Aromatic Character of Typical C_{60} Derivatives

Juni-ichi Aihara*[,a] **and Shigetoshi Takata**[b]
[a] Department of Chemistry, Faculty of Science, Shizuoka University, Oya, Shizuoka 422, Japan
[b] Information Processing Center, Shizuoka University, Oya, Shizuoka 422, Japan

The topological resonance energy (TRE) method has revealed that typical derivatives of C_{60} are moderately aromatic like the parent molecule C_{60}. For most C_{60} derivatives, polyvalent molecular anions are at least as aromatic as the neutral species, whereas polyvalent molecular cations are much less aromatic in nature. In general, addition and insertion reactions with C_{60} proceed in such a manner that the reaction products become as aromatic as possible.

Three years ago the route to production of a macroscopic amount of C_{60} or buckminsterfullerene (**1**) was described.[1] The molecule had been supposed to be highly aromatic due to cyclic conjugation,[2–12] but it soon proved to be fairly reactive. Various functionalization studies have been carried out with C_{60}.[13–15] Unlike planar aromatics, C_{60} has no hydrogen atoms or other groups attached, so is unable to undergo substitution reactions. This molecule instead undergoes addition reactions characteristic of alkenes. A number of C_{60} derivatives have been prepared successfully and characterized.[13–15]

We have shown that the topological resonance energy (TRE) method[16,17] is very useful for consistently interpreting energetic and magnetic properties of an aromatic molecule.[18–20] However, it is not easy to apply this method to large π-electron systems. In 1988 we managed to evaluate the TRE of C_{60}, and confirmed that this molecule is moderately aromatic with some olefinic character.[21,22] It is now tempting to explore electronic structures of various C_{60} derivatives. We applied the TRE method to these molecules to deepening our understanding of their aromatic character.

Theory.—In order for the TRE to be obtained, the reference (or matching) polynomial must first be constructed.[16,17] We used the computer program published by Ramaraj and Balasubramanian[23] to enumerate the coefficients in the reference polynomials of large π-electron systems. No attempt was made to correct for departures from perfect sp^2 hybridization caused by non-planarity. Hückel parameters compiled by Streitwieser were utilized.[24]

When aromatic properties of different molecules are compared, the percentage resonance energy (%RE) is very useful.[21,25,26] The %RE is defined as 100 times the TRE, divided by the total π-electron energy of the polyene reference.[25,26] Benzene is the prototype of aromatic molecules, having a %RE of 3.528.[21] In general, a highly aromatic molecule is kinetically stable or inert.[27,28]

There are two types of CC π bond in C_{60}. CC π bonds shared by pentagonal and hexagonal rings are denoted by 5,6 bonds, whereas those shared by two hexagonal rings are referred to as 6,6 bonds.[15]

Results and Discussion

The TREs were calculated for C_{60} and eleven kinds of its derivatives. Schlegel diagrams **1–12** in Fig. 1 represent the π-electron systems of these derivatives. Ten of them are found in existing C_{60} derivatives. The %REs and the energies of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs), obtained for these π-electron systems, are listed in Table 1. The HOMO–LUMO energy separation is a conventional index for kinetic stability.[27–29]

