

# Weighted HOMO-LUMO energy separations of properly closed-shell fullerene isomers

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*The HOMO–LUMO energy separation has been used as an index of kinetic stability for fullerenes. However, its utility is rather limited, in that a larger fullerene molecule in general has a smaller HOMO–LUMO energy separation even if it is kinetically stable. The T value, i.e., the HOMO–LUMO energy separation weighted with the number of carbon atoms, is free from this kind of difficulty. Properly closed-shell isomers of fullerenes with antibonding LUMOs were found to have an exceptionally large T value irrespective of the number of constituent carbon atoms and are hence predicted to be kinetically very stable. Thus, the antibonding character of the LUMOs is one of the determinants for kinetically stabilizing fullerene molecules. © 2001 by Elsevier Science Inc.*

## INTRODUCTION

The energy separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) has been used as a simple index of kinetic stability for fullerenes.<sup>1–6</sup> By kinetic stability, we mean stability against all possible chemical reactions and decomposition. It is true that fullerenes with no or very small HOMO–LUMO energy separation have not been isolated.<sup>3,5,6</sup> However, a closing of the HOMO–LUMO gap is to be expected for larger fullerenes as the number of hexagonal faces in the polyhedron increases and the graphite limit is approached.<sup>7,8</sup> Larger fullerenes in general have a smaller HOMO–LUMO energy separation even if they are kinetically stable.

Fowler et al. found that some limited types of fullerene isomers have a relatively large HOMO–LUMO energy separation,

together with antibonding or nonbonding LUMOs.<sup>8–11</sup> Typically, such fullerene isomers are called leapfrogs.<sup>4,8–10</sup> Fowler and Manolopoulos pointed out that, as the size of a fullerene cage increases, the HOMO–LUMO energy gap will become very small and then the distinction between leapfrogs and other closed-shell isomers and even between open and closed shells will be blurred.<sup>8</sup> Therefore, the HOMO–LUMO energy separation is not always suitable for predicting the degree of kinetic stability.

We previously reported that the T value, i.e., the HOMO–LUMO energy separation multiplied by the number of carbon atoms, is preferred as an index of kinetic stability.<sup>12–15</sup> All fullerene isomers that have been isolated so far have a T value >13.0.<sup>12,15</sup> Fullerenes with a large T value have a large minimum bond resonance energy.<sup>15</sup> In this article, we show that isolated-pentagon fullerene isomers with antibonding LUMOs have a very large T value, irrespective of the size of the molecule, and thus are predicted to be kinetically very stable. All T values were calculated using Hückel molecular orbital theory.

## ISOLATED-PENTAGON ISOMERS AND THEIR T VALUES

The T values for isolated-pentagon isomers of fullerenes with N = 120 are summarized in Table 1, where N is the number of constituent carbon atoms.<sup>13</sup> Most isolated-pentagon isomers have a pseudo-closed electronic shell with bonding LUMOs.<sup>16</sup> For example, 10,729 out of 10,774 isolated-pentagon isomers of C<sub>120</sub> have a pseudo-closed shell and have a relatively small T value. For isolated-pentagon isomers of C<sub>120</sub>, the T value lies in the range of 0.0–74.4. Thus, the T value varies very widely among the isolated-pentagon isomers. However, their average is as small as 13.7, reflecting the large proportion of pseudo-closed shell isomers.<sup>13</sup>

The T value can likewise be calculated for the polyene reference defined using a matching polynomial for any fullerene molecule.<sup>12,14</sup> The T value is very small for the

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**Table 1. T values for isolated-pentagon isomers of fullerenes with up to 120 carbon atoms**

N	number of isolated-pentagon isomers	T value		
		min <sup>a</sup>	max <sup>b</sup>	average
60	1	45.4 (0)	45.4 (1)	45.4
70	1	37.1 (0)	37.1 (0)	37.1
72	1	50.6 (0)	50.6 (1)	50.6
74	1	7.6 (0)	7.6 (0)	7.6
76	2	0.0 (1)	26.1 (0)	13.1
78	5	5.7 (0)	49.4 (1)	23.2
80	7	0.0 (2)	14.0 (0)	5.9
82	9	0.0 (1)	27.2 (0)	11.3
84	24	1.6 (0)	58.5 (2)	22.9
86	19	0.4 (0)	35.1 (0)	12.4
88	35	0.0 (1)	33.1 (0)	12.2
90	46	0.6 (0)	58.5 (3)	21.1
92	86	0.1 (0)	42.3 (0)	14.1
94	134	0.0 (3)	37.0 (0)	13.6
96	187	0.0 (1)	61.6 (6)	17.8
98	259	0.2 (0)	39.4 (0)	13.8
100	450	0.0 (4)	38.3 (0)	13.7
102	616	0.0 (1)	63.7 (6)	14.6
104	823	0.0 (1)	42.3 (0)	12.9
106	1233	0.0 (9)	40.4 (0)	13.1
108	1799	0.0 (2)	64.0 (15)	13.5
110	2355	0.0 (1)	43.4 (0)	12.9
112	3342	0.0 (8)	43.8 (1)	13.4
114	4468	0.0 (1)	67.2 (17)	13.6
116	6063	0.0 (3)	46.8 (1)	13.4
118	8148	0.0 (9)	45.3 (0)	13.4
120	10774	0.0 (4)	74.4 (41)	13.7

