

Aromaticity and kinetic stability of fullerene C₃₆ isomers and their molecular ions

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Abstract The aromatic character of fullerene C₃₆ isomers was examined by the Hess-Schaad resonance energy (HSRE), topological resonance energy (TRE) and the percentage topological resonance energy (%TRE) models. According to the nucleus-independent chemical shift (NICS) at the cage center, C₃₆ fullerene isomers must be highly aromatic with negative values. However, they are predicted to be antiaromatic with negative HSREs and negative TREs. The TRE method revealed that they all are aromatized by acquiring two or more electrons. NICSs at the cage center and the $2(N+1)^2$ rule cannot be used as an indicator of the aromatic stabilization for C₃₆ isomers and their molecular ions. We utilized the bond resonance energy (BRE) model to estimate the kinetic stability of C₃₆ isomers and their molecular ions. C₃₆ isomers are only stabilized kinetically in penta- and hexavalent molecular anions. All the results indicate that aromaticity and kinetic stability are closely related to the cyclic motion of π electrons.

Keywords Aromaticity · C₃₆ · Fullerene · NICS · Resonance energy

Introduction

Aromaticity is one of the most important and interesting concepts in modern organic chemistry. It has been defined in structural, magnetic and energetic terms [1]. In 1996, Schleyer et al. [2] proposed new magnetic criterion for

aromaticity: nucleus-independent chemical shift (NICS), which is defined as the negative value of the absolute shielding computed at the ring center or at some other interesting point of the system. Positive and negative NICS values are considered paramagnetic and diamagnetic ring currents, respectively. The more negative the NICS values, the more aromatic the molecules are. NICS (1) represent the value calculated at the ring center and 1 Å^o above the molecular plane.

Research on C₃₆ has attracted much attention in recent years. Chen et al. [3] reported NICS values of neutral C₃₆ fullerene molecules. Tanaka et al. [4] and Chen et al. [5–7] assigned the aromaticity of charged species some of the C₃₆ isomers. Then they found that neutral and charged isomers of C₃₆ have large negative NICS (1) values, suggesting that C₃₆ isomers must be highly aromatic. We noted that C₃₆ fullerene isomers are antiaromatic with negative topological resonance energy (TRE) [8, 9], even if they have negative NICS (1) values at the cage centers. In this paper, we attempt to critically evaluate the aromaticity of fullerene C₃₆ isomers using Hess-Schaad resonance energy (HSRE) [10, 11], TRE and percentage topological resonance energy (%TRE) methods. The absence of interrelation between aromaticity and diamagnetism is also discussed. Finally, we apply the bond resonance energy (BRE) model to C₃₆ isomers and their molecular ions to analyze their kinetic stability and isolability.

Methods of calculations

Aromaticity arises from extra thermodynamic stabilization due to cyclic conjugation. HSRE is defined as the difference between Hückel molecular orbital (HMO) π energy and the additive contribution obtained by summing

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individual bond energies. TRE is defined as the difference between the π -electron energy of a conjugated molecule and its hypothetical acyclic reference structure. Both the HSRE and TRE were defined using HMO theory and were found to be highly correlative with chemical reactivity for a variety of π -electronic systems. Positive and negative values of these resonance energies indicate aromaticity and antiaromaticity, respectively [8–11]. TRE can be evaluated not only for neutral but also for charged species. %TRE is defined as 100 times the TRE, divided by the total π -binding energy of the hypothetical acyclic reference structure. This index is useful for comparing the degree of aromaticity in different molecules, fullerene isomers and their molecular ions [12, 13]. The BRE represents the contribution of a given π -bond to TRE of the molecule [14]. The BRE is defined within the framework of HMO theory as follows. A hypothetical π -system, in which a given π -bond (e.g., the C_p - C_q bond) interrupts the cyclic conjugation of π -electrons thereat, is constructed by assuming $\beta_{pq} = i\beta$ and $\beta_{qp} = -i\beta$, where β is the standard resonance integral between two carbon $2p_z$ orbitals and i is the square root of -1 . In this π -system no circulation of π -electrons is expected along the circuits that share the C_p - C_q bond in common. BRE for the C_p - C_q bond can then be interpreted as a destabilization energy of this hypothetical π -system. In general, a molecule that has one or more π bonds with a large negative BRE is kinetically very unstable. The minimum (min) BRE signifies the smallest BRE in the molecule and is closely related to the kinetic stability of the molecule [15]. Aihara proved that if the min BRE is less than $-0.100 |\beta|$ the fullerenes will be kinetically very unstable [16]. This provides a simple index for determining the degree of kinetic stability for both isolated pentagon rule (IPR) and non-IPR fullerene isomers and their molecular ions [11, 12]. Note that not only TRE but also HSRE and BRE energy belong to the energetic criteria of aromaticity.

