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Weighted HOMO-LUMO energy separation as an index of kinetic stability for fullerenes*

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Abstract. A very simple but general index of kinetic stability, *T*, is proposed for π-electron systems, which is defined as a highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy separation multiplied by the number of conjugated atoms. This new index can be justified by relating it to the approximate form of the superdelocalizability, an index of chemical reactivity defined by Fukui et al. It is best suited for predicting the kinetic stability of fullerenes. All isolable fullerene isomers have *T* values larger than 13.

Key words: Fullerenes – Polyene reference – Kinetic stability – HOMO-LUMO gap – HMO theory

1 Introduction

Although many fullerenes are observable immediately after vaporization of graphite, most of them cannot be isolated from fullerite soot [1–3]. This well-known fact manifests that many fullerene molecules are rather comparable in thermodynamic stability but quite different in kinetic stability [4]. By kinetic stability we mean stability with respect to the activated complex of any further clustering or fragmentation reaction [5]. Kinetic stability has a crucial influence on the relative yields of different fullerene isomers. However, the kinetic stability of fullerenes is still poorly understood. It is not easy to estimate the degree of kinetic stability because it concerns innumerable chemical reactions.

The highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy separation has been used as a conventional measure of kinetic stability [6–10]. A large HOMO-LUMO gap can be associated with high kinetic stability because it is energetically unfavourable to add electrons to a high-lying LUMO and extract electrons from a low-lying HOMO, so forming the activated complexes of any potential reaction [5]. For planar polycyclic benzenoid hydrocarbons, a HOMO-LUMO gap is highly correlative with the Hess-Schaad resonance energy per π electron, a measure of thermodynamic stability due to cyclic conjugation [11–13]. This correlation implies that thermodynamically stable benzenoid systems are kinetically stable.

For spherical and spheroidal fullerene molecules, the energies of π-molecular orbitals calculated with a Hückel molecular orbital (HMO) method are highly correlative with those calculated using more sophisticated self-consistent field (SCF) molecular orbital methods [14]. Therefore, the kinetic stability of fullerenes has often been discussed in terms of the HOMO-LUMO gaps calculated using HMO theory [5, 7–10, 15]. Indeed, fullerene isomers with very small HOMO-LUMO gaps have not been isolated [5, 7, 10]. However, it is true that even kinetically stable species are not isolable if they are not thermodynamically stable [16]. HMO theory cannot be used to estimate the thermodynamic stability of fullerenes because σ strain contributes substantially to the thermodynamic stability [17].

In 1991, Fowler pointed out that a HOMO-LUMO energy separation is not always suited for predicting the kinetic stability of fullerenes [9]. As the cage size increases, the ratio of hexagonal to pentagonal rings increases but the HOMO-LUMO gap must decrease, in line with the semi-metallic nature of graphite. Thus, the HOMO-LUMO gap cannot be used as an index of kinetic stability for graphite. We found that the HOMO-LUMO energy separation can be modified to avoid this kind of difficulty. The modified index we propose in this paper is a HOMO-LUMO gap multiplied by the number of conjugated atoms. We show below that this weighted HOMO-LUMO energy separation can be interpreted as a general index of kinetic stability for fullerenes. All formulation is made within the framework of simple HMO theory.

2 Theory

In 1954 Fukui et al. derived a novel index of reactivity, called the superdelocalizability, by application of per-

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turbation theory to a model in which the incoming group forms a weak π bond to atom r of a given π-electron system [18–20]. This index stresses the importance of the HOMO and the LUMO for electrophilic and nucleophilic reactions, respectively. The superdelocalizabilities for electrophilic and nucleophilic reactions at the r position in the molecule, which are denoted by $S_r^{(E)}$ and $S_r^{(N)}$, respectively, are expressed as follows:

$$S_r^{(E)} = 2\sum_i^{\text{occ}} \frac{(C_{ir})^2}{m_i} \quad , \tag{1}$$

$$S_r^{(N)} = -2\sum_i^{\text{unocc}} \frac{(C_{ir})^2}{m_i} \quad . \tag{2}$$

Here, C_{ir} and m_i are the LCAO (linear combination of atomic orbitals) coefficient of the rth atom and the energy coefficient for the ith molecular orbital, respectively.

