap E_{gap} (eV) of the Top-Six Lowest-Energy C_{98} Isomers, for Which One Set of Data Are Based on the Optimized Geometry at the PBE1PBE/6-311G* Level and the Other Set Are Based on the DFTB Optimized Structure[a]

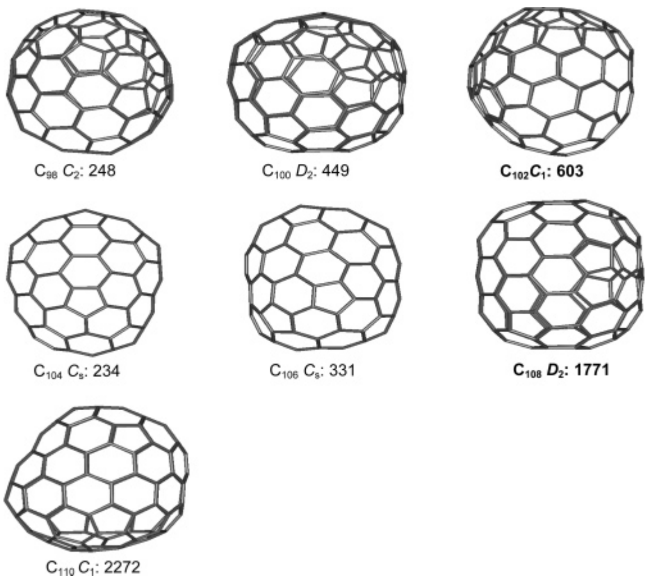
			PBE1PBE/6-311G*//DFTB		PBE1PBE/6-311G*	
C_N	label	symmetry	Δ*E*	E_{gap}	Δ*E*	E_{gap}
C_{98}	**248**	**C_2**	**0.000**	**1.837**	**0.000**	**1.971**
	120	C_s	1.166	1.690	1.162	1.791
	253	C_3	3.044	1.517	2.998	1.549
	254	C_2	3.207	1.415	3.217	1.459
	148	C_3	2.930	1.388	3.273	1.430
	244	C_1	4.079	1.252	4.140	1.301

[a] The boldface marks the lowest-energy isomer.

lowest-energy isomer are greater than 1.5 eV, indicating that these isomers are all chemically stable.

B. C_{98} as a Testing Case. An advantage of the DFTB method as a prescreening tool is that the optimized geometries are very close to those based on DFT optimization. This is because the DFTB method is designed to reproduce the results of DFT calculations at the outset. Because few ab initio studies have been reported for fullerenes beyond the size C_{96}, we used C_{98} as a testing case, for which full geometry optimization at PBE1PBE/6-311G* level was carried out for leading lowest-energy isomers. In Table 3, we show the relative energies and HOMO−LUMO gaps of top-six lowest-energy isomers of C_{98}, where one set of data were based on the DFTB optimized geometries whereas the other set were based on the full geometry optimization at the PBE1PBE/6-311G* level. It can be seen that the differences in the relative energies are only a few tenths of a kcal/mol, which proves the robustness of the energy ranking determined solely on the basis of the DFTB geometries.

C. Lowest-Energy IPR Isomers of $C_{98}-C_{110}$. First, all 7535 IPR isomers of $C_{98}-C_{110}$ were geometrically optimized using the DFTB method. Again, those isomers whose relative energies with respect to the lowest-energy DFTB isomer are within the energy cutoff value (6.3 kcal/mol) were collected. Next, single-point energy calculation at the PBE1PBE/6-311G* level was carried out to obtain the energy ranking and the top candidates for the lowest-energy isomer (highlighted in boldface in Table S1). It can be seen from Table S1 that all the lowest-energy isomers identified on the basis of the PBE1PBE/6-311G* calculation have corresponding (DFTB) energies within 5.1 kcal/mol from the lowest-lying DFTB isomer, which justifies the use of 6.3 kcal/mol as the energy cutoff criterion.



C_{98} C_2: 248 C_{100} D_2: 449 **C_{102} C_1: 603**

C_{104} C_s: 234 C_{106} C_s: 331 **C_{108} D_2: 1771**

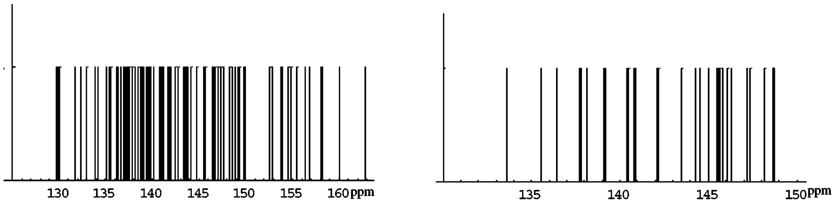
C_{110} C_1: 2272

Figure 1. Top candidate for the lowest-energy isomer of large-sized fullerenes $C_{98}-C_{110}$.