<sup>a</sup> Values in parentheses are the numbers of isolated-pentagon isomers with no HOMO-LUMO gap.

<sup>b</sup> Values in parentheses are the numbers of isolated-pentagon isomers with antibonding LUMOs.

polyene references. Those for the polyene references of fullerenes with  $60 \leq N \leq 100$  lie in the very narrow range 6.70–7.43.<sup>14</sup> This implies that these polyene references must really be olefinic and similar in chemical reactivity to each other. Thus, the T value can be regarded as an index of kinetic stability normalized with respect to the size of a conjugated system. The average T value for all isolated-pentagon isomers of C<sub>120</sub> (13.7) is about twice as large as that for the polyene references. It follows that most of the isomers must be less reactive than their polyene references.

A very small number of fullerene isomers have a properly closed-shell electronic configuration, in the sense that the LUMOs are antibonding or nonbonding.<sup>16</sup> Proper closed-shell isomers consist of leapfrogs, cylindrical closed shells, and sporadic closed shells.<sup>8–11</sup> Their T values are examined below.

### Leapfrog Isomers

Any fullerene isomer can, by leapfrogging, be converted into a closed-shell molecule with three times as many carbon at-

oms.<sup>4,8–10</sup> Whether a starting fullerene has a closed shell or not, its leapfrog always has a properly closed shell. C<sub>60</sub>:1 is the smallest leapfrog fullerene. Here, the number just after the colon is the isomer number given by Fowler and Manolopoulos.<sup>16</sup> We found that leapfrog isomers of fullerenes have, without exception, a very large T value. The T values for leapfrogs with N = 120 are presented in Table 2. For fullerenes that have leapfrog isomers, the isolated-pentagon isomer with the largest T value is always a leapfrog.

For example, C<sub>120</sub> has only 40 leapfrog isomers.<sup>8</sup> Their T values lie in the range of 44.5–74.4, the average being 64.0. Thus, the leapfrogs are very rare but have a very large T value. Considering that the polyene references have a T value of ~7, these leapfrogs are presumed to be chemically much less reactive. All leapfrog isomers of all fullerenes are likewise predicted to be kinetically very stable. It is interesting to note that for leapfrogs the T value tends to increase as the number of carbon atoms increases. At present we have no explanation for this aspect of the T value.

As has just been seen, the main difficulty with the use of the HOMO–LUMO energy separation can be avoided by weighting it with the number of carbon atoms. By using the T value, a marked distinction in kinetic stability can be appreciated between leapfrogs and other isomers and between properly closed and pseudo-closed shells. We previously reported that the T values can be used to classify the degrees of kinetic stability of polycyclic aromatic hydrocarbons (PAHs).<sup>17</sup>

### Icosahedral Closed-Shell Isomers.

Fullerene isomers with I<sub>h</sub> symmetry have a closed-shell electronic configuration if N is a multiple of 60.<sup>8,18–20</sup> They all are leapfrogs. C<sub>60</sub>:1 again is the smallest member in this group.<sup>8</sup> Tang and Huang evaluated the HOMO–LUMO energy gaps of such icosahedral closed-shell fullerenes with up to 37,500 carbon atoms.<sup>20</sup> The T values calculated using their result are listed in Table 3.

