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Kinetic Stability of Gold Fullerenes and the $2(N+1)^2$ Rule

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Gold fullerenes conform to the $2(N+1)^2$ skeletal electron counting rule, namely, they attain the maximum degree of kinetic stability when they have $2(N+1)^2$ mobile electrons. Icosahedral Au_{32} ($N = 3$) is predicted to possess the highest kinetic stability with the largest minimum bond resonance energy. Thus, gold fullerenes are much less sensitive to local ring structure than carbon fullerenes. In such a situation, the $2(N+1)^2$ rule works as a rule of kinetic stability rather than as that of spherical aromaticity.

It is not easy to estimate the kinetic stability of a polyatomic molecule, because innumerable chemical reactions are involved. In 1995, we found that bond resonance energy (BRE) reflects the kinetic stability of the cyclic π-system concerned.[1–6] This quantity is defined graph-theoretically as a contribution of a given π-bond to topological resonance energy (TRE).[3,4] In general, kinetic stability of a molecule is determined by the chemical reactivity at the most reactive site in the molecule. We have noted that the smallest or minimum BRE (min BRE) in a molecule can be used as a good measure of kinetic stability for polycyclic conjugated hydrocarbons and fullerenes.[2–6] Min BRE is obviously preferred as an indicator of kinetic stability to TRE. As far as fullerenes and their molecular ions are concerned, those with min BREs $< -0.100|\beta|$ are kinetically unstable and difficult to isolate.[2–6]

Like carbon atoms, gold atoms tend to form large hollow cages.[7–12] Small gold clusters, at least up to 13 atoms, favor planar trigonal raft structures.[13–16] Deltahedral gold cages are presumed to form if many Au atoms aggregate. Recently, Johansson et al. have predicted a highly stable icosahedral Au_{32} fullerene on the basis of DFT calculations.[7] This gold cluster has been predicted to be highly aromatic with a large negative nucleus independent chemical shift (NICS) value at the cage center. Other gold deltahedrons, such as $Au_{42}(I_h)$ and $Au_{50}(D_{6d})$, might also be more or less stable.[10–12] In this paper, we report that the kinetic stability of such gold deltahedrons can be examined consistently in terms of the $2(N+1)^2$ skeletal electron counting rule[17–20] and the BRE concept,[2–6] the former of which has been proposed by Hirsch et al. to rationalize the possible aromaticity of spherical molecules.[17–20]

Theory

A fullerene π-system can be viewed naively as an electron gas bound on the surface of a sphere.[21–23] Such a spherical quasi-free-electron system takes a closed-shell electronic configuration when it contains $2(N+1)^2$ mobile electrons, where N is a non-negative integer. In 2000, Hirsch et al. found that large negative NICS values occur at the centers of fullerene cages with $2(N+1)^2$ π-electrons.[17–20] This is the central idea of the $2(N+1)^2$ skeletal electron counting rule. Johansson et al. then reported the occurrence of a large negative NICS value at the center of the Au_{32} cage.[7] This fact strongly supports the view that 32 electrons arising from gold 6s valence shells can be depicted as free or mobile electrons bound on the surface of a sphere. BRE calculations were performed by applying Hückel molecular orbital (HMO) theory to such gold clusters. For the definition of BRE, see Ref. 3 or 4.

We used the min BRE of a molecule as an indicator of kinetic stability. Figure 1 summarizes the min BREs for $C_{60}(I_h)$ and all possible molecular ions, the numerical values of which have been published elsewhere.[5] The $C_{60}(I_h)$ molecular anions with 62–70 π-electrons are kinetically stable with min BREs $> -0.100|\beta|$. These molecular anions are in marked contrast in kinetic stability to the dication and tetracation, which are kinetically very unstable with min BREs $< -0.100|\beta|$. Note, however, that $C_{50}(D_{5h})$ ($N = 4$) is moderately aromatic (TRE $= 0.708|\beta|$) but is predicted to be kinetically very unstable (min BRE $= -0.308|\beta|$).[4] Such a trend in kinetic stability is fully congruent with experiment.[5] We have shown that the fullerenes and metallofullerenes with min BREs $< -0.100|\beta|$ have not been isolated from the fullerene soot.[6]