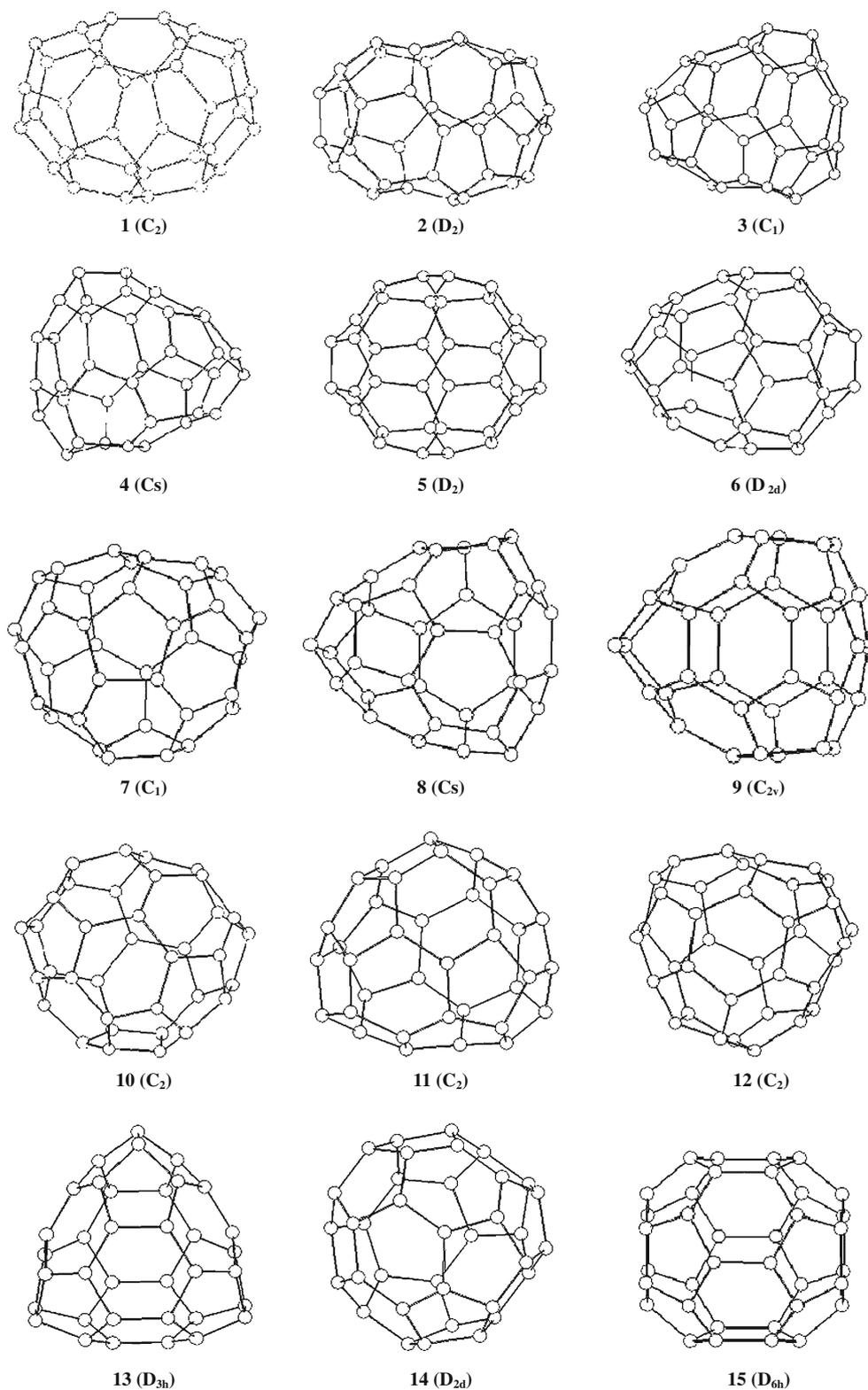
Results and discussion

Aromaticity of C_{36} isomers

In 1998, Piscoti et al. [17] synthesized C_{36} crystal and identified that C_{36} has a cage-like structure with D_{6h} symmetry from the solid state ^{13}C -NMR spectrum. In 2000, Shinohara and co-workers reported successful production of C_{36} related compounds, i.e., $C_{36}\text{H}_4$, $C_{36}\text{H}_6$, $C_{36}\text{H}_4\text{O}$, $C_{36}\text{H}_6\text{O}$, via the high-temperature laser-vaporization of metal-doped graphite rods [18, 19]. This result strongly indicates that C_{36} has very high reactivity. There are 15 conventional fullerene isomers for C_{36} [20]. These isomers are presented in Fig. 1.

The HSRE, TRE and %TRE have been computed for C_{36} isomers are listed in Table 1. The NICS (1) values, the number of pentagon adjacencies (e55) and the relative energies relevant to the present study are available from the literature [3, 21]. As shown in Table 1, all isomers but **14** have negative HSREs. HSRE is a simple but practical measure of aromaticity. C_{60} (I_h) has a HSRE of 1.866β [11]. C_{60} (I_h) has a %TRE of 1.795 [9, 12], which is about half that of benzene (3.528) [22]. Therefore, we might safely say that C_{60} is moderately aromatic with some olefinic character. TREs for C_{36} isomers studied are all negative in sign and predicted to be antiaromatic. In general, TRE is positive for fullerenes with more than 40 carbon atoms [13, 23]. It is noteworthy that isomer **14** is the most stable not only with small positive HSRE but also with a small negative TRE. Campbell et al. [24] indicated that stability of the small fullerenes correlates well with the minimum possible numbers of pentagon adjacencies. The most stable isomer is **14** with the smallest possible adjacency count (12). The most stable isomer of **14** also has been