TABLE 4: Relative Electronic Energies Δ*E* (kcal/mol), Symmetries, Ring Spiral Codes, and HOMO−LUMO Gaps (eV) of the Low-Lying Isomers of $C_{98}-C_{110}$[a]

				PBE1PBE/6-311G*//DFTB		
C_N[b]	label[c]	ring spiral code	symmetry	Δ*E*	E_{gap}	DFTB Δ*E*
C_{98}	**248**	**1 7 9 11 13 27 33 36 41 46 48 51**	**C_2**	**0.000**	**1.837**	**1.285**
(259)	120	1 7 9 11 13 27 33 36 41 44 48 50	C_s	1.166	1.690	2.247
	148	1 7 9 11 26 30 32 34 36 38 40 50	C_3	2.930	1.388	0.000
	253	1 7 9 14 18 22 34 36 38 40 43 49	C_3	3.001	1.524	2.557
C_{100}	**449**	**1 7 9 18 23 25 27 33 40 43 46 48**	**D_2**	**0.000**	**1.225**	**0.000**
(450)	**425**	**1 7 9 11 13 15 33 35 39 43 47 50**	**C_1**	**0.009**	**1.420**	**1.194**
	442	**1 7 9 11 13 27 34 38 41 44 47 51**	**C_2**	**0.260**	**1.282**	**1.379**
	173	1 7 9 11 13 15 38 33 40 43 46 52	C_1	1.204	1.180	1.088
	440	1 7 9 11 13 15 34 39 41 44 47 51	C_2	2.152	1.273	2.584
C_{102} (616)	**603**	**1 7 9 14 18 23 31 36 39 44 49 52**	**C_1**	**0.000**	**1.373**	**0.000**
C_{104}	**234**	**1 7 9 11 13 18 34 45 44 46 51 54**	**C_s**	**0.000**	**1.605**	**0.000**
(823)	**812**	**1 7 9 11 13 18 29 31 37 45 49 53**	**D_2**	**0.046**	**2.041**	**5.080**
	443	1 7 9 11 13 18 34 37 40 44 46 49	C_2	1.532	1.197	1.310
	766	1 7 9 11 26 28 31 35 45 48 51 53	C_2	2.074	1.170	3. 414
	106	1 7 9 11 13 18 37 40 43 45 51 53	C_1	2.478	1.361	6.113
C_{106}	**331**	**1 7 9 11 13 24 29 46 49 47 50 53**	**C_s**	**0.000**	**1.769**	**3.215**
(1233)	534	1 7 9 11 13 24 29 46 49 46 52 55	C_1	1.339	1.170	0.269
	1194	1 7 9 11 13 30 32 37 40 46 49 52	C_2	1.715	1.061	1.024
	318	1 7 9 11 13 24 29 46 46 49 51 53	C_1	2.776	1.878	6.113
	314	1 7 9 11 13 24 30 38 43 46 49 55	C_1	2.838	1.633	4.658
C_{108} (1799)	**1771**	**1 7 9 11 13 18 43 45 48 44 51 55**	**D_2**	**0.000**	**1.660**	**0.036**
C_{110}	**2272**	**1 7 9 11 13 15 47 49 44 46 52 56**	**C_1**	**0.000**	**1.388**	**2.115**
(2355)	**1262**	**1 7 9 11 13 15 47 39 42 46 48 54**	**C_{2v}**	**0.355**	**0.980**	**0.776**
	2293	**1 7 9 11 13 15 47 49 41 49 52 54**	**C_1**	**0.404**	**1.442**	**1.422**
	2232	1 7 9 11 13 15 47 49 41 46 50 57	C_1	1.793	1.442	3.166
	1946	1 7 9 11 13 15 47 49 43 45 51 56	C_1	2.364	1.252	3.200
	2070	1 7 9 11 13 15 34 36 41 44 49 57	C_1	2.768	1.225	2.792

[a] The energies are calculated at the PBE1PBE/6-311G* level of theory and based on DFTB optimized geometries. The boldface marks the top candidates for the lowest-energy isomer [b] The number of IPR isomers is given in parentheses. [c] The labels are according to Fowler and Manolopoulos.[21]



C_{102} C_1: 603

C_{108} D_2: 1771

Figure 2. Calculated ^{13}C NMR spectra of C_{102} (C_1: 603) and C_{108} (D_2: 1771). The two isomers are predicted to be more easily isolated by the experiment than other large-sized fullerenes.