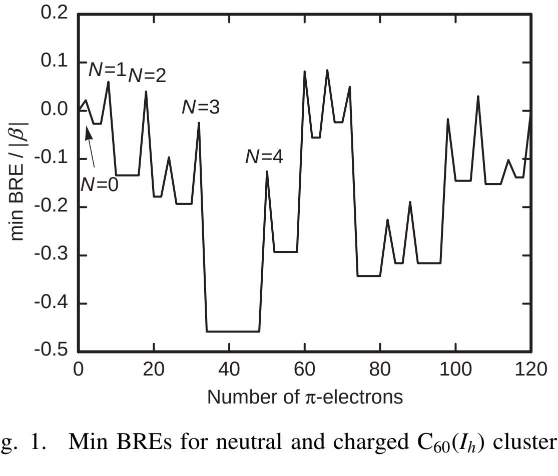

Fig. 1. Min BREs for neutral and charged $C_{60}(I_h)$ clusters.

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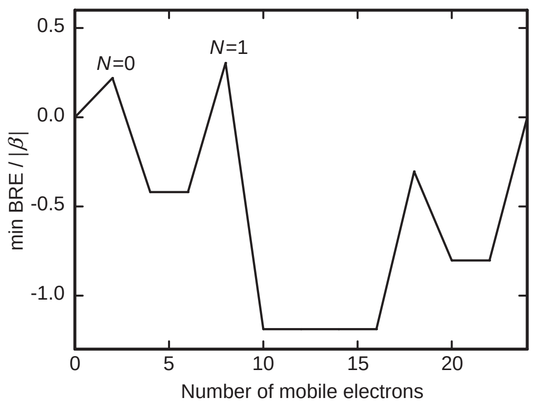

Fig. 2. Min BREs for neutral and charged $Au_{12}(I_h)$ clusters.

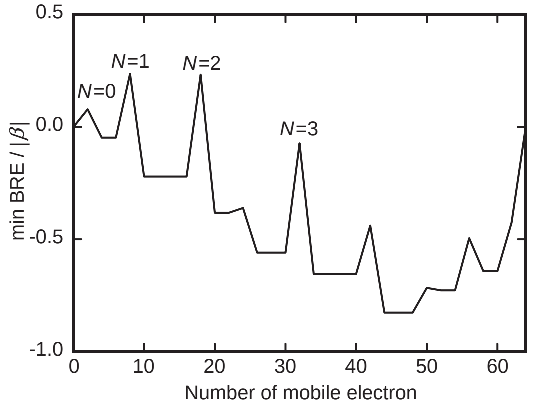

Fig. 3. Min BREs for neutral and charged $Au_{32}(I_h)$ clusters.

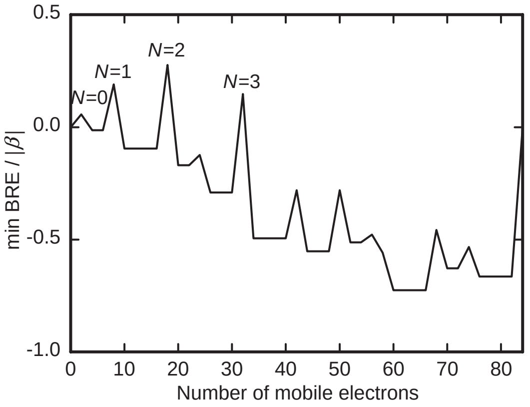

Fig. 4. Min BREs for neutral and charged $Au_{42}(I_h)$ clusters.

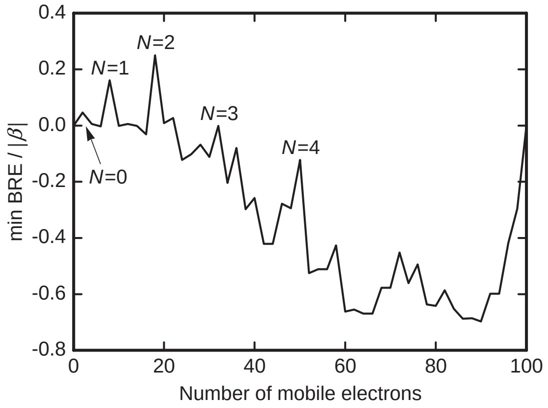

Fig. 5. Min BREs for neutral and charged $Au_{50}(D_{6d})$ clusters.