Fukui et al. then proposed the use of approximate superdelocalizabilities based on the use of the HOMO or the LUMO only [18]. As the term associated with the HOMO or the LUMO is dominant in Eqs. (1) and (2), the superdelocalizabilities can be approximated in the form:

$$S_r^{(E)} \approx \frac{2(C_{\text{HOMO},r})^2}{m_{\text{HOMO}}} \quad , \tag{3}$$

$$S_r^{(N)} \approx -\frac{2(C_{\text{LUMO},r})^2}{m_{\text{LUMO}}} \quad . \tag{4}$$

In general, the average of the LCAO coefficients squared decreases as the number of conjugated atoms increases. For each molecular orbital the following relationship holds exactly:

$$\overline{(C_{ir})^2} = \frac{1}{N}\sum_{r=1}^{N} (C_{ir})^2 = \frac{1}{N} \quad , \tag{5}$$

where N is the number of conjugated atoms. We then replace $(C_{\text{HOMO},r})^2$ in Eq. (3) and $(C_{\text{LUMO},r})^2$ in Eq. (4) by this averaged value and obtain the approximate superdelocalizabilities averaged over all conjugated atoms:

$$\overline{S_r^{(E)}} \approx \frac{2}{N\, m_{\text{HOMO}}} \quad , \tag{6}$$

$$\overline{S_r^{(N)}} \approx -\frac{2}{N\, m_{\text{LUMO}}} \quad . \tag{7}$$

Thus, chemical reactivity, averaged over the entire molecule, is inversely proportional not only to the energy coefficient of the HOMO but also to the number of conjugated atoms.

It is reasonable to assume that the kinetic stability of a molecule is attributable to the reactivity of the most reactive sites in the molecule. That is, whether a molecule is thermodynamically stable or not, its kinetic stability is determined primarily by the reactivity of the most reactive sites. The most reactive sites are the ones with the largest value of $(C_{\text{HOMO},r})^2$ and/or $(C_{\text{LUMO},r})^2$. What we want to say in this context is that these LCAO coefficients squared must also be roughly proportional to $1/N$. Therefore, it is not unreasonable to assume that Eqs. (6) and (7) represent the general propensity toward chemical reaction at the most reactive site in the molecule.

With this aspect of superdelocalizability in mind, we define a new index of kinetic stability, T, which is obtained by multiplying the HOMO-LUMO energy separation by the number of conjugated atoms, namely

$$T = N\,(m_{\text{HOMO}} - m_{\text{LUMO}}) \quad . \tag{8}$$

Letter T is adopted here as it comes after letter S for superdelocalizability. The reciprocal of T (i.e. $1/T$) takes the size of the π-electron system into account just in the same manner as Eqs. (6) and (7). Note that both $S_r^{(E)}$ and $1/T$ increase when m_{HOMO} descreases. Likewise, $S_r^{(N)}$ and $1/T$ increase when m_{LUMO} decreases. Therefore, the value of $1/T$ can be interpreted as an approximate but general index of chemical reactivity. Exactly in the same sense, its reciprocal, T, can be considered to represent the general tendency to resist chemical reactions or the degree of kinetic stability. The use of the T value as an index of kinetic stability has an advantage, in that it does not diverge even if the HOMO and the LUMO are degenerate.

3 Discussion

We first examine the validity of the above theory by making some numerical calculations. In our graph theory of aromaticity [4, 15, 21–27], a hypothetical polyene-like reference structure is defined for any cyclic π-electron system. Thus, the polyene references constructed graph-theoretically for fullerenes are olefinic by definition, so are supposed to be similar in reactivity to each other. We evaluated T values for the polyene references of 23 arbitrarily chosen fullerenes in the range $N = 20$–70. Calculated T values and related quantities are presented in Table 1. It is not easy to obtain matching polynomials for fullerenes with more than 70 carbon atoms [26].

