Theoretical Prediction of Isolable Fullerene Isomers

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Isolable fullerene isomers must be kinetically very or fairly stable. It was found that both the minimum bond resonance energy (min BRE) and the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energy separation are useful for estimating the kinetic stability of fullerene molecules. A fullerene isomer must be difficult to isolate from the arc-produced soot if it has a min BRE of less than $-0.100\ |\beta|$ and/or a HOMO-LUMO energy separation smaller than $0.130\ |\beta|$. All fullerene isomers so far isolated are kinetically stable in this sense. Candidates for isolable fullerene isomers were chosen by evaluating these two indices.

Although many fullerenes are observable immediately after laser vaporization of graphite, most of them cannot be isolated from arc-produced soot.[1—5] This well-known fact manifests that many fullerene molecules are rather comparable in thermodynamic stability but quite different in kinetic stability.[6] By kinetic stability we mean stability with respect to the activated complex of any further clustering or fragmentation reaction.[7] The kinetic stability has a crucial influence on the relative yields of different fullerene isomers. However, it is not easy to estimate the degree of kinetic stability, because it has to do with many possible chemical reactions.

We previously defined the bond resonance energy (BRE)[6,8—11] as the contribution of each π bond to the topological resonance energy (TRE).[12,13] The smallest or minimum BRE in a molecule, abbreviated hereafter as min BRE, usually arises from the most reactive substructure in the molecule. In many cases, the kinetic stability is determined based on the reactivity of the most reactive site in the molecule. Therefore, the min BRE can be used as a practical index of the kinetic stability for cyclic π-electron systems. This index proved to be best suited for justifying the isolated pentagon rule (IPR) for fullerenes.[6,14,15]

The highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energy separation has also been used for predicting the degree of kinetic stability.[7,10,15,16] A large HOMO-LUMO gap can be associated with high kinetic stability because it is energetically unfavorable to add electrons to a high-lying LUMO, and to extract electrons from a low-lying HOMO, and so to form the activated complexes of any potential reaction.[7] At present, fullerene isomers with very small HOMO-LUMO gaps are not isolable, even if they are generated in an arc-discharge reactor.[5]

We found that both the min BRE and the HOMO-LUMO energy separation are necessary to estimate the kinetic stability of fullerene molecules. In this paper, we attempt to predict candidates for isolable IPR isomers of fullerenes with up to 84 carbon atoms by referring to these two indices of kinetic stability and some other factors.

Theoretical Backgrounds

Since the definition of BRE has been described several times,[6,8—11] it is not repeated here. This index represents well the kinetic stability of a molecule in which there are highly reactive substructures. If a min BRE has a large negative value, the molecule is expected to exhibit high chemical reactivity or high kinetic instability somewhere around the very bond. Negative BREs indicate that the CC bonds concerned are the origin of antiaromatic destabilization. For neutral IPR fullerene molecules, in which there are no 5/5 bonds, the min BRE occurs at one or more of the 5/6 bonds. Here, *m*/*n* bonds stand for CC bonds shared by *m*- and *n*-membered rings. Most 6/6 bonds have large positive BREs.

It has been established that IPR-violating fullerenes are kinetically very unstable.[14,15] A 5/5 bond has a large negative BRE, but most others do not.[6,10] In other words, a min BRE has a large negative value if the fullerene molecule violates the IPR. It is such large negative min BREs that sharply distinguish IPR-violating fullerene isomers from most IPR-satisfying ones. This never implies that there are no IPR-satisfying fullerene isomers with large negative min BREs.[10] In general, fullerene molecular cations are kinetically much more unstable than the molecular anions derived from the same fullerene molecule.[8]

The HOMO-LUMO energy separation is indeed a very simple and general index of the kinetic stability for cyclic π-electron systems including fullerenes.[5,7,15,16] Manolopoulos et al. found an interesting correlation between the yields of fullerenes observed immediately after the vaporization of graphite and their HOMO-LUMO energy separations.[7] Recently, Diener and Afford decisively showed that fullerene molecules with small HOMO-LUMO gaps cannot be isolated, even if they are produced by arc synthesis.[5]