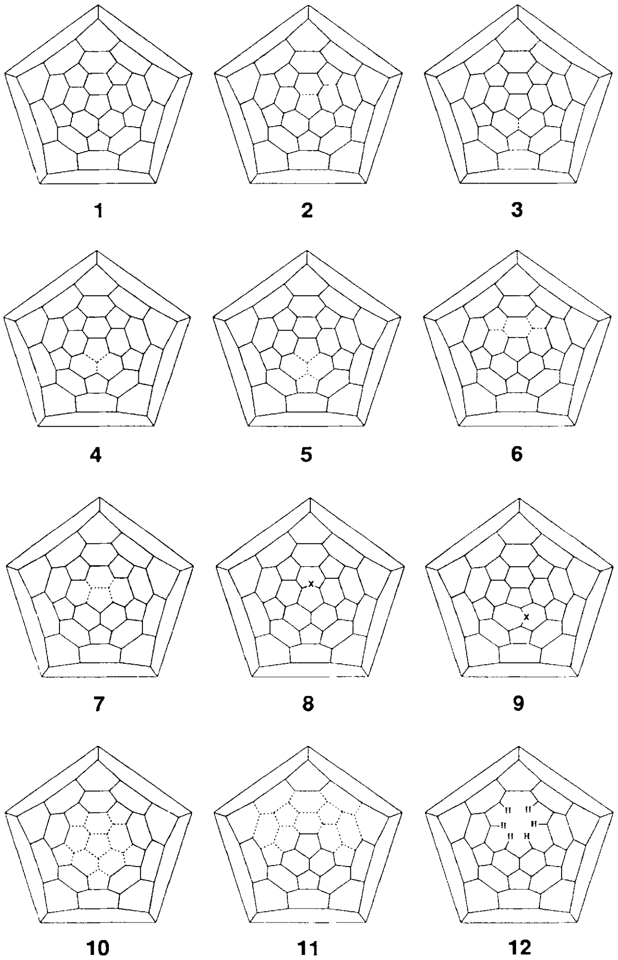

1 **2** **3**
4 **5** **6**
7 **8** **9**
10 **11** **12**

Fig. 1 Schlegel diagrams for the π-electron systems of typical C_{60} derivatives. Solid lines indicate the paths along which π electrons can move.

As reported previously,[30] C_{60} (**1**) is more stable than any of smaller fullerenes. It has the largest HOMO–LUMO energy separation.[29,30] However, the %RE of this molecule is not very large, being about a half that of benzene.[21] Therefore, we might safely say that C_{60} is moderately aromatic with some olefinic character.

We found that functionalization does not change the aromaticity of C_{60} markedly. All C_{60} derivatives studied are moderately aromatic with moderately large positive %REs.

Table 1 The TREs and the energies of the HOMOs and the LUMOs for neutral C_{60} derivatives and corannulene

Species	TRE ($\lvert\beta\rvert$)	%RE	HOMO (β)	LUMO (β)
1	1.643	1.795	0.6180	−0.1386
2	1.631	1.792	0.4695	−0.0959
3	1.327	1.459	0.3705	0.0150
4	1.391	1.560	0.1383	0.1383
5	1.644	1.881	0.4774	−0.1272
6	1.517	1.746	0.4716	−0.0717
7	1.261	1.444	0.2953	0.0540
8 (X = O)	1.632	1.785	0.3355	−0.0959
8 (X = NH)	1.630	1.781	0.2963	−0.0959
9 (X = O)	1.151	1.260	0.1239	0.0150
9 (X = NH)	1.107	1.210	0.0593	0.0150
10	1.656	2.245	0.6180	−0.2158
11	1.246	1.858	0.4786	−0.0841
12	1.550	1.920	0.4633	−0.1097
13	0.735	2.626	0.7376	−0.4773

They are necessarily more or less olefinic, like C_{60} itself. Hydrogenation, fluorination and chlorination yield mixtures containing many different species.[13-15] Multiple addition to C_{60} is associated with its olefinic character. Fortunately, the pattern of additions to C_{60} under controlled conditions appreciably reflect the aromaticity.

Fulleroids are inflated fullerenes where up to six carbon atoms are added systematically to C_{60}.[31] Reaction of C_{60} with diazomethane yields the simplest fulleroid $C_{60}CH_2$ (**8**, X = CH_2).[31] In this reaction carbene is inserted into a 5,6 bond. The π-electron system of this fulleroid molecule (**2**) has a larger positive %RE than that of the isomeric structure (**3**).

Herndon and Randić have shown that for polycyclic aromatic molecules, relatively small even-membered π-electron rings are the main source of aromaticity.[32,33] For benzenoid systems and fullerenes, hexagonal rings must be primarily responsible for aromaticity.[11,32,33] Insertion of carbene into a 5,6 bond of C_{60} leads to the loss of one hexagonal π-electron ring, whereas insertion into a 6,6 bond gives rise to the loss of two such rings. Thus, the loss of aromaticity is minimized if carbene is inserted into a 5,6 bond to give the π-electron system **2**. In other words, carbene insertion tends to take place in such a manner that it gives the product of highest aromaticity.