It is noteworthy that in contrast to the widely varied HOMO-LUMO energy separation, the T values are fairly constant for all polyene references of fullerenes. All T values lie in the relatively narrow range 5.78–7.42, the average being 6.66. This strongly supports our view that the hypothetical polyene references are olefinic in nature and would exhibit similar chemical reactivity. Hence, the T value is preferred to the unweighted HOMO-LUMO energy separation, at least for fullerenes. As fullerenes consist of three-coordinate carbon atoms only, the π-binding energy per carbon atom is almost constant for their polyene references. The near constancy of π-binding energy per conjugated atom conforms to that of the T values. According to the Hess-Schaad resonance energy model [11, 28], the π-binding energy per carbon atom is constant for the polyene references of all fullerenes.

In fact, the T values for the polyene references of planar cyclic conjugated hydrocarbons vary widely [29]. For example, the T values for the polyene references of benzene ($N = 6$) and angulated or zigzag polyacene

Table 1. *T* values and related quantities for the polyene references of 23 fullerenes. See footnotes a–e for molecular topologies

Species	π-binding energy per carbon atom/$\lvert\beta\rvert$	$m_{\mathrm{HOMO}} - m_{\mathrm{LUMO}}$	*T* value
C_{20} (I_h)[a]	1.5256	0.3635	7.27
C_{24} (D_{6d})[a,b]	1.5247	0.2729	6.55
C_{26} (D_{3h})[a,b]	1.5242	0.2344	6.09
C_{28} (T_d)[a,b]	1.5239	0.2065	5.78
C_{30} (C_{2v})[a]	1.5242	0.2008	6.02
C_{30} (D_{5h})[b]	1.5251	0.2413	7.24
C_{32} (D_3)[a,c]	1.5242	0.1915	6.13
C_{36} (D_{2d})[a]	1.5245	0.1837	6.61
C_{36} (D_{6h})[b]	1.5244	0.1773	6.38
C_{38} (D_{3h})[b]	1.5251	0.1851	7.03
C_{40} (D_{5d})[b,c]	1.5248	0.1733	6.93
C_{40} (T_d)[b]	1.5249	0.1706	6.82
C_{42} (C_3)[b]	1.5247	0.1550	6.51
C_{44} (D_{3h})[b]	1.5249	0.1496	6.58
C_{44} (D_2)[a]	1.5216	0.1576	6.94
C_{44} (T)[a]	1.5248	0.1395	6.14
C_{48} (C_1)[c]	1.5249	0.1367	6.56
C_{50} (D_{5h})[a,b]	1.5250	0.1344	6.72
C_{50} (D_3)[a]	1.5249	0.1286	6.43
C_{56} (C_{2v})[c]	1.5251	0.1208	6.77
C_{60} (I_h)[a,c,d]	1.5253	0.1237	7.42
C_{60} (C_{2v})[a]	1.5252	0.1175	7.05
C_{70} (D_{5h})[e]	1.5254	0.1029	7.20

[a] Ref. [25]
[b] Ref. [24]
[c] Ref. [27]
[d] Ref. [23]
[e] Ref. [26]

Table 2. Highest occupied molecular orbital (HOMO) lowest unoccupied molecular orbital (LUMO) energy separations and *T* values for real molecules of fullerenes listed in Table 1

Species	$m_{\mathrm{HOMO}} - m_{\mathrm{LUMO}}$	*T* value
C_{20} (I_h)	0.0000	0.00
C_{24} (D_{6d})	0.0000	0.00
C_{26} (D_{3h})	0.0669	1.74
C_{28} (T_d)	0.0000	0.00
C_{30} (C_{2v})	0.0584	1.75
C_{30} (D_{5h})	0.0000	0.00
C_{32} (D_3)	0.3639	11.65
C_{36} (D_{2d})	0.3002	10.81
C_{36} (D_{6h})	0.0000	0.00
C_{38} (D_{3h})	0.0000	0.00
C_{40} (D_{5d})	0.3731	14.93
C_{40} (T_d)	0.0000	0.00
C_{42} (C_3)	0.2801	11.76
C_{44} (D_{3h})	0.4241	18.66
C_{44} (D_2)	0.2460	10.82
C_{44} (T)	0.4059	17.86
C_{48} (C_1)	0.3843	18.45
C_{50} (D_{5h})	0.1031	5.16
C_{50} (D_3)	0.4679	23.40
C_{56} (C_{2v})	0.0717	4.02
C_{60} (I_h)[a]	0.7566	45.40
C_{60} (C_{2v})	0.1870	11.22
C_{70} (D_{5h})[a]	0.5293	37.05

with 15 benzene rings ($N = 62$) are 6.21 and 18.19, respectively, which suggests that the polyene references of planar molecules might be fairly different in chemical reactivity, depending on the geometry of the π-electron system. As the situation with planar molecules is somewhat complicated, it will be discussed elsewhere. The *T* value is fairly constant among the polyene references of appropriate homologous hydrocarbons [29]. It seems that fullerenes constitute the best homologous series.