We previously pointed out that for IPR isomers of fullerenes, the min BRE is correlative with the HOMO-LUMO energy separation.[10] However, such a correlation is not found for many non-IPR and some IPR fullerene isomers. The HOMO-LUMO energy separation failed to predict the kinetic instability of many non-IPR fullerene isomers. Many non-IPR fullerene isomers have fairly large HOMO-LUMO energy separations.[10] It seems that the HOMO-LUMO energy separation is suited for predicting the kinetic stability of a molecule in which there are no highly reactive sites. In any case, it is safe to say that isolable fullerenes not only have large min BREs, but also large HOMO-LUMO gaps.

Candidates for Isolable Fullerene Isomers

All min BREs and HOMO-LUMO energy separations, calculated with simple Hückel theory, are listed in Tables 1, 2, 3, 4, 5, and 6. Isomer numbers given by Fowler et al.[2,17,18] were used for the convenience of readers. For the molecular geometries of all IPR fullerene isomers studied, see Refs. 2, 17, and 18. The relative energies of the isomers calculated by Fowler et al. using the QCFF/PI model[19—22] are cited in Tables 1, 2, 3, 4, 5, and 6. Note that the Hückel theory cannot be used to estimate the thermodynamic stability of fullerenes because the σ strain contributes substantially to it. The number in parensethese just after every relative energy represents the order of the thermodynamic stability. So far, eleven fullerene isomers have been isolated and identified by ^{13}C NMR spectroscopy.[23—30] They are denoted by asterisks in Tables 1, 2, 3, 4, 5, and 6.

Table 1. Relative Energies, HOMO-LUMO Energy Separations, and min BREs for IPR Isomers of Fullerenes with up to 74 Carbon Atoms

Species	Relative energy	HOMO-LUMO gap/$\|\beta\|$	min BRE
	kJ mol^{-1}		$\|\beta\|$
C_{60} (I_h)* a)	—	0.7566	0.0822
C_{70} (D_{5h})* a)	—	0.5293	0.0519
C_{72} (D_{6d})	—	0.7023	0.0845
C_{74} (D_{3h})	—	**0.1031**	−0.0053

a) Ref. 23.

Table 2. Relative Energies, HOMO-LUMO Energy Separations, and min BREs for IPR Fullerene Isomers of C_{76}

Isomer	Relative energy$^{a)}$	HOMO-LUMO gap/$\|\beta\|$	min BRE
	kJ mol^{-1}		$\|\beta\|$
1 (T_d)	59 (2)	**0.0000**	**−0.1086**
2 (D_2)* b)	0 (1)	0.3436	0.0074

a) Ref. 20. b) Ref. 24.

Table 3. Relative Energies, HOMO-LUMO Energy Separations, and min BREs for IPR Fullerene Isomers of C_{78}

Isomer	Relative energy$^{a)}$	HOMO-LUMO gap/$\|\beta\|$	min BRE
k	kJ mol		$\|\beta\|$
1 (D_3)* b,c)	43.5 (4)	0.2532	−0.0098
2 (C_{2v})* b,c)	25.9 (3)	0.3481	−0.0440
3 (C_{2v})* c)	0.0 (1)	0.1802	−0.0887
4 (D_{3h})	87.4 (5)	0.6333	0.0795
5 (D_{3h})	10.5 (2)	**0.0730**	**−0.1470**

a) Ref. 22. b) Ref. 25. c) Ref. 26.

Table 4. Relative Energies, HOMO-LUMO Energy Separations, and min BREs for IPR Fullerene Isomers of C_{80}

Isomer	Relative energy$^{a)}$	HOMO-LUMO gap / $\|\beta\|$	min BRE
	kJ mol^{-1}		$\|\beta\|$
1 (D_{5d})	1.3 (2)	**0.0728**	−0.0681
2 (D_2)* b)	0.0 (1)	0.1749	−0.0368
3 (C_{2v})	11.4 (3)	**0.0338**	**−0.1526**
4 (D_3)	75.6 (6)	0.1351	−0.0175
5 (C_{2v})	29.3 (4)	**0.0987**	**−0.1192**
6 (D_{5h})	42.9 (5)	**0.0000**	**−0.1247**
7 (I_h)	143.8 (7)	**0.0000**	**−0.1479**

a) Ref. 21. b) Ref. 27.

