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## **Kinetic Instability of Neutral and Charged Fullerenes with Four–Membered Rings**

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# Kinetic Instability of Neutral and Charged Fullerenes with Four-Membered Rings<sup>#</sup>

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## Abstract

The kinetic instability of neutral and charged fullerenes was estimated with good accuracy by the bond resonance energy (BRE) model. Classical fullerenes with or without adjacent pentagons are stabilized kinetically by acquiring two or more electrons. However, the same is not true for fullerenes with one four-membered ring. Such non-classical fullerene isomers are predicted to be very reactive even if they carry large negative charge. It must be difficult for such fullerenes to form kinetically stable metallofullerenes.

**Keywords.** Fullerene with four-membered rings; kinetic stability; BRE; bond resonance energy; TRE; topological resonance energy.

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## 1 INTRODUCTION

Isolable metallofullerenes consist of a negatively charged fullerene cage and one or more metal cations within it [1–3]. Such a charged fullerene cage must be kinetically stable since it survives the harsh synthetic conditions. By kinetic stability, we mean stability with respect to the activated complex of any possible chemical reaction [4,5]. Carbon cages in all metallofullerenes isolated so far are classical fullerenes with five- and six-membered rings only. Recently isolated  $\text{Sc}_2@C_{66}$  and  $\text{Sc}_3\text{N}@C_{68}$  contain fullerene cages with adjacent pentagons [6,7]. These carbon cages must likewise be kinetically stable.

Not only classical but also non-classical fullerenes may be capable of forming kinetically stable metallofullerenes. Among such candidates are fullerenes with four-membered rings. In 1993 Gao and Herndon suggested that fullerenes with fewer than 60 carbon atoms might be stabilized thermodynamically by inserting square faces into them [8]. Babić and Trinajstić estimated the degrees of aromaticity for such fullerenes [9–11]. Fowler *et al.* systematically designed a series of

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higher fullerenes with one four-membered ring and examined their thermodynamic stability in some detail [12]. Their QCFF/PI (quantum consistent force field/ $\pi$ ) calculations for selected isomers of  $C_{62}$  to  $C_{68}$  revealed that some square-containing isomers are fairly low in energy.

If fullerene cages with square faces are not thermodynamically very unstable in the neutral electronic state, there is a possibility that some of them might be stabilized kinetically by acquiring some extra electrons and form isolable metallofullerenes [13]. However, no one has ever investigated the kinetic stability of such fullerene molecular ions. We established that the minimum bond resonance energy (min BRE) in a fullerene  $\pi$ -system represents well the degree of kinetic stability [2,3,5,14–19]. In this paper, we predict the kinetic stability of neutral and negatively charged fullerenes with four-membered rings using the BRE model.

## 2 THEORY

Detailed definition of the BRE has been described elsewhere [14,15]. It represents the contribution of a given  $\pi$  bond to the topological resonance energy (TRE) [20,21]. The min BRE is one of the practical indices of kinetic stability [2,3,14–19]. If the min BRE of a given molecule has a large negative value, it will be kinetically unstable with chemically reactive sites in it [2,3,14–19]. We have presumed that if the min BRE is less than  $-0.100 |\beta|$ , the species will be kinetically very unstable. All metallofullerenes so far extracted and structurally identified have a negatively charged carbon cage with a min BRE  $> -0.100 |\beta|$  [2,3], where  $\beta$  is the Hückel resonance integral. Metallofullerenes that contain a carbon cage with adjacent pentagons are not exceptional [19].

## 3 RESULTS AND DISCUSSION

The min BREs calculated for classical fullerene isomers with 62–68 carbon atoms are listed in Table 1. All these isomers are the lowest-energy one and the ones that are at most 11 kcal/mol less stable than it [12]. Isomer numbers given in this table are those proposed by Fowler *et al.* [12]. For molecular structures of these isomers, see spiral codes in [12]. Isomers with a min BRE  $< -0.100 |\beta|$  are denoted in boldface. It is noteworthy that all of these classical isomers have a min BRE  $< -0.100 |\beta|$  in the neutral electronic state, showing that all of them are kinetically unstable. These large negative min BREs arise from the CC bonds shared by two pentagons [14]. This constitutes the very reason why the isolated pentagon rule holds for fullerenes.