C_{60} reacts with Bu^tLi to form the stable Bu^tC_{60} anion, which contains the π-electron system **4**.[34] In this relation, the stability of the $C_{60}H$ cation was probed by collision-induced dissociation in a vacuum.[35] As shown in Table 2(*d*), both $C_{60}H^-$ and $C_{60}H^+$ are moderately aromatic.

Treatment of the Bu^tC_{60} anion with acid affords two Bu^tHC_{60} isomers.[34] Their π-electron systems are given in **5** and **6**. The latter easily rearranges to the former.[34] The %RE of **5** is large compared with those of the isomeric structures **6** and **7**. Higher aromaticity of **5** must be a driving force for the **6**→**5** rearrangement. The reaction of C_{60} with BH_3–tetrahydrofuran in dry toluene followed by hydrolysis yields $C_{60}H_2$.[36] This is the simplest hydrocarbon with the π-electron system **5**.

The fact that 1,2-addition occurs largely at 6,6 bonds can be rationalized again in terms of local aromatic structures. Two and three hexagonal π-electron rings are lost by 1,2-additions to 6,6 and 5,6 bonds, respectively. This causes **5** to be more aromatic than **6** and **7**. The π-electron system **5** is formed in many other C_{60} derivatives, such as the epoxide, Diels–Alder adducts, osmate esters and some iridium and platinum complexes.[13 15] This implies that in general, addition reactions with C_{60} proceed in such a manner that the reaction products achieve as much aromaticity as possible.

Oxofulleroid is formed either by ultraviolet irradiation or

Table 2 TREs of molecular ions for C_{60} and its derivatives

Charge	TRE ($\lvert\beta\rvert$)	%RE
(*a*) Buckminsterfullerene (**1**)		
+6	−1.064	−1.175
+5	−0.717	−0.790
+4	−0.371	−0.407
+3	0.080	0.087
+2	0.530	0.580
+1	1.087	1.188
0	1.643	1.795
−1	1.566	1.712
−2	1.489	1.629
−3	1.518	1.664
−4	1.547	1.699
−5	1.680	1.851
−6	1.813	2.003
(*b*) Dihydrofulleroid A (**2**)		
+4	−0.084	−0.093
+3	0.366	0.404
+2	0.816	0.899
+1	1.223	1.346
0	1.631	1.792
−1	1.597	1.757
−2	1.564	1.721
−3	1.593	1.756
−4	1.622	1.792
(*c*) Dihydrofulleroid B (**3**)		
+4	−0.208	−0.229
+3	0.248	0.273
+2	0.703	0.774
+1	1.015	1.117
0	1.327	1.459
−1	1.400	1.541
−2	1.474	1.623
−3	1.498	1.653
−4	1.522	1.682
(*d*) $C_{60}H$ (**4**)		
+4	−0.155	−0.174
+3	0.243	0.274
+2	0.748	0.840
+1	1.252	1.405
0	1.391	1.560
−1	1.529	1.715
−2	1.504	1.689
−3	1.479	1.663
−4	1.560	1.759
(*e*) Dihydrobuckminsterfullerene A (**5**)		
+4	−0.063	−0.072
+3	0.379	0.436
+2	0.822	0.942
+1	1.233	1.411
0	1.644	1.881
−1	1.583	1.812
−2	1.522	1.744
−3	1.559	1.790
−4	1.596	1.836
(*f*) Dihydrobuckminsterfullerene B (**6**)		
+4	−0.186	−0.216
+3	0.258	0.298
+2	0.703	0.810
+1	1.110	1.278
0	1.517	1.746
−1	1.510	1.739
−2	1.502	1.731
−3	1.537	1.775
−4	1.572	1.819
(*g*) Dihydrobuckminsterfullerene C (**7**)		
+4	−0.110	−0.127
+3	0.341	0.391

Table 2 (*continued*)