Table 5. Relative Energies, HOMO-LUMO Energy Separations, and min BREs for IPR Fullerene Isomers of C_{82}

Isomer	Relative energy$^{a,b)}$	HOMO-LUMO gap/$\|\beta\|$	min BRE
	kcal mol^{-1}		$\|\beta\|$
1 (C_2)	5.7 (3)	0.1495	−0.0607
2 (C_s)	6.1 (4)	0.3313	0.0096
3 (C_2)* c)	0.0 (1)	0.2568	−0.0405
4 (C_s)	3.8 (2)	0.2450	−0.0314
5 (C_2)	6.9 (5)	**0.1300**	**−0.1172**
6 (C_s)	9.7 (6)	**0.0683**	**−0.1619**
7 (C_{3v})	25.1 (9)	**0.0000**	**−0.2412**
8 (C_{3v})	23.7 (8)	**0.0467**	**−0.1883**
9 (C_{2v})	13.0 (7)	**0.0160**	**−0.2266**

a) 1 kcal mol^{-1} = 4.184 kJ mol^{-1}. b) Ref. 19. c) Refs. 26 and 39.

First, some general aspects of higher fullerenes are surveyed. Isolable fullerene molecules must be not only kinetically, but also thermodynamically, stable. The thermodynamically most unstable isomer so far isolated may be isomer **4** (D_{2d}) of C_{84} in Table 6. This isomer is 111 kJ mol^{-1} higher in energy than the lowest-energy isomer, **22** (D_2). Thus, it is difficult to say how thermodynamically stable isolable fullerene isomers are. It is highly desirable that isolable fullerene isomers are located at the global or local minima in the Stone–Wales interconversion map.[17,31,32] In fact, high-energy isomer **4** of C_{84} is located at the local minimum in the interconversion map.[31,32]

We have presumed that fullerene isomers with a min BRE less than $-0.100\ |\beta|$ must be kinetically very unstable, and labile in the arc-discharge reactor.[6,8—11] At present, there are no exceptions to this presumption. IPR fullerene isomers whose min BREs are less than $-0.100\ |\beta|$ are supposed to be comparable in reactivity to non-IPR ones, which generally have min BREs of less than $-0.100\ |\beta|$.[6,10] Most of them have small HOMO-LUMO energy separations. The

Table 6. Relative Energies, HOMO-LUMO Energy Separations, and min BREs for IPR Fullerene Isomers of C_{84}

Isomer	Relative energy[a)] kJ mol^{-1}	HOMO-LUMO gap/$\|\beta\|$	min BRE $\|\beta\|$
1 (D_2)	255.3 (24)	0.6143	0.0819
2 (C_2)	185.3 (23)	0.3523	-0.0390
3 (C_s)	155.1 (22)	**0.0191**	**-0.1615**
4 (D_{2d})* [b)]	111.1 (16)	0.3519	0.0108
5 (D_2)	119.0 (17)	0.2403	-0.0574
6 (C_{2v})	74.0 (12)	0.1892	-0.0414
7 (C_{2v})	101.0 (14)	0.1892	-0.0748
8 (C_2)	121.0 (19)	0.1776	-0.0119
9 (C_2)	120.8 (18)	**0.0556**	**-0.1561**
10 (C_s)	153.2 (21)	**0.0916**	-0.0725
11 (C_2)	34.5 (6)	0.2540	-0.0501
12 (C_1)	51.5 (7)	0.2164	-0.0415
13 (C_2)	102.6 (15)	**0.0988**	**-0.1473**
14 (C_s)	68.4 (10)	0.4054	0.0202
15 (C_s)	52.6 (8)	0.2191	-0.0732
16 (C_s)	28.4 (4)	0.3369	-0.0316
17 (C_{2v})	78.5 (13)	0.1745	**-0.1084**
18 (C_{2v})	60.3 (9)	0.3285	-0.0543
19 (D_{3d})	28.9 (5)	0.1861	-0.0702
20 (T_d)	123.2 (20)	0.6962	0.0771
21 (D_2)	69.5 (11)	0.1381	-0.0401
22 (D_2)* [c)]	0.0 (1)	0.3449	-0.0254
23 (D_{2d})* [c)]	1.8 (2)	0.3449	-0.0564
24 (D_{6h})	24.7 (3)	0.5293	0.0351