found at the B3LYP/6-31G* level of theory. As shown in Table 1, all the isomers have negative NICS (1) values. It lies in the range of from -38.2 to -2.3 . According to the original interpretation of NICS, all the isomers must be aromatic with negative NICS values. The NICS (1) values at the cage center calculated is -11.5 for benzene at the same level [2]. From the NICS values, we obtain the absurd conclusion that some C_{36} isomers are more aromatic than benzene. Some of the isomers have three or four times larger NICS values than benzene. The sign and magnitude of NICS values are not suited for estimating the degree of aromaticity of C_{36} isomers. Fullerenes are characterized by the presence of 12 pentagons and varying number of hexagons in their structure. For fullerenes hexagons and pentagons are the main source of aromaticity and antiaromaticity, respectively. The study of the aromaticity of C_{36} and C_{60} revealed that C_{60} has higher aromaticity than C_{36} [12, 13]. It is attributable that the larger proportion of hexagons in C_{60} than in C_{36} . C_{36} isomers have eight hexagons but many highly antiaromatic pentalene-like substructures. Thus, there is no reason to deny that all C_{36} isomers are almost antiaromatic.

Next, we examined the TRE for C_{36} isomers molecular ions. The TRE and %TRE for 15 different isomers of fullerene C_{36} from hexacations to hexaanions were given in Table 2. As shown in Table 2 multiple charged cations are antiaromatic with negative resonance energy, whereas its multiple charged anions are aromatic with positive resonance energy. When C_{36} accepts two or more π electrons, it becomes aromatic with a positive TRE. The TREs for C_{36} molecular ions markedly decrease by forming multiple charged cations. In contrast, the TREs markedly increase by forming multiple charged anions. In case of neutral

