July, 1993] © *1993 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***66***, *1955—1958(1993)* 1955

Aromaticity of Multiply Charged Fullerene Ions

Jun-ichi AIHARA* and Haruo HOSOYA†
Department of Chemistry, Faculty of Science, Shizuoka University, Oya, Shizuoka 422
† Department of Information Sciences, Faculty of Science, Ochanomizu University, Bunkyo-ku, Tokyo 112

(Received March 8, 1993)

The topological resonance energies (TREs) indicate that mono- to hexaanions of C_{60} are as aromatic as the neutral species. The tendency of multiply charged C_{60} anions to retain their own spherical conjugated systems can be attributed to aromatic character. Tetraanions of C_{28}, C_{36}, and C_{44} are likewise predicted to be highly aromatic. Thus, the formation of metallofullerenes, such as U@C_{28}, U@C_{36}, and U@C_{44}, can be rationalized in terms of aromaticities of the ligands.

Aromaticity is one of the determinants for the kinetic stability of a cyclic conjugated system. Several theoretical models have predicted that the neutral buckminsterfullerene molecule (C_{60}, **1**) has a certain degree of aromaticity (Chart 1).[1—15] We previously showed that it is moderately aromatic with a positive topological resonance energy (TRE).[14] This molecule reacts with alkali metals to form multiply charged molecular anions.[16—21] Many salts of the C_{60} trianion such as K_3C_{60} have metallic properties, some being superconductive at low temperature.[16—19] One of the important unresolved problems is whether such multiply charged fullerene ions are aromatic or not. This paper presents the first theoretical argument for the aromaticity of typical multiply charged fullerene ions. We utilize the topological resonance energy (TRE) model[22,23] as before, which solely is suited for estimating the aromaticity of charged species.

Table 1. The TREs of C_{60} Ions (I_h Symmetry)

Charge	TRE/$\lvert\beta\rvert$	%RE	REPE/$\lvert\beta\rvert$
+6	−1.064	−1.175	−0.0197
+5	−0.717	−0.790	−0.0130
+4	−0.371	−0.407	−0.0066
+3	+0.080	+0.087	+0.0014
+2	+0.530	+0.580	+0.0091
+1	+1.087	+1.188	+0.0184
0	+1.643	+1.795	+0.0274
−1	+1.566	+1.712	+0.0257
−2	+1.489	+1.629	+0.0240
−3	+1.518	+1.664	+0.0241
−4	+1.547	+1.699	+0.0242
−5	+1.680	+1.851	+0.0258
−6	+1.813	+2.003	+0.0275

Results and Discussion

The TREs calculated for multiply charged C_{60} cations and anions are listed in Table 1. We assumed that all C_{60} ions have a truncated icosahedral structure.[24—26] Curvature corrections were not made for π-electron energies of C_{60} and other fullerene molecules. Since the reference (or matching) polynomial for C_{60} has already been published,[14,29] it is not repeated here. The percent resonance energy (%RE) and the resonance energy per electron (REPE) have been acknowledged as good measures of aromatic stabilization.[3,23,27,28] The %RE is given as 100 times the TRE, divided by the total π-electron energy of the graph-theoretically defined polyene reference,[27,28] whereas the REPE is defined as the TRE divided by the number of π electrons.[23] The %REs and REPEs of C_{60} molecular ions are also given in Table 1.

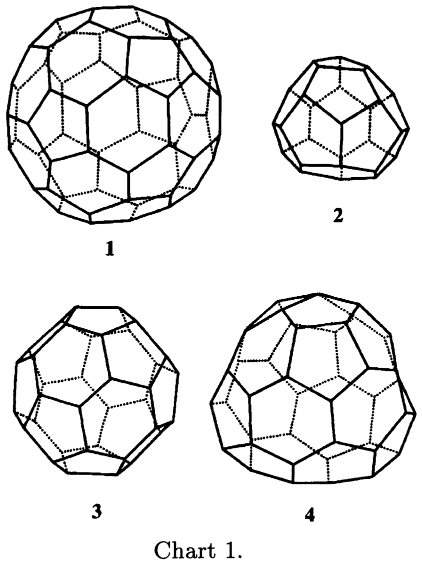
1 **2** **3** **4**

Chart 1.