a) Ref. 21. b) Refs. 29 and 30. c) Refs. 26 and 28.

min BREs less than -0.100 $|\beta|$ are indicated in boldface in Tables 2, 3, 4, 5, and 6.

Besides, it should be noted that fullerene isomers with a HOMO-LUMO energy separation of less than 0.170 $|\beta|$ have not been isolated, even if their min BREs are larger than -0.100 $|\beta|$. The smallest HOMO-LUMO energy separation among the fullerene isomers so far isolated is 0.1749 $|\beta|$ for isomer **2** (D_2) of C_{80}. Therefore, fullerene isomers with the HOMO-LUMO energy separation less than 0.130 $|\beta|$ will tentatively be presumed to be kinetically very unstable. This critical value was chosen in such a manner that the number of species with the HOMO-LUMO gap less than this value is close to that of species with the min BRE less than -0.100 $|\beta|$. The values of the HOMO-LUMO gap less than 0.130 $|\beta|$ are indicated in boldface in Tables 1, 2, 3, 4, 5, and 6.

It now is reasonable to say that if a fullerene isomer has a min BRE larger than -0.100 $|\beta|$ and/or a HOMO-LUMO energy separation larger than 0.130 $|\beta|$, it must be kinetically stable and has a large possibility of surviving the harsh synthetic process. It goes without saying that isolable fullerenes should not be thermodynamically very unstable. We are ready to choose isolable species from the list of IPR fullerene isomers.

C_{60} (I_h) and C_{70} (D_{5h}) are produced in the highest yields by arc synthesis.[1—4,23] Table 1 shows that their min BREs are positive in sign, indicating that all CC bonds in the two molecules have positive BREs.[6,8] All CC bonds contribute more or less to the TRE or to the aromatic stabilization of the molecule. In addition, both have large HOMO-LUMO energy separations. C_{60} and C_{70} have no other IPR fullerene isomers.

C_{72} (D_{6d}) and C_{74} (D_{3h}) have not been isolated, although their min BREs are larger than -0.100 $|\beta|$. The failure to isolate these molecules cannot be explained in terms of the min BRE. The binding energy per carbon atom of C_{72} (D_{6d}) is small compared to those of C_{70} (D_{5h}) and C_{74} (D_{3h}).[33,34] It is said that C_{72} (D_{6d}) is unstable because it has two quasi-planar coronene substructures.[35,36] There is evidence that C_{74} (D_{3h}) is generated on a macroscopic scale, but cannot be isolated from the soot.[5] The kinetic instability of this molecule is consistent with its very small HOMO-LUMO energy separation. No other IPR fullerene isomers are conceivable for C_{72} and C_{74}.

As shown in Table 2, C_{76} has two possible IPR fullerene isomers.[2,17] One of them, isomer **2** (C_2), is lower in energy with a positive min BRE and a fairly large HOMO-LUMO gap, so has naturally been isolated.[24] In contrast, isomer **1** (T_d) is a bit higher in energy with a min BRE smaller than -1.00 $|\beta|$. This isomer has no HOMO-LUMO energy gap as the HOMOs and the LUMOs are degenerate. According to our chemical common sense, molecules with no HOMO-LUMO gap are extremely reactive.