In Table 4, we summarize the main results of this work, including the identified top candidates for the lowest-energy isomers of C_{98}−C_{110} (see Figure 1), the relative energies, ring spiral codes, and the HOMO−LUMO gaps. In light of the intrinsic error bar for the DFT electronic-energy calculation[18b] and possible temperature effects on the relative stability, those low-lying isomers within 3.0 kcal/mol from the top candidate are also listed in Table 4. For C_{98} and C_{100}, (C_2: 248) and (D_2: 449) are the leading candidate for the lowest-energy isomer, the same as those identified on the basis of semiempirical methods.[13,14,16a] However, the second lowest isomers differ from those determined from previous semiempirical calculation. Note that for the third and fourth lowest-energy isomers of C_{98}, (C_3: 148) and (C_3: 253), previous semiempirical (SAM1) calculation predicted that they are ranked 36th and 71st, respectively.[13] For C_{100}, the second and third lowest-energy isomers (C_1: 425) and (C_2: 442) are only 0.009 and 0.26 kcal/mol higher in energy than the leading candidate (D_2: 449). We therefore view the three C_{100} isomers iso-energetic.

Particular noteworthy are the lowest-energy isomers of C_{102} and C_{108} (C_1: 603 and D_2: 1771). Being 5.1 and 3.2 kcal/mol more stable than their second lowest-energy isomer (Table S1), these two isomers are more likely to be isolated experimentally among the large-sized fullerenes. For this reason, we calculated the ^{13}C NMR chemical shift of the two isomers at the PBE1PBE/6-311G* level of theory (Table S2). The simulated NMR spectra are plotted in Figure 2, which are readily compared with experimental spectra. On the other hand, our calculation indicates that there exist at least three nearly iso-energetic isomers for C_{100} and C_{110}. As a result, these isomers are likely to coexist in the soot and hard to separate experimentally. Of course, confirmation of the predicted lowest-energy isomers must await future experiments.

As in the case of C_{82}−C_{96}, the HOMO−LUMO gaps of fullerene C_{98}−C_{110} do not show strong correlation with the relative energy. In Table 4 and Table S1, it can be seen that C_{98} (C_2: 248) is the only isomer that has both the lowest energy and the largest HOMO−LUMO gap. Among all the large fullerene considered in this study, it appears that C_{104} (D_2: 812) has the largest HOMO−LUMO gap of 2.04 eV. Finally, comparing Table 1 with Table S1, it seems that the HOMO−LUMO gaps tend to decrease with increasing the size of fullerene.

IV. Conclusions

We have shown that the semiempirical DFTB method can be a highly efficient pre-screening tool, when combined with the DFT single-point energy calculation, to determine the best candidates for the lowest-energy isomer of large fullerenes. Our studies reveal new candidate isomers C_{92} (D_3: 28) and C_{94} (C_2: 43) to be the lowest-energy isomer of C_{92} and C_{94}. Moreover, for the first time, the lowest-energy structures of C_{98}−C_{110} (as well as new low-lying structures) are identified on the basis of DFT calculation. In particular, the predicted lowest-energy isomers of C_{102} (C_1: 603) and C_{108} (D_2: 1771) are notably lower in energy than their corresponding low-lying IPR isomers, suggesting that the two isomers are more readily isolated experimentally than other large-sized fullerenes in the size range C_{98}−C_{110}.

Acknowledgment. We thank Professor Th. Frauenheim and Dr. M. Ebstner for sending us the DFTB program. This research was supported in part by grants from DOE (DE-FG02-04ER46164), the Nebraska Research Initiative and the John Simon Guggenheim Foundation (X.C.Z.) and by the Research Computing Facility at University of Nebraska−Lincoln.

Supporting Information Available: Data of electronic energies for C_{98}−C_{110}, ^{13}C NMR chemical shifts for C_{102} (C_1: 603) and C_{108} (D_2: 1771) are collected. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Ugarte, D. *Nature* **1992**, *359*, 707−709. (b) Becker, L.; Poreda, R. J.; Bunch, T. E. *Lunar Planetary Sci.* **2000**, *31*, 1803. (c) Lu, J. P.; Yang, W. *Phys. Rev. B* **1994**, *49*, 11421−11424.

(2) Yang, S.; Dunsch, L. *Angew. Chem., Int. Ed.* **2006**, *45*, 1299−1302.

(3) (a) Hennrich, F. H.; Michel, R. H.; Fischer, A.; Richard, S. S.; Gilb, S.; Kappes, M. M.; Fuchs, D.; Burk, M.; Kobayashi, K.; Nagase, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1732−1734. (b) Achiba, Y.; Kikuchi, K.; Aihara, Y.; Wakabayashi, T.; Miyake, Y.; Kainosho, M. In *The Chemical Physics of Fullerenes 10 (And 5) Years Later*; Andreoni, W., Ed.; Kluwer Academic Publishers: Dordrecht, 1996; pp 139−147. (c) Goel, A.; Howard, J. B.; Vander, S. J. B. *Carbon* **2004**, *42*, 1907−1915. (d) Wang, G. W.; Saunders, M.; Khong, A.; Cross, R. J. *J. Am. Chem. Soc.* **2000**, *122*, 3216−3217.