Fig. 1 Fifteen structural isomers of C_{36} 

fullerenes, each hexagon bears about six π -electrons and must be aromatic. However, each pentagon bears about five π -electrons and must be antiaromatic or at best nonaromatic. When one or more π -electrons were added into the pentagons aromatic hexagons arose; when one or more π -electrons were

removed from the hexagons an antiaromatic pentagon ring arose. If a C_{36} molecule bears a negative charge, constituent pentagons are more or less aromatized. Thus, one or more π -electrons added into the pentagons increases TRE. Conversely, the TRE decreases by removing one or more

Table 1 Resonance energies and NICS(1) values for C₃₆ fullerene isomers

Isomer	HSRE (β)	TRE (β)	%TRE	NICS(1) ^a	e55	Relative energy(kcal/mol) ^b
1(C ₂)	-0.479	-0.587	-1.070	-2.3	16	80.5
2(D ₂)	-0.259	-0.379	-0.690	-15.0	18	110.6
3(C ₁)	-0.367	-0.478	-0.871	-8.8	15	60.2
4(C _s)	-0.383	-0.497	-0.906	-14.0	16	78.2
5(D ₂)	-0.079	-0.185	-0.337	-24.3	16	91.1
6(D _{2d})	-0.143	-0.252	-0.458	-11.2	14	32.4
7(C ₁)	-0.174	-0.281	-0.512	-15.8	14	37.8
8(C _s)	-0.173	-0.285	-0.519	-32.5	14	24.7
9(C _{2v})	-0.113	-0.226	-0.412	-17.6	13	7.4
10(C ₂)	-0.212	-0.314	-0.573	-21.0	14	48.3
11(C ₂)	-0.111	-0.213	-0.388	-34.2	13	13.4
12(C ₂)	-0.176	-0.283	-0.516	-15.1	13	17.9
13(D _{3h})	-0.311	-0.437	-0.796	-29.8	15	40.7
14(D _{2d})	0.009	-0.097	-0.176	-15.4	12	0.0
15(D _{6h})	-0.362	-0.465	-0.847	-38.2	12	3.3

^a NICS(1) values at the GIAO-SCF/6-31G**/B3LYP/6-31G* level of theory [3]

^b Relative energies at the B3LYP/6-31G* level of theory [3]

π -electrons. Hückel theory indicated that C₃₆ molecules are an electron deficient system [25, 26]. If it takes six π -electrons it achieves a closed-shell electronic configuration. It has a tendency to accept up to six electrons from reducing species to form multiple charged anions. If six π -electrons are added to the lower-lying vacant orbitals, the molecules are highly aromatized. Thus the hexaanions have the largest TREs and are predicted to be the most aromatic over the other anions. On the other hand, fullerene cations of C₃₆ are predicted to be more antiaromatic with negative TREs. Molecular cations of any fullerene have not been isolated yet. It is much more

difficult to remove one or more π -electrons from the neutral species than to add one or more π -electrons, thus, C₃₆ cations have strong antiaromatic character. The TREs are fully consistent with the electron deficiency of these molecules.

Chen et al. [5, 6] found large negative NICS(1) values of -57.9, -64.0 and -28.3 at the cage center for the tetracations of isomer **9** and **14**, and dications of isomer **15** at the GIAO-SCF/6-31G* level although they have negative TREs. On the basis of the calculated NICS values Tanaka et al. [4] assigned the degree of aromaticity of the isomers **14** and **15** tends to decrease gradually from neutral

Table 2 TREs of C₃₆ isomers molecular ions ($|\beta|$)