It is noteworthy that C_{60} anions are all as aromatic as the neutral species. Hückel theory indicates that the lowest unoccupied molecular orbitals (LUMOs) of C_{60} are triply degenerate. These LUMOs can accept up to six π electrons to form multiply charged C_{60} anions. As these LUMOs lie very low in energy, the %RE remains large for mono- to hexaanions. Accordingly, C_{60} is able to undergo up to six reversible reduction steps in cyclic voltammetry.[30—32] Highly charged C_{60} anions are very stable if it is placed in vacuum.[17—21] Thus, the predicted aromaticity of multiply charged C_{60} anions is quite consistent with experiment. The stability of the endohedral complex La@C_{60} can likewise be rationalized whatever the positive charge on the lanthanum atom might be.[33—35] Here, the symbol @ denotes the metal atom encapsulated by the fullerene molecule.[35]

The highest occupied molecular orbitals (HOMOs) of C_{60} are quintuply degenerate at relatively low energy. As seen from Table 1, multiply charged C_{60} cations have small positive or negative %REs, so these must be essentially nonaromatic or antiaromatic. Therefore, the removal of π electrons from the HOMOs destabilizes the molecular framework to a great extent. No reversible oxidation waves have been observed in the cyclic voltammogram of C_{60}.[30,36] In contrast to the anions, it seems unlikely that multiply charged cations are isolated without decomposition.

Recently Smalley and co-workers observed that the metallofullerene endohedral complex U@C_{28} is formed in abundance by laser vaporization of UO_2-impregnated graphite, suggesting that this complex is very stable.[37—39] They speculated that in C_{28} (**2**) the pentagons are grouped in four sets of three arranged in a tetrahedron.[37,38] Table 2 lists the TREs, %REs, and REPEs of multiply charged C_{28} ions calculated on the assumption that the C_{28} cage has T_d symmetry.[37—39] The reference (or matching) polynomial $R(X)$ for C_{28} is given below:

$$\begin{aligned}R(X) = {} & X^{28} - 42X^{26} + 777X^{24} - 8344X^{22} \\ & +57708X^{20} - 269628X^{18} + 868440X^{16} \\ & -1932444X^{14} + 2932008X^{12} - 2944708X^{10} \\ & +1859652X^{8} - 678312X^{6} + 123387X^{4} \\ & -8274X^{2} + 75 \end{aligned} \tag{1}$$

Hückel theory indicates that the neutral C_{28} molecule has an open-shell structure that effectively lacks four π electrons. The HOMOs are quadruply degenerate with only two π electrons in them. In general, cyclic conjugated systems with partially filled degenerate HOMOs, such as [4N]annulenes, are antiaromatic.[22,23] In accord with this, the neutral C_{28} molecule is predicted to be highly antiaromatic with a large negative %RE. C_{28} is scarcely formed by vaporization of graphite.[40,41]

However, when C_{28} accepts three or more π electrons, it becomes aromatic with a positive %RE. The C_{28} tetraanion is predicted to be the most aromatic of all the C_{28} ions. The %RE of C_{28}^{4-} (3.177) is much larger than that of C_{60} (1.188), being comparable to those of benzene (3.528) and corannulene (2.626).[14] It then follows that M@C_{28} must be thermodynamically very stable if M is uranium or any other tetravalent metal atom.[37—39] This supports Smalley's view that C_{28}^{4-} might possesse a uniquely stable structure like C_{60}.[37—39] C_{28} cations are highly antiaromatic with large negative %REs.

Smalley and co-workers also detected the formation of U@C_{36} and U@C_{44} in substantial amounts. We then calculated the TREs of C_{36} in D_{2d} symmetry (**3**) and C_{44} in T symmetry (**4**), which are listed in Tables 3 and 4, respectively. We chose these structural isomers from all possible structures of C_{36} and C_{44} since they have the largest HOMO–LUMO energy separations.[15] Eqs. 2 and 3 represent the reference polynomials for **3** and **4**, respectively:

$$\begin{aligned}R(X) = {} & X^{36} - 54X^{34} + 1323X^{32} - 19476X^{30} \\ & +192321X^{28} - 1346910X^{26} + 6898019X^{24} \\ & -26255052X^{22} + 74743467X^{20} - 158920874X^{18} \\ & +250185213X^{16} - 286861644X^{14} + 233449143X^{12} \\ & -129746290X^{10} + 46494509X^{8} - 9822212X^{6} \\ & +1050796X^{4} - 42320X^{2} + 288 \end{aligned} \tag{2}$$

$$\begin{aligned}R(X) = {} & X^{44} - 66X^{42} + 2013X^{40} - 37664X^{38} \\ & +483978X^{36} - 4531152X^{34} + 32000462X^{32} \\ & -174145908X^{30} + 739662345X^{28} \\ & -2468621666X^{26} + 6487126077X^{24} \\ & -13393722960X^{22} + 21594114326X^{20} \\ & -26905576992X^{18} + 25514074656X^{16} \\ & -18024278416X^{14} + 9210020709X^{12} \\ & -3266975370X^{10} + 758493495X^{8} \\ & -105468900X^{6} + 7588950X^{4} \\ & -212136X^{2} + 864 \end{aligned} \tag{3}$$