Five IPR fullerene isomers conceivable for C_{78} are listed in Table 3.[2,17] Isomers **1** (D_3), **2** (C_{2v}), and **3** (C_{2v}) have been isolated.[25,26] The min BREs of these three isomers are larger than -0.100 $|\beta|$. Their HOMO-LUMO gaps are much larger than 0.130 $|\beta|$. Isomer **5** (D_{2h}) is comparable in energy to isomers **1** and **2**, but must be difficult to isolate because its min BRE is smaller than -0.100 $|\beta|$. Its HOMO-LUMO energy separation is also very small. Isomer **4** (D_{3h}) has the largest min BRE and the largest HOMO-LUMO energy separation among the IPR isomers of C_{78}. All of the CC bonds in this isomer contribute to the aromaticity of the molecule. However, since this is the highest-energy isomer, it must be generated in a much smaller yield.

Wakabayashi et al. observed that the relative yields of C_{78} fullerene isomers are very sensitive to the conditions in the reaction chamber.[37] When the He pressure in the arc-discharge reactor is as low as 10 Torr (1 Torr = 133.322 Pa), isomers **1** (D_3) and **2** (C_{2v}) are obtainable, but **3** (C_{2v}) is not. Note that isomer **3** is the lowest energy isomer. However, if the He pressure is raised up to 200 Torr, isomer **3** is generated in the highest yield. This seems to reflect not only its highest thermodynamic stability, but also its fairly large negative min BRE. Isomer **3** has the second smallest HOMO-LUMO gap among the isolated fullerene isomers.

C_{80} has seven possible IPR fullerene isomers,[2,17] which are listed in Table 4. All IPR fullerene isomers of C_{80} are predicted to be kinetically very or fairly unstable. Four of them, isomers **3** (C_{2v}), **5** (C_{2v}), **6** (D_{5h}), and **7** (I_h), have large negative min BREs and very small HOMO-LUMO energy separations. These must be difficult to isolate even if they are generated at all. Isomers **6** and **7** have no HOMO-LUMO gaps. Isomer **2** (D_2), which is the lowest-energy isomer with a small negative min BRE, was isolated rather recently.[27] The HOMO-LUMO energy separation of this isomer is the smallest among the isolated fullerene isomers. Its yield is very low in harmony with its fairly small HOMO-LUMO gap. Isomer **4** (D_3) with a positive min BRE may be isolable, although the HOMO-LUMO gap is fairly small. The HOMO-LUMO gap of isomer **1** (D_{5d}) is very small, so must be difficult to isolate.

As shown in Table 5, C_{82} has nine possible IPR fullerene isomers.[2,17] One of the three isomers with C_2 symmetry was isolated from the soot extract.[26,38] It was idientified as **3** (C_2) by tenperature-dependent molecular orbital calculations.[39] The present study supports this identification. Isomer **3** is the lowest in energy with a small negative min BRE and a fairly large HOMO-LUMO gap. Five of the remaining isomers [**5** (C_2), **6** (C_s), **7** (C_{3v}), **8** (C_{3v}), and **9** (C_{2v})], have large negative min BREs and very small HOMO-LUMO energy separations. Isomer **7** has no HOMO-LUMO gap. Therefore, these must be difficult to isolate. Isomers **1** (C_2), **2** (C_s), and **4** (C_s) are predicted to be kinetically fairly stable. Although isomers **2** and **4** are as low in energy as isomer **3**, these three are interrelated with each other via Stone–Wales rearrangements.[32] Isomer **1** is located at the shallow local minimum in the interconversion map.[32]

Twenty-four IPR fullerene isomers are conceivable for C_{84},[2,18] all of which are listed in Table 6. In 1992 isomers **22** (D_2) and **23** (D_{2d}) were isolated as major C_{84} products.[26,28] They are lowest energy isomers and are, of course, located at the global energy minimum in the Stone–Wales interconversion map.[18,32] These isomers have min BREs larger than $-0.100\ |\beta|$ and fairly large HOMO-LUMO energy separations. Apart from C_{60} (I_h) and C_{70} (D_{5h}), they are the IPR fullerene isomers obtainable in the highest yield. This fact is consistent with their relatively large binding energies per carbon atom, which are larger than those of the lowest energy C_{82} and C_{86} isomers.[33,34]