The HOMO-LUMO energy separations and *T* values calculated for real molecules of fullerenes listed in Table 1 are presented in Table 2. C_{60} (I_h) and C_{70} (D_{5h}) have very large *T* values, as expected from the fact that they can be isolated in macroscopic quantities. No other highly stable species are found in Table 2. This also agrees with the fact that the fullerenes other than C_{60} (I_h) and C_{70} (D_{5h}) violate the isolated pentagon rule (IPR) [7, 30]. A fullerene molecule with $T <$ ca. 6 is presumably more reactive than the polyene reference. Open-shell species with $T = 0$ must be extremely reactive. Manolopoulos et al. found an interesting correlation between the yields of fullerenes observed immediately after vaporization of graphite and their unweighted HOMO-LUMO energy separations [5]. In view of the present study, they appear to have overestimated the kinetic stability of smaller fullerenes.

The HOMO-LUMO energy separations and *T* values calculated for IPR isomers of higher fullerenes with 60–84 carbon atoms are summarized in Table 3. Isomer numbers given by Fowler et al. are cited in this table for the convenience of the reader [3, 31, 32]. Molecular structures of 11 fullerene isomers have so far been determined without ambiguity by ^{13}C NMR spectroscopy [33–39]. In Table 3 these structurally identified isomers are indicated in boldface with the references concerned. Their *T* values are all larger than 13. As the HOMO-LUMO gap of each isolable fullerene is more than twice as large as that of the polyene reference, it is supposed to be kinetically more stable than the polyene reference.

In general, isolable fullerene isomers are the thermodynamically most stable ones [17, 40–43]. C_{78} is a notable exception. The yields of C_{78} fullerene isomers are very sensitive to arc-discharge reactor conditions. The lowest-energy isomer is C_{78} (3) [17]. This isomer is not isolable at low helium pressure although two higher-energy isomers are isolable [16]. The relatively small *T* value for C_{78} (3) reflects such kinetic instability. All IPR fullerene isomers of C_{80} are predicted to be kinetically very or fairly unstable. C_{80} (2) is the only isolable one at present [38], but its yield is very low in harmony with its relatively small *T* value. The *T* values for C_{78} (3) and C_{80} (2) are the smallest ones among the fullerenes isolated so far.

Interestingly, some higher fullerenes have isomers that are kinetically as stable as C_{60} (I_h). Among them are C_{72} (D_{5h}), C_{78} (4), C_{84} (1), C_{84} (20), and C_{84} (24), all of which have *T* values comparable to that of C_{60}. Unfortunately, these species have not been isolated yet because they are not thermodynamically stable [17]. Isolable fullerene molecules must not only be kinetically stable but also thermodynamically stable. Therefore, all fullerene isomers with large *T* values cannot be isolated. On the other hand, it is highly probable that fullerene isomers with $T < 10$ will be kinetically very unstable and

Table 3. HOMO-LUMO energy separations and T values for isolated pentagon rule (IPR) isomers of higher fullrenes