Icosahedral closed-shell fullerene isomers have not only quintuply degenerate HOMOs but also triply degenerate LUMOs.<sup>18</sup> Quintuply degenerate HOMOs in such an isomer must be lower in energy than the nondegenerate HOMO in many

**Table 2. T values for leapfrog isomers of fullerenes with N ≤ 120**

N	number of leapfrog isomers	HOMO-LUMO gaps <sup>a</sup> / β	T values	
			T values	average T value
60	1	0.7566	45.4	45.4
72	1	0.7023	50.6	50.6
78	1	0.6333	49.4	49.4
84	2	0.6143–0.6962	51.6–58.5	55.0
90	3	0.4989–0.6499	44.9–58.5	52.4
96	6	0.5173–0.6418	49.7–61.6	56.4
102	6	0.5466–0.6249	55.8–63.7	60.1
108	15	0.4819–0.5929	52.0–64.0	60.0
114	17	0.4409–0.5895	50.3–67.2	61.7
120	40	0.3707–0.6201	44.5–74.4	64.0

<sup>a</sup> Reference 8.

**Table 3. T values for selected icosahedral closed-shell isomers of fullerenes**

N	HOMO-LUMO gap <sup>a</sup> /  $\beta$	T value	N	HOMO-LUMO gap <sup>a</sup> /  $\beta$	T value
60	0.7566	45.4	10140	0.0896	909
240	0.4964	119	13500	0.0778	1050
540	0.3578	193	17340	0.0687	1190
1500	0.2256	338	21660	0.0615	1330
2940	0.1638	482	26460	0.0557	1470
4860	0.1284	624	31740	0.0509	1620
7260	0.1056	767	37500	0.0469	1760

<sup>a</sup> Reference 20.

other isomers, since the average energy of the five uppermost occupied molecular orbitals will not vary markedly. Likewise, triply degenerate LUMOs must be higher in energy than the nondegenerate LUMO in many other isomers. Therefore, the HOMO–LUMO gap must be much larger if the HOMOs and/or the LUMOs are highly degenerate. This must be the primary reason that  $I_h$  closed-shell isomers have a large T value. In fact, the density of  $\pi$ -molecular orbitals is very small near the HOMOs and the LUMOs in the  $\pi$ -energy level diagrams.<sup>18</sup>

Like other leapfrog isomers summarized in Table 2, the T value of icosahedral closed-shell fullerene increases in rough proportion to the square root of N. This is consistent with the observation made by Liu et al. that for leapfrog isomers the average HOMO–LUMO gap energy is inversely proportional to the square root of N.<sup>4</sup> A similar trend in the magnitude of the T value has been observed for some kinetically stable series of PAHs, such as zigzag polyacenes.<sup>17</sup> They all are kinetically very stable species.

### Sporadic Closed-Shell Isomers

In addition to leapfrogs, there are occasional closed-shell fullerene isomers with antibonding LUMOs. These isomers are called sporadic closed-shell isomers.<sup>8</sup> There are 48 sporadic closed-shell isomers in the range of  $112 \leq N \leq 140$ , most of which are of  $C_1$  symmetry, being less symmetric than most of the leapfrogs.<sup>8</sup> The T values calculated for these fullerene isomers are given in Table 4. There are no such isomers for fullerenes with  $N \leq 110$ .

The T values for sporadic closed-shell isomers are again larger than 40, but seem to be somewhat small compared with those for leapfrog isomers with the same number of carbon atoms. This is probably because the LUMOs of these isomers are very close to the nonbonding level.<sup>8</sup> All LUMOs for the isomers listed in Table 4 are lower in energy than  $\alpha - 0.030 \beta$ , where  $\alpha$  and  $\beta$  are the Coulomb integral for a carbon  $2p_z$  orbital and the resonance integral between two adjacent such orbitals, respectively. This is in marked contrast to, say, leapfrog isomers of  $C_{120}$ , for which the LUMOs are higher in energy than  $\alpha - 0.060 \beta$ .<sup>8</sup>

### Cylindrical Closed-Shell Isomers

Fowler et al. noted that two types of cylindrical fullerene isomers have a closed-shell electronic configuration with non-

**Table 4. T values for sporadic closed-shell isomers of fullerenes with  $N \leq 140$** 

N	Number of sporadic closed- shell isomers	HOMO-LUMO gaps <sup>a</sup> /  $\beta$	T values	average T value
112	1	0.3645	40.8	40.8
116	1	0.3626	42.1	42.1
120	1	0.3643	43.7	43.7
122	1	0.3648	44.5	44.5
124	3	0.3604–0.3910	44.7–48.5	46.7
128	3	0.3493–0.3837	44.7–49.1	46.6
130	3	0.3689–0.3834	48.0–49.8	48.7
132	4	0.3504–0.3753	46.3–49.5	48.0
134	7	0.3356–0.3793	45.0–50.8	48.8
136	9	0.2301–0.3783	31.3–51.4	47.3
138	4	0.3480–0.3675	48.0–50.7	49.6
140	12	0.3404–0.3745	47.7–52.4	50.1