As pointed out by Fowler and Zerbetto [13], the variation of the charge markedly affects the relative energies of fullerene isomers. Kinetic stability of each fullerene isomer also varies markedly by the variation of the charge [2,3,14–19]. As shown in Table 1, classical fullerene isomers with adjacent pentagons are all stabilized by acquiring one or more excess electrons. All molecular di- to tetra-anions have a min BRE  $> -0.100 |\beta|$ , indicating that such molecular anions

are kinetically stable. It is clear that even CC bonds shared by two pentagons are stabilized kinetically in polyvalent molecular anions. This is a feature common to many classical fullerene isomers with or without adjacent pentagons [2,3,15–19].

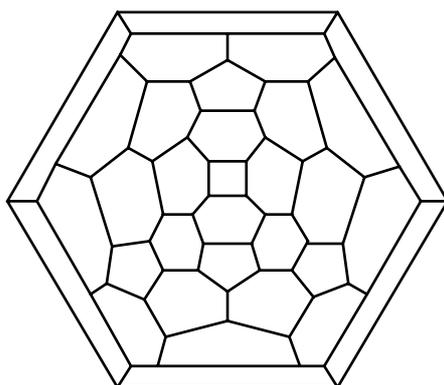
The min BREs calculated for low-energy isomers with one square ring of C<sub>62</sub> to C<sub>68</sub> fullerenes are listed in Table 2. All C<sub>62</sub> isomers in this table are 34–82 kcal/mol less stable than the most stable isomer, C<sub>62</sub>(**2194**,C<sub>1</sub>) in Table 1 [12]. C<sub>64</sub>, C<sub>66</sub>, and C<sub>68</sub> isomers in Table 2 are more than 70 kcal/mol higher than their respective lowest-energy isomers. Isomer numbers given in this table are again those proposed by Fowler *et al.* [12]. For molecular structures of these isomers, see spiral codes in [12]. Isomers with a min BRE < -0.100 |β| are denoted in boldface. This table shows that fullerene isomers with one four-membered ring in general have a min BRE < -0.100 |β| in the neutral electronic state, indicating that they must be kinetically very unstable. C<sub>66</sub>(**14298**,C<sub>2v</sub>) is apparently exceptional as its min BRE is slightly larger than -0.100 |β|. However, this C<sub>66</sub> isomer is 89 kcal/mol higher than the most stable classical isomer, C<sub>66</sub>(**4169**,C<sub>s</sub>) [12].

For fullerenes with one square face, min BREs always occurs at the CC bonds in the square ring. In general, CC bonds in the four-membered rings have larger negative BREs than those shared by two pentagons. The Schlegel diagram for C<sub>62</sub>(**9620**,C<sub>2v</sub>) is shown in Figure 1. This is the lowest-energy fullerene isomers with one square face, which is only 34 kcal/mol higher than the lowest-energy classical isomer, C<sub>62</sub>(**2194**,C<sub>1</sub>) [12]. Since C<sub>62</sub>(**9620**,C<sub>2v</sub>) has no adjacent pentagons, only CC bonds of the square face have a BRE < -0.100 |β|. Note that a fullerene molecule with a square face has two less pentagons [12]. Thus, not only adjacent pentagons but also square faces proved to be the main origins of kinetic instability.

**Table 1.** Min BREs for Low-Energy Classical Isomers of Fullerenes with 62–68 Carbon Atoms and Their Molecular Anions. Species with a min BRE < -0.100 |β| are Denoted in Boldface.