Isomer	Charge											
	+6	+5	+4	+3	+2	+1	-1	-2	-3	-4	-5	-6
1(C ₂)	-1.464	-1.419	-1.373	-1.247	-1.120	-0.854	-0.154	0.280	0.764	1.247	1.578	1.909
2(D ₂)	-1.534	-1.429	-1.324	-1.106	-0.887	-0.633	-0.076	0.228	0.588	0.948	1.433	1.918
3(C ₁)	-1.461	-1.394	-1.327	-1.180	-1.032	-0.755	-0.060	0.358	0.861	1.364	1.558	1.752
4(C _s)	-1.470	-1.386	-1.302	-1.181	-1.060	-0.779	-0.050	0.397	0.763	1.129	1.535	1.940
5(D ₂)	-1.834	-1.595	-1.355	-1.084	-0.812	-0.499	0.154	0.492	0.760	1.027	1.480	1.932
6(D _{2d})	-1.714	-1.466	-1.217	-0.993	-0.769	-0.511	0.048	0.347	0.825	1.303	1.510	1.717
7(C ₁)	-1.624	-1.388	-1.151	-0.996	-0.841	-0.561	0.120	0.521	0.853	1.184	1.536	1.888
8(C _s)	-1.601	-1.373	-1.145	-1.014	-0.882	-0.584	0.101	0.487	0.902	1.317	1.513	1.708
9(C _{2v})	-1.581	-1.317	-1.052	-0.900	-0.748	-0.487	0.106	0.437	0.741	1.045	1.49	1.934
10(C ₂)	-1.731	-1.460	-1.188	-1.031	-0.874	-0.594	0.099	0.512	0.943	1.374	1.585	1.795
11(C ₂)	-1.671	-1.385	-1.099	-0.957	-0.814	-0.514	0.201	0.615	0.915	1.214	1.509	1.804
12(C ₂)	-1.672	-1.357	-1.041	-0.898	-0.754	-0.519	0.131	0.545	0.844	1.143	1.506	1.869
13(D _{3h})	-1.497	-1.368	-1.239	-1.093	-0.946	-0.692	0.021	0.479	0.747	1.014	1.457	1.900
14(D _{2d})	-1.731	-1.391	-1.051	-0.896	-0.741	-0.419	0.109	0.315	0.689	1.062	1.508	1.953
15(D _{6h})	-1.362	-1.391	-1.420	-1.268	-1.116	-0.791	0.038	0.541	0.803	1.065	1.509	1.952

Table 3 %TREs of C₃₆ isomers molecular ions

Isomer	Charge											
	+6	+5	+4	+3	+2	+1	-1	-2	-3	-4	-5	-6
1(C ₂)	-2.749	-2.642	-2.535	-2.291	-2.046	-1.558	-0.279	0.512	1.408	2.303	2.943	3.583
2(D ₂)	-2.881	-2.663	-2.445	-2.034	-1.622	-1.156	-0.554	-0.417	0.667	1.750	2.676	3.601
3(C ₁)	-2.741	-2.596	-2.450	-2.169	-1.887	-1.379	-0.108	0.655	1.587	2.518	2.904	3.289
4(C _s)	-2.760	-2.582	-2.403	-2.171	-1.938	-1.422	-0.091	0.725	1.405	2.085	2.864	3.642
5(D ₂)	-3.442	-2.972	-2.501	-1.993	-1.484	-0.911	0.281	0.899	1.398	1.896	2.761	3.626
6(D _{2d})	-3.217	-2.732	-2.246	-1.826	-1.405	-0.932	0.088	0.634	1.520	2.405	2.814	3.223
7(C ₁)	-3.047	-2.586	-2.124	-1.831	-1.538	-1.025	0.220	0.952	1.569	2.185	2.865	3.544
8(C _s)	-3.005	-2.560	-2.114	-1.864	-1.613	-1.066	0.186	0.891	1.661	2.430	2.818	3.206
9(C _{2v})	-2.967	-2.455	-1.942	-1.655	-1.367	-0.890	0.194	0.799	1.364	1.929	2.779	3.629
10(C ₂)	-3.250	-2.721	-2.192	-1.895	-1.598	-1.086	0.182	0.936	1.736	2.535	2.952	3.369
11(C ₂)	-3.137	-2.583	-2.029	-1.759	-1.488	-0.938	0.368	1.123	1.682	2.241	2.813	3.385
12(C ₂)	-3.138	-2.530	-1.922	-1.651	-1.379	-0.948	0.240	0.996	1.554	2.111	2.810	3.508
13(D _{3h})	-2.810	-2.549	-2.288	-2.009	-1.729	-1.263	0.040	0.875	1.374	1.872	2.719	3.566
14(D _{2d})	-3.248	-2.594	-1.939	-1.647	-1.355	-0.766	0.200	0.576	1.268	1.960	2.813	3.665
15(D _{6h})	-2.556	-2.589	-2.621	-2.331	-2.040	-1.444	0.071	0.989	1.478	1.966	2.814	3.662