Charge	TRE ($|\beta|$)	%RE
+2	0.792	0.908
+1	1.026	1.176
0	1.261	1.444
−1	1.376	1.576
−2	1.490	1.708
−3	1.519	1.744
−4	1.547	1.781
(*h*) Oxofulleroid A (**8**; X = O)		
+4	0.123	—
+3	0.589	—
+2	1.055	—
+1	1.343	—
0	1.632	1.785
−1	1.611	—
−2	1.591	—
−3	1.634	—
−4	1.676	—
(*i*) Azafulleroid A (**8**; X = NH)		
+4	0.182	—
+3	0.653	—
+2	1.123	—
+1	1.377	—
0	1.630	1.781
−1	1.613	—
−2	1.597	—
−3	1.643	—
−4	1.689	—
(*j*) Oxofulleroid B (**9**; X = O)		
+4	0.031	—
+3	0.504	—
+2	0.976	—
+1	1.064	—
0	1.151	1.260
−1	1.237	—
−2	1.323	—
−3	1.360	—
−4	1.397	—
(*k*) Azafulleroid B (**9**; X = NH)		
+4	0.099	—
+3	0.576	—
+2	1.052	—
+1	1.080	—
0	1.107	1.210
−1	1.198	—
−2	1.288	—
−3	1.329	—
−4	1.370	—
(*l*) Main π-electron system in $C_{60}Br_6$ (**10**)		
+4	−0.223	−0.305
+3	0.183	0.249
+2	0.589	0.800
+1	1.122	1.523
0	1.656	2.245
−1	1.525	2.069
−2	1.393	1.893
−3	1.390	1.894
−4	1.386	1.894
(*m*) Main π-electron system in $C_{60}Br_8$ (**11**)		
+4	−0.278	−0.419
+3	0.094	0.142
+2	0.467	0.699
+1	0.857	1.279
0	1.246	1.858
−1	1.251	1.869
−2	1.256	1.879
−3	1.254	1.881
−4	1.251	1.884
(*n*) Open-cage $C_{54}H_6$ (**12**)		
+4	0.004	0.005
+3	0.387	0.482
+2	0.771	0.956
+1	1.160	1.438
0	1.550	1.920
−1	1.514	1.877
−2	1.478	1.834
−3	1.426	1.773
−4	1.374	1.712

by heating of the epoxide.[14,15] Taylor and Walton predicted that oxygen is inserted into a 5,6 bond of C_{60}.[14,15] If this is so, the resulting π-electron system must be given by **8**, where X is O. Azafulleroids (**8**; X = NCH_2R) are formed as reaction products of organic azides with C_{60}.[37] Nitrogen is likewise inserted into a 5,6 bond. It is interesting to see that the two insertion reactions lead to the formation of the same π-electron system **8**.

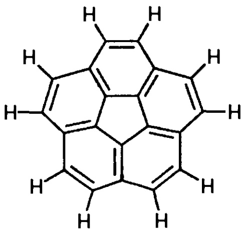
In the π-electron system **8** one hexagonal ring is replaced by an antiaromatic oxepine- or azepine-type ring, whereas in the isomeric system **9** two hexagonal rings are replaced by oxepine- or azepine-type rings. Therefore, **8** is predicted to be more aromatic than **9**. In Table 2 it is highlighed that whatever X might be, **8** has a larger %RE than **9**. Thus, insertion reactions also tend to minimize the loss of aromaticity in the product.

C_{60} bromination illustrates the most controlled halogenation. Reaction of C_{60} with Br_2 in CCl_4 and C_6H_6 yields $C_{60}Br_6$.[38] The main π-electron system of this molecule (**10**) consists of 50 carbon atoms and has a larger %RE than C_{60}. Enhanced aromaticity is attributable to the decreased ratio of pentagonal to hexagonal rings. Reaction of C_{60} with Br_2 in CS_2 yields $C_{60}Br_8$.[38] The main π-electron system (**11**) consists of 46 carbon atoms, and is moderately aromatic.

There are likely to be different viewpoints concerning the derivatization of C_{60}. Since 6,6 bonds in C_{60} have large double-bond character, it may be predicted that 1,2-addition occurs there. Taylor and Walton applied the Mills–Nixon effect[39] to C_{60}, and proposed that the need to avoid double bonds in the pentagonal rings largely governs the stability of C_{60} derivatives.[15] These viewpoints coincide with the present interpretation based on aromaticity.