Results and Discussion

We examined the kinetic stability of four gold fullerenes explicitly, all of which are deltahedral in geometry. Min BREs calculated for neutral species and all possible molecular ions are graphically summarized in Figs. 2–5. With the exception of the species with $2(N+1)^2$ mobile electrons, every gold fullerene tended to decrease the min BRE as the number of mobile electrons increased. Min BRE is often maximized when neutral or charged gold fullerene has $2(N+1)^2$ mobile electrons.

The number of mobile electrons in $Au_{12}(I_h)$ is not equal to $2(N+1)^2$, and thus, it is predicted to be kinetically very unstable with an open-shell electronic configuration.[24] As shown in Fig. 2, the neutral species with 12 mobile electrons has a very large negative min BRE ($-1.187|\beta|$), which is by far smaller than the critical value of $-0.100|\beta|$. $Au_{12}{}^{10+}(I_h)$ ($N=0$), which bears unrealistically large charge, has a large positive min BRE of $0.220|\beta|$. A bit more realistic $Au_{12}{}^{4+}(I_h)$ ($N=1$) must be kinetically stable with a min BRE of as large as $0.305|\beta|$, which indicates that all Au–Au bonds contribute appreciably to aromaticity. However, $Au_{12}{}^{6-}(I_h)$ ($N=2$) must be kinetically very unstable with 18 mobile electrons.

Icosahedral Au_{32} has been predicted to be aromatic, because it has 32 mobile electrons ($N=3$).[7] This cluster is formally obtained by using the carbon fullerene $C_{60}(I_h)$ as a template; if an Au atom is placed at the center of each face of $C_{60}(I_h)$, a $Au_{32}(I_h)$ deltahedron forms. It has a very large energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) ($1.303|\beta|$), a conventional indicator of kinetic stability.[7,8] In harmony with this, $Au_{32}(I_h)$ is remarkably diamagnetic at the cage center (NICS $= -100$ ppm).[7] Min BRE for this gold cluster is $-0.074|\beta|$, which is somewhat larger than the critical value. In fact, this min BRE is the largest one among the neutral gold deltahedrons studied. Therefore, $Au_{32}(I_h)$ appears to be more or less stable in a kinetic sense.

Min BREs for all possible molecular ions of $Au_{32}(I_h)$ are listed in Table 1, together with the HOMO energies. Table 1 and Figure 2 show that not only neutral but also charged species with $2(N+1)^2$ mobile electrons have a closed-shell electronic configuration with maximum min BREs even if their min BRE values are not always larger than $-0.100|\beta|$. Thus, this gold cluster satisfies the $2(N+1)^2$ rule. Since gold deltahedrons are not carbon fullerenes, we are not sure that a min BRE value larger than the critical value really indicates the high kinetic stability enough to isolate the species. The near-icosahedral structure remains the lowest-energy structure for $Au_{32}{}^-$.[9]

$Au_{42}(I_h)$ is formally obtained by using the carbon fullerene $C_{80}(\mathbf{7},I_h)$[25] as a template.[10] The number of mobile electrons in it is not equal to $2(N+1)^2$; thus, the cluster does not satisfy the $2(N+1)^2$ skeletal electron counting rule. In marked contrast to $Au_{32}(I_h)$, this gold cluster has a large positive NICS value at the cage center (>100 ppm)[10] and is predicted to be kinetically very unstable with a large negative min BRE of $-0.281|\beta|$, although the HOMO–LUMO gap ($0.483|\beta|$) is moderately large. In fact, $Au_{42}(I_h)$ has been reported to be