to dianions. In 2000, Hirsch et al. calculated the NICS values at the cage centers of neutral and charged fullerenes and proposed the so-called $2(N+1)^2$ rule of spherical aromaticity [27], where N is zero or an arbitrary positive integer. They found that neutral and charged fullerenes with $2(N+1)^2$ π -electrons have a large negative NICS values, suggesting that these fullerenes must be highly aromatic. All the tetracation ions of C₃₆ isomers have $2(N+1)^2$ π -electrons with $N=3$. As can be seen from Table 3, all the tetracations have negative TREs. There is no doubt that all these C₃₆ tetracations are antiaromatic although they have $2(N+1)^2$ π -electrons, together with large negative NICS value at the cage centers. It is evident that the $2(N+1)^2$ rule cannot be used as an indicator of the aromatic stabilization for C₃₆ isomers molecular ions. This convinced us that the NICS values at the cage center are not related directly to aromaticity and cannot be used as an indicator of aromaticity for C₃₆ isomers. The negative NICS values simply indicate that the species concerned is diatropic at the cage center. We long ago reported the aromaticity and magnetic properties of cycl[3.2.2]azines and cycl[3.3.3]azines [28]. On the basis of ¹H NMR spectra of these compounds, cycl[3.2.2]azines are predicted to be diatropic, on the other hand cycl[3.3.3]azines paratropic. But both are aromatic with positive TREs. It has been seen that diatropicity and paratropicity coexist in some of the polycyclic aromatic compounds. The diatropicity and paratropicity mainly come from the peripheral structure of the polycyclic compounds. But the aromaticity mainly comes from all the possible relatively small rings or circuits in the polycyclic compounds [28]. According to Haddon et

al. [29, 30] the ring currents in C₆₀ (I_h) can be thought of as the superposition of the induced currents in the individual rings and those circulating all around the molecule. The small ring current for C₆₀ (I_h) results from a compensating effect of strong paramagnetic currents induced in the five-membered rings and diamagnetic ones flowing around the molecule. As far as C₃₆ is concerned, the π -electron currents induced along the equatorial belt of the molecule contribute much to not only the NICS value at the cage center but also those at the individual rings center. In contrast, aromaticity is determined primarily by the relatively small circuits. Large circuits are much less responsible for aromaticity.

Kinetic stability of C₃₆ isomers

It is not easy to estimate the kinetic stability of a polyatomic molecule, because innumerable chemical reactions are involved. By kinetic stability, we mean stability against any possible chemical reaction and decomposition. In general, kinetic instability is very sensitive to the presence or absence of anti-or non-aromatic substructures. This substructure must be very reactive and fragile. Aromaticity cannot always be regarded as an indication of kinetic stability because aromatic non-benzenoid molecules are not always kinetically stable. The IPR rule holds for isolable or extractable fullerenes. The energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) has been used successfully to predict the degree of kinetic stability in neutral fullerenes [31]. Unfortunately, both the IPR rule and

the HOMO-LUMO gap do not apply to charged fullerenes. Thus, we estimated the kinetic stability of C_{36} isomers and their molecular anions by the BRE model [14–16]. The min BREs for all C_{36} isomers and their molecular anions are listed in Table 4. The min BREs $> -0.100|\beta|$ are underlined. It is noteworthy that isomer **14** has the largest min BRE in the neutral state, but its value is less than $-0.100|\beta|$, showing that all of the isomers are kinetically unstable in the neutral state. According to BRE studies, adjacent pentagons often exhibit large negative BREs [14, 32]. Therefore, it seems quite likely that such antiaromatic pentalene like substructures are the main source of kinetic instability or synthetic difficulty.