Tables 3 and 4 suggest that although these two fullerene molecules have large HOMO–LUMO energy separations, the neutral species are essentially nonaromatic in nature. However, their tetraanions are predicted to be highly aromatic with large positive %REs and REPEs. This might again constitute the primary reason why U@C_{36} and U@C_{44} are formed and detected by mass spectrometry. Multiply charged cations

Table 2. The TREs of C_{28} Ions (T_d Symmetry)

Charge	TRE/$\lvert\beta\rvert$	%RE	REPE/$\lvert\beta\rvert$
+4	−1.986	−4.754	−0.0828
+3	−1.914	−4.544	−0.0766
+2	−1.841	−4.336	−0.0708
+1	−1.530	−3.595	−0.0567
0	−1.219	−2.858	−0.0436
−1	−0.702	−1.649	−0.0242
−2	−0.184	−0.434	−0.0061
−3	+0.571	+1.357	+0.0184
−4	+1.327	+3.177	+0.0415

Table 3. The TREs of C_{36} Ions (D_{2d} Symmetry)

Charge	TRE/$\lvert\beta\rvert$	%RE	REPE/$\lvert\beta\rvert$
+4	−1.051	−1.939	−0.0328
+3	−0.896	−1.646	−0.0272
+2	−0.741	−1.355	−0.0218
+1	−0.419	−0.764	−0.0120
0	−0.097	−0.176	−0.0027
−1	+0.109	+0.200	+0.0030
−2	+0.315	+0.576	+0.0083
−3	+0.689	+1.265	+0.0177
−4	+1.062	+1.960	+0.0266

Table 4. The TREs of C_{44} Ions (T Symmetry)

Charge	TRE/$\|\beta\|$	%RE	REPE/$\|\beta\|$
+4	−1.470	−2.210	−0.0367
+3	−1.158	−1.736	−0.0283
+2	−0.847	−1.265	−0.0202
+1	−0.377	−0.563	−0.0088
0	+0.093	+0.138	+0.0021
−1	+0.296	+0.442	+0.0066
−2	+0.500	+0.747	+0.0109
−3	+0.862	+1.292	+0.0183
−4	+1.224	+1.841	+0.0255

of such fullerenes are all predicted to be highly antiaromatic. The electronic structures of U@C_{28}, U@C_{36}, and U@C_{44} somewhat resemble that of uranocene $(C_8H_8)_2U$, in that U^{4+} is bonded to the aromatized hydrocarbon ligand(s). Uranocene was indeed obtained as a thermally stable green solid.[42—44)]

Concluding Remarks

As has been seen above, the TRE turned out to be a simple but practical measure for predicting the aromaticity of fullerene ions. We can say that aromatic character is the most likely explanation for the tendency of the multiply charged anions of C_{60}, C_{28}, C_{36}, and C_{44} to retain their own spherical conjugated systems. Thus, the formation of C_{60}-based superconductors and such metallofullerenes as U@C_{28}, U@C_{36}, and U@C_{44} can be rationalized in terms of aromaticities of the ligands.

Because of their non-alternant geometry, all fullerenes are anyhow predicted to be more aromatic in negatively or positively charged states than in the neutral state. In this context, Manolopoulos and co-workers pointed out that the LUMOs of all fullerenes in the C_{34} to C_{70} range, with the sole exception of icosahedral C_{60}, are either slightly bonding or nonbonding.[15)] Thus, the LUMOs of all fullerene molecules lie very low in energy, so the negatively charged states must be thermodynamically very stable as compared to the positively charged ones. This aspect of electronic structure is fully consistent with the present results. For neutral fullerenes, the TRE is in good agreement with the Hess–Schaad resonance energy.[3)]

We thank Professor Hisanori Shinohara of Mi'e University for helpful discussion. This work was supported by the Grant-in-Aid for Scientific Research on Priority Area "The Theory of Chemical Reactions" from the Ministry of Education, Science and Culture. All calculations were carried out at the Information Processing Center of Shizuoka University.

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