Table 1. Min BREs and HOMO Energies for $\mathrm{Au}_{32}(I_h)$ Molecular Ions

Number of mobile electrons	(HOMO energy − α) /β	Min BRE /$\lvert\beta\rvert$
2 ($N = 0$)	5.653	0.078
4	4.393	−0.048
6	4.393	−0.048
8 ($N = 1$)	4.393	0.236
10	2.303	−0.221
12	2.303	−0.221
14	2.303	−0.221
16	2.303	−0.221
18 ($N = 2$)	2.303	0.232
20	0.215	−0.382
22	0.215	−0.382
24	0.215	−0.361
26	0.000	−0.560
28	0.000	−0.560
30	0.000	−0.560
32 ($N = 3$, neutral species)	0.000	−0.074
34	−1.303	−0.654
36	−1.303	−0.654
38	−1.303	−0.654
40	−1.303	−0.654
42	−1.303	−0.439
44	−2.000	−0.827
46	−2.000	−0.827
48	−2.000	−0.827
50 ($N = 4$)	−2.000	−0.716
52	−2.156	−0.728
54	−2.156	−0.728
56	−2.156	−0.495
58	−2.451	−0.642
60	−2.451	−0.642
62	−2.451	−0.426
64	−2.653	0.000

higher in energy than some space-filling isomers.[10] As can be seen from Fig. 4, the molecular cations of $\mathrm{Au}_{42}(I_h)$ with $2(N+1)^2$ mobile electrons have the maximum min BREs.

$\mathrm{Au}_{50}(D_{6d})$ is presumably the lowest-energy isomer of Au_{50}.[12] This closed-shell gold cluster is formally obtained by using the carbon fullerene $\mathrm{C}_{96}(\mathbf{185},D_{6d})$[25] as a template. The neutral species has been predicted to be aromatic, because it has 50 mobile electrons ($N = 5$). Although this molecule is not icosahedral in symmetry, it exhibits a fairly large HOMO–LUMO energy gap ($0.837\lvert\beta\rvert$). The NICS value at the cage center is predicted to be around −80 ppm.[11,12] However, the min BRE is $-0.122\lvert\beta\rvert$, which is somewhat smaller than the critical value. Therefore, $\mathrm{Au}_{50}(D_{6d})$ must be kinetically rather unstable. Figure 5 indicates that not only neutral but also positively charged $\mathrm{Au}_{50}(D_{6d})$ species with $2(N+1)^2$ mobile electrons have the maximum min BREs.

As has been seen above, the $2(N+1)^2$ skeletal electron counting rule, combined with the BRE concept, is very useful for predicting the kinetic stability of highly symmetric gold fullerenes. Kinetic stability of gold deltahedrons is maximized when they have $2(N+1)^2$ mobile electrons. In fact, this rule can be applied to less symmetric gold fullerenes, as can be expected from its applicability to a wide variety of carbon fullerenes.[18] This does not mean that deltahedral species are always the lowest-energy isomers of large gold clusters. For example, tube-like structures have been predicted to be the most stable isomers of Au_{24} and Au_{26}.[26,27]

Concluding Remarks

The $2(N+1)^2$ skeletal electron counting rule was originally proposed as a rule of spherical aromaticity for cage molecules, such as carbon fullerenes.[17–20] However, serious difficulties are encountered when it is applied to carbon fullerenes.[28–32] For example, neither kinetic stability of $\mathrm{C}_{60}(I_h)$ nor kinetic instability of $\mathrm{C}_{50}(D_{5h})$ can be explained with this rule. It, however, is true that carbon fullerenes with $2(N+1)^2$ π-electrons have relatively large min BREs, although the converse does not always hold. Therefore, it is worth noting that neutral and charged gold deltahedrons with $2(N+1)^2$ mobile electrons are predicted to be less reactive with relatively large min BREs than other species. The maximum min BREs for gold deltahedrons are associated with the species with $2(N+1)^2$ mobile electrons, even if this does not always indicates high kinetic stability. As pointed out previously,[28–32] the aromaticity of fullerenes relies primarily on their local ring structure. It seems that for deltahedral gold clusters aromaticity is not sensitive to the arrangement of individual rings. In such a situation, the $2(N+1)^2$ rule works well as a rule of kinetic stability.

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