We see from the Table 4 that kinetic stability of all the isomers varies markedly by the variation of the charge. This means that the kinetic stability of pentagonal rings and constituent π bonds in C_{36} isomers is enhanced when the molecule bears more negative charge. All the isomers in mono- or dianionic states also have the min BREs smaller than $-0.100|\beta|$. These anions have not been isolated, either. Because it has an empty bonding orbital in the neutral state, but two electrons added are not enough to stabilize it. We conclude that C_{36} must be unable to form kinetically stable metallofullerenes in neutral or mono- or dianionic states. This is its difference from the C_{36} isomers with IPR fullerenes. Among the tetraanions some isomers min BREs $> -0.100|\beta|$. These tetravalent isomers are moderately aromatic with C_{60} . Guo et al. [33] detected the formation of $U@C_{36}$. Uranium atom usually forms a tetracation. Among the tetra-anions, isomer **10** is predicted to be the most stable with the largest %TRE (2.535). As shown in Table 3, the %TRE of penta- and

hexaanions are large positive values. The %TRE of hexaanions of all isomers is much larger than the C_{60} (1.795) and as large as benzene (3.528) [22]. These isomers also have a min BREs $> -0.100|\beta|$. Thus, $M@C_{36}$ must also be thermodynamically very stable, if M denotes metal atoms from pentavalent to hexavalent. According to the %TREs and min BREs, we can predict that penta- and hexavalent metallofullerenes may be extracted from the arc-produced soot as a salt.

Conclusions

Studies have demonstrated that NICS values calculated for C_{36} isomers and the $2(N+1)^2$ rule are not associated with aromaticity of fullerene C_{36} isomers and their molecular ions. There is no correlation with the energetic criteria of aromaticity. Note that aromaticity in principle is a state of energy [34]. It comes from all the possible circuits in the molecule. In this sense, the main source of antiaromaticity in C_{36} isomers is a large proportion of pentagons to hexagons or the pentalene like substructures. Both the NICS values and the $2(N+1)^2$ rule does not take into account the effect of such local structures on aromaticity. This is why the NICS values and the $2(N+1)^2$ rule failed to predict the aromaticity of the C_{36} molecule and their molecular ions. The HSRE and TRE defined above can be used to estimate the degree of aromaticity for fullerene C_{36} isomers. Note that variation of total charge markedly affects the aromaticity and the kinetic stability of C_{36} isomers. At the penta- or hexavalent anionic states, the C_{36}

Table 4 Min BREs of C_{36} isomers molecular anions ($-\beta$)

Isomer	Charge						
	0	-1	-2	-3	-4	-5	-6
1 (C_2)	-0.5147	-0.4226	-0.3589	-0.1872	-0.0499	0.0976	0.1330
2 (D_2)	-0.3616	-0.2838	-0.2683	-0.2348	-0.2410	0.0076	0.1526
3 (C_1)	-0.5177	-0.4518	-0.4201	-0.1440	0.0300	0.1024	0.0761
4 (C_s)	0.5272	-0.3589	-0.2145	-0.1365	-0.1497	0.0553	0.1580
5 (D_2)	-0.2788	-0.2019	-0.1822	-0.1822	-0.2255	0.0149	0.1483
6 (D_{2d})	-0.3471	-0.3554	-0.3667	-0.1432	0.0412	0.1009	0.0760
7 (C_1)	-0.4974	-0.2891	-0.2169	-0.1318	-0.1042	0.0687	0.1247
8 (C_s)	-0.3769	-0.3249	-0.3366	-0.1073	0.0158	0.0896	0.0645
9 (C_{2v})	-0.4634	-0.2690	-0.1657	-0.1621	-0.1660	0.0284	0.1367
10 (C_2)	-0.4012	-0.3238	-0.2837	-0.0629	0.0557	0.1125	0.1142
11 (C_2)	-0.4753	-0.2501	-0.1685	-0.0686	-0.0234	0.0859	0.1151
12 (C_2)	-0.4241	-0.2659	-0.1898	-0.1209	-0.0915	0.0636	0.1160
13 (D_{3h})	-0.3870	-0.2561	-0.1251	-0.1634	-0.2016	0.0325	0.1659
14 (D_{2d})	-0.1766	-0.2331	-0.2895	-0.1976	-0.1382	0.0508	0.1602
15 (D_{6h})	-0.4826	-0.3019	-0.1212	-0.1212	-0.1212	0.0451	0.1607

isomers are predicted to be not only highly aromatic with a large TRE but also highly kinetically stable without any min BREs $< -0.100|\beta|$ bonds.

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