The carriers of the unidentified infrared (UIR) bands seen in many celestial objects have been assigned to emission from polycyclic aromatic hydrocarbons (PAHs).[40,41] In 1990 Balm and Kroto proposed novel candidates for the UIR bands.[42] They postulated that open carbon cages in which edge carbon atoms bond to hydrogen atoms might be responsible for the UIR bands. Many such hydrocarbons have solo hydrogens (*i.e.*, non-adjacent peripheral hydrogen atoms), the presence of which is necessary for explaining the UIR band at 885 cm^{-1}. Hydrocarbons such as **12** meet this requirement. This compound is moderately aromatic, and may be considered to be one of the candidates for the UIR bands.

Next, let us consider the aromaticity of molecular ions of C_{60} derivatives. The %REs of such ionic species are listed in Table 2. As reported previously,[30] mono- and poly-valent anions of C_{60} are as aromatic as C_{60} itself. In contrast, the mono- and poly-valent cations are much less aromatic than the mono- and poly-valent anions. Such a trend in aromaticity is consistent with experiment. Mono- and poly-valent anions of C_{60} are isolable, but its cations are not.[43–46] C_{60} undergoes up to six reversible reduction processes in cyclic voltammetry.[47–49] However, no reversible oxidation steps have been observed.[47,50,51]



13

Fig. 2 Molecular structure of corannulene (**13**)

Table 3 TREs of corannulene molecular ions (**13**)

Charge	TRE (|β|)	%RE
+4	−0.848	−3.184
+3	−0.601	−2.217
+2	−0.354	−1.284
+1	0.190	0.685
0	0.735	2.626
−1	0.451	1.621
−2	0.166	0.602
−3	0.180	0.663
−4	0.193	0.726

Similar situations are observed for the C_{60} derivatives studied. For these molecules, singly and multiply charged anions are never much less aromatic than the neutral species. However, multiply charged cations are much less aromatic than the neutral species. Consequently, tetracations of all C_{60} derivatives are essentially nonaromatic with very small negative or positive %REs. Many C_{60} derivatives undergo several reversible reduction processes in cyclic voltammetry, but no reversible oxidation steps have been observed.[31,34,37,52]

Manolopoulos and co-workers pointed out that the LUMOs of fullerenes are very low-lying.[29] Examination of Table 1 reveals that C_{60} derivatives not only have low-lying LUMOs but also low-lying HOMOs. Such arrangements of π-electron orbitals determine the aromatic character of C_{60} derivatives in ionized states. Then, even if one or more π electrons are added to low-lying vacant orbitals, the π-electron system retains most of the aromaticity. Conversely, if one or more π electrons are removed from highly bonding orbitals, the π-electron system is destabilized to a great extent.

There are many non-benzenoid hydrocarbons consisting of pentagonal and hexagonal rings only. Among them are pentalene, indacenes, pyracylene and dibenzo[*cd*,*gh*]pentalene. Adding π electrons to such molecules is likely to create aromaticity in the pentagonal rings.[14,15] These non-alternant hydrocarbons tend to form stable molecular anions.[53] π-Electron systems of C_{60} derivatives likewise consist of pentagonal and hexagonal rings only. Therefore, it is highly probable that the pentagonal rings in C_{60} derivatives are responsible for the aromaticity of the molecular anions.

Corannulene (**13**) (Fig. 2) also belongs to this type of molecule. As shown in Table 3, multiply charged cations of this molecule are antiaromatic with negative %REs, whereas its multiply charged anions are aromatic with positive %REs. Consistent with this, **13** can easily be reduced to a stable tetraanion.[54] One should remember that tetraanions of PAHs have only rarely been observed.[54] We might say that many C_{60} derivatives have the propensity to form highly charged molecular anions since these molecules have many local corannulene structures.

Conclusions

The advantages of using the TRE method have been pointed out repeatedly.[16-22] In addition, there are no other analytical methods for estimating the aromaticity of molecular ions. The %RE was indeed found to be a simple but practical measure for predicting the stability of C_{60} derivatives and their molecular ions. We showed that gross features of fullerene chemistry can be described in terms of aromatic stabilization. As pointed out by Dixon and co-workers,[55] the most favourable pattern for addition may change when the functional groups are bulky.

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