(4) (a) Bauernschmitt, R.; Ahlrichs, R.; Hennrich, F. H.; Kappes, M. M. *J. Am. Chem. Soc.* **1998**, *120*, 5052−5059. (b) Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2001**, *114*, 10362−10367. (c) Sun, G. Y.; Kertesz, M. *Chem. Phys. Lett.* **2000**, *328*, 387−395.

(5) (a) Wang, X. Q.; Wang, C. Z.; Zhang, B. L.; Ho, K. M. *Chem. Phys. Lett.* **1994**, *217*, 199−203. (b) Sun, G. Y.; Kertesz, M. *J. Phys. Chem. A* **2001**, *105*, 5468−5472.

(6) (a) Bettinger, H. F.; Scuseria, G. E. *Chem. Phys. Lett.* **2000**, *332*, 35−42. (b) Furche, F.; Ahlrichs, R. *J. Am. Chem. Soc.* **2002**, *124*, 3804−3805. (c) Sun, G. Y.; Kertesz, M. *J. Phys. Chem. A* **2001**, *105*, 5212−5220. (d) Mizorogi, N.; Aihara, J. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3368−3371.

(7) (a) Kiuchi, M.; Aihara, J. *J. Mol. Struct.: Theochem* **2004**, *685*, 97−100. (b) Sun, G. Y.; Kertesz, M. *Chem. Phys.* **2002**, *276*, 107−114.

(8) (a) Sun, G. Y. *Chem. Phys. Lett.* **2003**, *367*, 26−33. (b) Watanabe, M.; Ishimaru, D.; Mizorogi, N.; Kiuchi, M.; Aihara, J. *J. Mol. Struct.: Theochem.* **2005**, *726*, 11−16.

(9) (a) Sun, G. Y. *Chem. Phys.* **2003**, *289*, 371−380. (b) Slanina, Z.; Zhao, X.; Lee, S. L.; Osawa, E. *Chem. Phys.* **1997**, *219*, 193−200.

(10) Slanina, Z.; Zhao, X.; Deota, P.; Osawa, E. *J. Mol. Model.* **2000**, *6*, 312−317.

(11) Zhao, X.; Slanina, Z.; Goto, H.; Osawa, E. *J. Chem. Phys.* **2003**, *118*, 10534−10540.

(12) (a) Murry, R. L.; Scuseria, G. E. *J. Phys. Chem.* **1994**, *98*, 4212−4214. (b) Zhao, X.; Slanina, Z.; Goto, H. *J. Phys. Chem. A* **2004**, *108*, 4479−4484.

(13) Zhao, X.; Slanina, Z. *J. Mol. Struct.: Theochem.* **2003**, *636*, 195−201.

(14) Zhao, X.; Goto, H.; Slanina, Z. *Chem. Phys.* **2004**, *306*, 93−104.

(15) Achiba, Y.; Fowler, P. W.; Mitchell, D.; Zerbetto, F. *J. Phys. Chem. A* **1998**, *102*, 6835−6841.

(16) (a) Cai, W. S.; Xu, L.; Shao, N.; Shao, X. G.; Guo, Q. X. *J. Chem. Phys.* **2005**, *122*, 184318. (b) Cioslowski, J.; Rao, N.; Moncrieff, D. *J. Am. Chem. Soc.* **2000**, *122*, 8265−8270.

(17) Brinkmann, G.; Dress, A. W. M. *Adv. Appl. Math.* **1998**, *21*, 473−480.

(18) (a) Porezag, D.; Frauenheim, Th.; Köhler, Th.; Seifert, G.; Kaschner, R. *Phys. Rev. B* **1995**, *51*, 12947−12957. (b) Elstner, M.; Porezag, D.; Jungnickel, G.; Elsner, J.; Haugk, M.; Frauenheim, Th.; Suhai, S.; Seifert, G. *Phys. Rev. B* **1998**, *58*, 7260−7268. (c) Albertazzi, E.; Domene, C.; Fowler, P. W.; Heine, T.; Seifert, G.; Van, A. C.; Zerbetto, F. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2913−2918. (d) Fowler, P. W.; Heine, T.; Zerbetto, F. *J. Phys. Chem. A* **2000**, *104*, 9625−9629.

(19) (a) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996,** *77*, 3865−3868. (b) An, W.; Gao, Y.; Bulusu, S.; Zeng, X. C. *J. Chem. Phys.* **2005**, *122*, 204109.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.03; Gaussian, Inc.: Wallingford, CT, 2004.

(21) Fowler, P. W.; Manolopoulos, D. E. *An Atlas of Fullerenes*; Clarendon: Oxford, U.K., 1995.