Species	min BRE /  β						
	neutral	anion	dianion	trianion	teraanion	pentaanion	hexaanion
C <sub>62</sub> ( <b>2194</b> ,C <sub>1</sub> )	<b>-0.3486</b>	<b>-0.1304</b>	0.0772	0.0417	-0.0133	-0.0396	-0.0924
C <sub>62</sub> ( <b>2378</b> ,C <sub>2</sub> )	<b>-0.2786</b>	<b>-0.1550</b>	-0.0469	-0.0013	0.0133	0.0723	0.0975
C <sub>62</sub> ( <b>2377</b> ,C <sub>1</sub> )	<b>-0.2754</b>	<b>-0.1205</b>	-0.0980	0.0386	0.0659	-0.0078	<b>-0.1083</b>
C <sub>64</sub> ( <b>3451</b> ,D <sub>2</sub> )	<b>-0.1206</b>	-0.0661	-0.0116	-0.0036	-0.0124	0.0630	0.0964
C <sub>64</sub> ( <b>3452</b> ,C <sub>s</sub> )	<b>-0.1101</b>	-0.0834	-0.0567	0.0612	0.0525	-0.0052	<b>-0.1026</b>
C <sub>64</sub> ( <b>3457</b> ,C <sub>2</sub> )	<b>-0.2195</b>	-0.0302	0.0733	0.0299	-0.0272	-0.0496	-0.0930
C <sub>66</sub> ( <b>4169</b> ,C <sub>s</sub> )	<b>-0.2128</b>	-0.0223	0.0642	0.0537	0.0009	-0.0450	<b>-0.1334</b>
C <sub>66</sub> ( <b>4348</b> ,C <sub>2v</sub> )	<b>-0.4281</b>	<b>-0.1362</b>	0.0899	0.0102	-0.0707	<b>-0.1022</b>	<b>-0.1338</b>
C <sub>66</sub> ( <b>4466</b> ,C <sub>2</sub> )	<b>-0.2884</b>	-0.0829	0.0815	0.0186	-0.0553	-0.0574	-0.0596
C <sub>68</sub> ( <b>6290</b> ,C <sub>2</sub> )	<b>-0.1081</b>	-0.0561	-0.0040	0.0130	-0.0149	0.0537	0.0872
C <sub>68</sub> ( <b>6328</b> ,C <sub>2</sub> )	<b>-0.1973</b>	-0.0187	0.0664	0.0290	-0.0416	-0.0432	-0.0542
C <sub>68</sub> ( <b>6198</b> ,C <sub>1</sub> )	<b>-0.3196</b>	-0.0781	0.0733	0.0414	-0.0116	-0.0533	<b>-0.1148</b>
C <sub>68</sub> ( <b>6270</b> ,C <sub>1</sub> )	<b>-0.2400</b>	-0.0922	-0.0839	0.0053	0.0061	0.0373	0.0376
C <sub>68</sub> ( <b>6094</b> ,C <sub>s</sub> )	<b>-0.3704</b>	-0.0945	0.0619	0.0714	0.0482	-0.0414	<b>-0.1399</b>
C <sub>68</sub> ( <b>6146</b> ,C <sub>2</sub> )	<b>-0.1766</b>	<b>-0.1073</b>	-0.0380	0.0210	0.0702	0.0838	0.0855

Qian *et al.* carried out molecular orbital calculation on  $C_{62}(\mathbf{9620}, C_{2v})$  at the B3LYP/6–31G\* level of theory [22], which revealed that the optimized structure favors the [4]radialene rather than the cyclobutadiene resonance to relax the antiaromatic character of the four-membered ring. Its frontier molecular orbitals are localized mainly around the four-membered ring in agreement with the location of CC bonds with large negative BREs [22]. Therefore, this molecule is presumed to be quite reactive under normal isolation conditions. Qian *et al.* attempted to prepare it from  $C_{60}(I_h)$  in solution [22,23].



**Figure 1.** The Schlegel diagram for  $C_{62}(\mathbf{9620}, C_{2v})$ .

**Table 2.** Min BREs for Low-Energy Isomers with One Square Face of Fullerenes with 62–68 Carbon Atoms and Their Molecular Anions. Species with a min BRE  $< -0.100 |\beta|$  are Denoted in Boldface.