Species	$m_{\mathrm{HOMO}} - m_{\mathrm{LUMO}}$	T value
A. C_{60}–C_{74}		
C_{60} (I_h)[a]	**0.7566**	**45.40**
C_{70} (D_{5h})[a]	**0.5293**	**37.05**
C_{72} (D_{6d})	0.7023	50.57
C_{74} (D_{3h})	0.1031	7.63
B. C_{76}		
1 (T_d)	0.0000	0.00
2 (D_2)[b]	**0.3436**	**26.11**
C. C_{78}		
1 (D_3)[c,d]	**0.2532**	**19.75**
2 (C_{2v})[c,d]	**0.3481**	**27.15**
3 (C_{2v})[d]	**0.1802**	**14.06**
4 (D_{3h})	0.6333	49.40
5 (D_{3h})	0.0730	5.69
D. C_{80}		
1 (D_{5d})	0.0728	5.82
2 (D_2)[e]	**0.1749**	**13.99**
3 (C_{2v})	0.0338	2.71
4 (D_3)	0.1351	10.81
5 (C_{2v})	0.0987	7.90
6 (D_{5h})	0.0000	0.00
7 (I_h)	0.0000	0.00
E. C_{82}		
1 (C_2)	0.1495	12.26
2 (C_s)	0.3313	27.17
3 (C_2)[d]	**0.2568**	**21.06**
4 (C_s)	0.2450	20.09
5 (C_2)	0.1300	10.66
6 (C_s)	0.0683	5.60
7 (C_{3v})	0.0000	0.00
8 (C_{3v})	0.0467	3.83
9 (C_{2v})	0.0160	1.31
F. C_{84}		
1 (D_2)	0.6143	51.60
2 (C_2)	0.3523	29.59
3 (C_s)	0.0191	1.60
4 (D_{2d})[f]	**0.3519**	**29.56**
5 (D_2)	0.2403	20.19
6 (C_{2v})	0.1892	15.89
7 (C_{2v})	0.1892	15.89
8 (C_2)	0.1776	14.92
9 (C_2)	0.0556	4.67
10 (C_s)	0.0916	7.70
11 (C_2)	0.2540	21.34
12 (C_1)	0.2164	18.18
13 (C_2)	0.0988	8.30
14 (C_s)	0.4054	34.06
15 (C_s)	0.2191	18.41
16 (C_s)	0.3369	28.30
17 (C_{2v})	0.1745	14.66
18 (C_{2v})	0.3285	27.59
19 (D_{3d})	0.1861	15.63
20 (T_d)	0.6962	58.48
21 (D_2)	0.1381	11.60
22 (D_2)[d,g]	**0.3449**	**28.97**
23 (D_{2d})[d,g]	**0.3449**	**28.97**
24 (D_{6h})	0.5293	44.46

[a] Ref. [33]
[b] Ref. [34]
[c] Ref. [35]
[d] Ref. [36]
[e] Ref. [38]
[f] Ref. [39]
[g] Ref. [37]

unable to survive harsh experimental conditions. At present there are no exceptions.

We previously estimated the percentage topological resonance energy (%TRE) for graphite [44]. The %TRE, defined as 100 times the topological resonance energy (TRE) divided by the total π-binding energy of the polyene reference, is useful for comparing the degrees of aromaticity of different molecules [15, 23, 25]. The %TRE was estimated to be 3.061 for graphite [44]. This value is comparable to the %TRE of benzene (3.528). Apparently such a large %TRE value for graphite is not compatible with its zero HOMO-LUMO gap. This kind of difficulty was overcome by using the T value instead of the unweighted HOMO-LUMO energy separation. Nevertheless, we cannot estimate the T value of graphite yet.

4 Concluding remarks

The T value is a HOMO-LUMO energy separation weighted with the number of conjugated atoms. It is extremely simple to calculate. The present study confirmed that the T value can be used as a practical index for estimating the degree of kinetic stability. The unweighted HOMO-LUMO separation does not permit comparison between different molecules, but the T value does. Thus, the difficulty with the use of the unweighted HOMO-LUMO energy eparation apparently disappeared. The T value could become useful not only in fullerene chemistry but also in general organic chemistry. Readers are requested to refer to Table 3 if isolation of new fullerene isomers are reported.

Finally, one possible flaw must be mentioned with respect to the definition of the T value. Since this index is formally related to the approximate superdelocalizabilities averaged over all conjugated atoms, there is some possibility that it might not reflect fully the reactivity of the most reactive sites in the molecule. In particular, if there are extremely reactive sites, the T value may fail to take them fully into account. Probably for this reason, the T value is not best suited for explaining a striking difference in kinetic stability between IPR and non-IPR isomers of fullerenes [15]. In such a case, the use of the bond resonance energy (BRE) is highly recommended [4, 15]. The BRE is an index of kinetic stability closely related to the reactivity of a local structure in the molecule.

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