<sup>a</sup> Reference 8.

bonding LUMOs.<sup>8,11</sup> Their molecular structures can be constructed in the following manner. First, fullerenes with fivefold and sixfold symmetry are formed by expansion of  $C_{40}$ :**39** and  $C_{48}$ :**186** with a belt of 5k and 6k hexagons at the equator, respectively, where k is the arbitrary integer. Insertion of hexagons, one belt of five or six hexagonal rings at a time, makes the cylindrical portion of the fullerene larger, leaving the caps unchanged.<sup>8</sup> With every third added belt, a closed shell with a nonbonding LUMO is produced. The smallest members in these two series are  $C_{70}$ :**1** and  $C_{84}$ :**24**.

Fowler evaluated the HOMO–LUMO energy gaps for such cylindrical closed-shell species.<sup>11</sup> The T values obtained using his result are listed in Table 5. These T values are larger than 30, but are appreciably smaller than those for leapfrogs of similar size.<sup>11</sup> This may possibly be associated with the nonbonding LUMO, which is no doubt lower in energy than the antibonding one. Furthermore, the energy of the nondegenerate

**Table 5. T values for cylindrical closed-shell isomers of fullerenes with a nonbonding LUMO**

fivefold symmetry ( $D_{5h}$ or $D_{5d}$ )			sixfold symmetry ( $D_{6h}$ or $D_{6d}$ )		
N	HOMO-LUMO gap <sup>a</sup> /  $\beta$	T value	N	HOMO-LUMO gap <sup>a</sup> /  $\beta$	T value
70	0.529	37.0	84	0.529	44.4
100	0.350	35.0	120	0.350	42.0
130	0.260	33.8	156	0.260	40.6
160	0.207	33.1	192	0.207	39.7
190	0.171	32.5	228	0.171	39.0
220	0.146	32.1	264	0.146	38.5
250	0.127	31.8	300	0.127	38.1

<sup>a</sup> Reference 11.

HOMO must be more or less high. Thus, cylindrical closed-shell isomers must be kinetically less stable than leapfrog isomers. However, they are still predicted to be kinetically stable enough to survive the harsh synthetic conditions if they are generated in macroscopic amounts.

The T value of a cylindrical closed-shell isomer decreases gradually with increasing number of carbon atoms. This reminds us of the fact that higher members of PAH with a periodic structure have a smaller T value if the corresponding infinite benzenoid polymer has no band gap.<sup>17</sup> For example, higher members of linear polyacene have smaller T values as infinite polyacene has no band gap. If one uses Hamada's nomenclature of carbon nanotubes,<sup>21</sup> cylindrical portions of the cylindrical closed-shell isomers with fivefold and sixfold symmetry are identical with metallic tubules (5,5) and (6,6), respectively. The absence of a band gap in these tubules may possibly be related to the diminished T values for larger cylindrical closed-shell isomers.

## CONCLUSIONS

Thermodynamic stability of a fullerene cage increases as the size increases.<sup>22,23</sup> That is, the binding energy per carbon atom increases as the number of carbon atoms increases. However, most isomers of fullerenes cannot be isolated from the arc-produced soot irrespective of their cage size. This clearly indicates that thermodynamically stable fullerene isomers are not always kinetically stable.

As has been seen, fullerene isomers with antibonding LUMOs are characterized by a T value > 40. These isomers must be kinetically very stable, however stable they might be thermodynamically. Even the T value of 40 is six times as large as those for the polyene references. Thus, the antibonding character of the LUMO seems to be one of the determinants for kinetically stabilizing fullerene cages. The contribution of these properly closed-shell isomers to the average T value should not be overestimated because they are very small in number.

We have hypothesized that the kinetic stability of a fullerene molecule is determined mainly by the  $\pi$ -electronic system. This has been supported by the practical utility of the T value for many fullerenes and PAHs.<sup>12,13,15,17</sup> In fact, all isolable fullerene isomers have a fairly large T value.<sup>12,15</sup> However, the converse is not always true. Typical leapfrogs such as C<sub>72</sub>:1, C<sub>78</sub>:4, C<sub>84</sub>:1, and C<sub>84</sub>:20 have not been isolated from the soot made in the arc reactor, although their T values are very large. This suggests that some other factors, such as thermodynamic stability,<sup>22,23</sup> strain,<sup>2,24,25</sup> and kinetic control of synthetic routes,<sup>26,27</sup> must also be considered to complement the discussion based solely on the T value.

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