Species	min BRE / $ \beta $						
	neutral	anion	dianion	trianion	teraanion	pentaanion	hexaanion
$C_{62}(\mathbf{9620}, C_{2v})$	<b>-0.3691</b>	<b>-0.2411</b>	<b>-0.1940</b>	<b>-0.1923</b>	<b>-0.1905</b>	<b>-0.1971</b>	<b>-0.2036</b>
$C_{62}(\mathbf{8255}, C_1)$	<b>-0.1838</b>	<b>-0.2322</b>	<b>-0.2813</b>	<b>-0.2259</b>	<b>-0.2626</b>	<b>-0.2670</b>	<b>-0.2714</b>
$C_{62}(\mathbf{9899}, C_s)$	<b>-0.4329</b>	<b>-0.3237</b>	<b>-0.2201</b>	<b>-0.2046</b>	<b>-0.2772</b>	<b>-0.2721</b>	<b>-0.2670</b>
$C_{62}(\mathbf{9618}, C_1)$	<b>-0.3821</b>	<b>-0.3594</b>	<b>-0.3424</b>	<b>-0.2521</b>	<b>-0.2013</b>	<b>-0.1923</b>	<b>-0.1948</b>
$C_{62}(\mathbf{10323}, C_{2v})$	<b>-0.3089</b>	<b>-0.3641</b>	<b>-0.4192</b>	<b>-0.3040</b>	<b>-0.1889</b>	<b>-0.1674</b>	<b>-0.1613</b>
$C_{62}(\mathbf{9117}, C_s)$	<b>-0.4837</b>	<b>-0.4355</b>	<b>-0.3873</b>	<b>-0.2400</b>	<b>-0.1356</b>	<b>-0.1453</b>	<b>-0.1550</b>
$C_{62}(\mathbf{8256}, C_1)$	<b>-0.1932</b>	<b>-0.2000</b>	<b>-0.2067</b>	<b>-0.2673</b>	<b>-0.3279</b>	<b>-0.2550</b>	<b>-0.2394</b>
$C_{62}(\mathbf{9611}, C_1)$	<b>-0.3009</b>	<b>-0.3409</b>	<b>-0.3843</b>	<b>-0.2678</b>	<b>-0.1653</b>	<b>-0.1703</b>	<b>-0.1754</b>
$C_{62}(\mathbf{8157}, C_1)$	<b>-0.1942</b>	<b>-0.2446</b>	<b>-0.2950</b>	<b>-0.2228</b>	<b>-0.1936</b>	<b>-0.2545</b>	<b>-0.3174</b>
$C_{62}(\mathbf{8156}, C_1)$	<b>-0.2558</b>	<b>-0.2063</b>	<b>-0.1657</b>	<b>-0.2103</b>	<b>-0.2638</b>	<b>-0.2429</b>	<b>-0.2770</b>
$C_{62}(\mathbf{9345}, C_1)$	<b>-0.4308</b>	<b>-0.3508</b>	<b>-0.2756</b>	<b>-0.2271</b>	<b>-0.2173</b>	<b>-0.1727</b>	<b>-0.1905</b>
$C_{62}(\mathbf{8542}, C_2)$	<b>-0.1189</b>	<b>-0.1149</b>	<b>-0.1109</b>	<b>-0.1653</b>	<b>-0.2400</b>	<b>-0.2841</b>	<b>-0.3281</b>
$C_{64}(\mathbf{9902}, C_s)$	<b>-0.3005</b>	<b>-0.2170</b>	<b>-0.1596</b>	<b>-0.2108</b>	<b>-0.2620</b>	<b>-0.2595</b>	<b>-0.2571</b>
$C_{66}(\mathbf{14298}, C_{2v})$	<b>-0.0779</b>	<b>-0.1580</b>	<b>-0.2382</b>	<b>-0.2835</b>	<b>-0.3289</b>	<b>-0.3016</b>	<b>-0.2744</b>
$C_{68}(\mathbf{15749}, C_s)$	<b>-0.1281</b>	<b>-0.2099</b>	<b>-0.3229</b>	<b>-0.2543</b>	<b>-0.2073</b>	<b>-0.2076</b>	<b>-0.2078</b>

It is noteworthy that fullerenes with one square face have a large negative min BRE even if they carry negative charge. In marked contrast to classical fullerenes, all mono- and poly-valent molecular anions of such non-classical fullerenes are predicted to be kinetically very unstable with a min BRE  $< -0.100 |\beta|$ . Four peripheral CC bonds of the square ring still have very large negative BREs. Most fullerenes with a square face listed in Table 2 have one empty bonding orbital in the neutral electronic state, but two additional electrons are not enough to stabilize the four-membered ring. Therefore, such fullerenes must be unable to form kinetically stable metallofullerenes.

Gao and Herndon designed five fullerene molecules with two square faces and suggested that some of them might be kinetically very stable because they have a large highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) energy separation [8]. We found that some of them have a min BRE  $> -0.100 |\beta|$  [11]. This may be due partly to the fact that they have only eight five-membered rings. The min BREs for five fullerenes with two square faces and their molecular anions are listed in Table 3. For their molecular structures, see [8]. All the molecular trianions and tetraanions have a min BRE  $< -0.100 |\beta|$ .