Isomer **4** (D_{2d}) of C_{84} was recently isolated and identified by ^{13}C NMR spectroscopy.[29,30] The presence of this isomer had been suggested by the ^{3}He endohedral chemical shifts of C_{84} fullerene isomers.[40] As pointed out by Osawa et al.,[32] **4** is fairly high in energy, but it is located at the local energy minimum in the Stone–Wales interconversion map. The min BRE is positive in sign, indicating that all of the constituent CC bonds contribute to the aromaticity of the molecule. Its HOMO-LUMO energy separation is fairly large.

Among the IPR fullerene isomer of C_{84}, **3** (C_s), **9** (C_2), **13** (C_2), and **17** (C_{2v}) of C_{84} have large negative BREs. Isomers **3**, **9**, **10** (C_s), and **13** have very small HOMO-LUMO gaps. These have not been isolated from the soot extract, and must be difficult to isolate if they are generated in the reactor. Thus, it is only six out of 24 possible IPR fullerene isomers that have large negative BREs and/or small HOMO-LUMO energy separations. All other isomers are kinetically stable and have a possibility of being isolable. In fact, there still are many fullerene isomers of C_{84} that will possibly be isolated in the near future.[41,42] C_{84} has no IPR fullerene isomers with no HOMO-LUMO gap.

According to Achiba and others.,[29,30,38,43] two fullerene isomers of C_2 symmetry and one isomer of D_2 symmetry were isolated as minor C_{84} products, but their molecular structures have not been determined. C_{84} fullerene has five IPR isomers of C_2 symmetry, namely, isomers **2**, **8**, **9**, **11**, and **13**. Since two of them, **9** and **13**, not only have large negative min BREs, but also small HOMO-LUMO gaps, the isolated C_2 species must be chosen from isomers **2**, **8**, and **11**. Isomer **11** may be isolable, because it is low in energy and located near to the local energy minimum in the Stone–Wales interconversion map.[32] However, isomers **2** and **8** are high in energy and not located at the local energy minima.[18,32] For the moment, we cannot decide which of the two will be isolated preferentially.

C_{84} has four isomers of D_2 symmetry (**1**, **5**, **21**, and **22**), the last of which has already been isolated and identified. Isomer **1** is the highest energy IPR isomer, and is necessarily located at the energy maximum in the Stone–Wales interconversion map.[18,32] It is thus highly probable that the D_2 isomer, isolated but unidientified, is isomer **5**.[32] Although it is as high in energy as isomer **4**, it is likewise located at the local energy minimum in the interconversion map. Isomer **21** is fairly high in energy and not located at the energy minimum.[18,32]

Interestingly, some IPR fullerene isomers are predicted to be kinetically as stable as C_{60} (I_h). Among them are isomers **1** and **20** (T_d) of C_{84}. C_{72} (D_{5h}) and isomer **4** of C_{78} belong to this group, too. These fullerene isomers not only have positive min BREs values, but also large HOMO-LUMO energy separations, comparable to those of C_{60} (I_h). These molecules are highly symmetric in geometry, and have multiply degenerate HOMOs completely filled with π electrons. Unfortunately, none of them have been isolated, at least as major products, because they are not thermodynamically very stable. Except for C_{72} (D_{5h}), they are not located at the energy minima in the interconversion maps.[17,18,32]

Concluding Remarks

There have been a couple of problems with regard to the kinetic stability of fullerene molecules. The IPR cannot be explained in terms of the HOMO-LUMO gap, whereas the failure to isolate some IPR fullerene isomers, such as C_{74} (D_{3h}), cannot be predicted from their min BREs. As has shown above, the HOMO-LUMO gap alone or the min BRE alone is not sufficient for predicting the kinetic stability of fullerene isomers. When both the min BRE and the HOMO-LUMO energy separation are taken into account, candidates for isolable fullerene isomers can be narrowed down effectively. Both indices can be calculated very easily, even for very large π-electron systems, such as much higher fullerenes and carbon nanotubes.

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