Among the species designed by Gao and Herndon is the C<sub>40</sub> isomer with D<sub>4h</sub> symmetry [8], which is identical with isomer **542** in the list of C<sub>40</sub> isomers presented later by Fowler et al. [12]. This isomer is 110 kcal/mol higher in energy than the most stable classical isomer although it is the lowest-energy isomer with two square faces. This isomer happens to have a large negative min BRE. Fowler *et al.* pointed out that lowest-energy C<sub>40</sub> cages with one or more squares are much higher in energy than the best conventional fullerene isomer [12]. Larger fullerenes must likewise be thermodynamically very unstable if they have two or more square faces.

**Table 3.** Min BREs for Five Fullerenes with Two Square Faces and Their Molecular Anions. Species with a min BRE  $< -0.100 |\beta|$  are Denoted in Boldface.

Species	min BRE / $ \beta $						
	neutral	anion	dianion	trianion	teraanion	pentaanion	hexaanion
C <sub>32</sub> (S <sub>4</sub> )	-0.0726	-0.0726	-0.0726	<b>-0.2950</b>	<b>-0.5173</b>	<b>-0.2937</b>	-0.0701
C <sub>40</sub> ( <b>542</b> ,D <sub>4h</sub> )	<b>-0.3343</b>	<b>-0.1019</b>	<b>-0.0529</b>	<b>-0.3185</b>	<b>-0.5841</b>	<b>-0.5520</b>	<b>-0.5200</b>
C <sub>48</sub> (D <sub>4d</sub> )	-0.0581	<b>-0.1078</b>	<b>-0.1575</b>	<b>-0.3274</b>	<b>-0.4974</b>	<b>-0.4452</b>	<b>-0.3930</b>
C <sub>56</sub> (D <sub>4h</sub> )	-0.0496	-0.0496	-0.0496	<b>-0.2941</b>	<b>-0.5387</b>	<b>-0.5010</b>	<b>-0.4634</b>
C <sub>60</sub> (C <sub>2v</sub> )	<b>-0.1139</b>	<b>-0.1786</b>	<b>-0.2857</b>	<b>-0.3090</b>	<b>-0.3323</b>	<b>-0.3319</b>	<b>-0.3315</b>

In 1994 Dunlap and Taylor designed a C<sub>48</sub> fullerene isomer with O<sub>h</sub> symmetry [24]. This molecule is constructed formally from C<sub>60</sub>(I<sub>h</sub>) by removing six pairs of carbon atoms, which fuse two six-membered rings at the ends of three mutually perpendicular axes, and then connecting the ensuing dangling bonds. All the carbon atoms are equivalent, being shared by one four-, one six-, and one eight-membered ring. For the molecular structure, see [24]. They calculated the HOMO–LUMO energy gap of C<sub>48</sub>(O<sub>h</sub>) to be less than one-third that of C<sub>60</sub>(I<sub>h</sub>) and predicted that C<sub>48</sub>(O<sub>h</sub>) is

considerably less stable [24]. This prediction is consistent with the very large negative min BRE. The min BREs for C<sub>48</sub>(O<sub>h</sub>) and its molecular anions are listed in Table 4. It appears that this alternant molecule is never stabilized by acquiring one or more excess electrons.

**Table 4.** Min BREs for the Octahedral C<sub>48</sub> Fullerene and Its Molecular Anions. Species with a min BRE < -0.100 |β| are Denoted in Boldface.

Species	min BRE /  β						
	neutral	anion	dianion	trianion	teraanion	pentaanion	hexaanion
C <sub>48</sub> (O <sub>h</sub> )	<b>-0.4045</b>	<b>-0.4045</b>	<b>-0.4045</b>	<b>-0.3024</b>	<b>-0.2004</b>	<b>-0.2302</b>	<b>-0.2600</b>

## 4 CONCLUSIONS

Although many of the classical fullerene isomers are reactive in the neutral electronic state, they are often employed to construct isolable metallofullerenes [1–3]. Even if fullerene cages contain adjacent pentagons, they are markedly stabilized by accepting one or more extra electrons from metal atoms [6,7,19]. Non-classical fullerenes with a four-membered ring were predicted to behave in quite a different manner. They are predicted to be kinetically very unstable in the neutral electronic state and still so even if they carry large negative charge. In addition, they must suffer from the strain energy due to the presence of square and pentagonal faces. Therefore, it must be very difficult for this kind of fullerene isomers to form isolable or extractable metallofullerenes. This aspect of kinetic stability clearly distinguish the non-classical fullerenes with square faces from the classical ones with or without adjacent pentagons.

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## Biographies

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