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Ab initio molecular-orbital calculation for C_{70} and seven isomers of C_{80}

Kenji Nakao
Institute of Materials Science, University of Tsukuba, Tsukuba 305, Japan

Noriyuki Kurita
Energy Research Laboratory, Hitachi Ltd., Hitachi 319-12, Japan

Mitsutaka Fujita
Institute of Materials Science, University of Tsukuba, Tsukuba 305, Japan

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We investigate stable structures and electronic properties for isolated C_{70} and nonisolated C_{80}, by performing an *ab initio* molecular-orbital calculation based on a nonlocal density-functional formalism and a Harris-functional approximation. We first show the stable structure for C_{70} and give the explanation for the experimental inconsistency in structure by revealing the existence of a metastable structure. Concerning the seven isomers of C_{80} satisfying an isolated pentagon rule, it is found that the isomer with nearly D_2 symmetry (D_2-C_{80}) has a large bond energy and highest-occupied molecular-orbital–lowest unoccupied molecular-orbital (HOMO-LUMO) energy gap which are comparable to those for isolated higher fullerenes. Therefore we propose that D_2-C_{80} should be detectable in an experiment. Since C_{80} does not belong to the sequence of fullerenes with magic numbers, we discuss the problem of whether it is really unstable or not from the viewpoint of the electronic properties. Further, we consider the structures of C_{80} ions and show the great stability of the $C_{80}{}^{6-}$ with nearly I_h symmetry which has a larger HOMO-LUMO gap than both C_{60} and C_{70}.

I. INTRODUCTION

Since a series of higher fullerenes, i.e., C_{70}, C_{76}, C_{84}, C_{90}, and C_{94} have been isolated,[1] much attention has been focused on the existence of magic numbers among possible fullerene structures with an even number of carbon atoms from both the experimental and theoretical viewpoints. Furthermore, the NMR characterization for fullerene isomers[2,3] reveals the selectivity among possible topological structures of the isomers. For instance, Ettl *et al.* identified a C_{76} isomer as having D_2 symmetry, which is known to be chiral.[2] Theoretically, some stable fullerenes have been proposed based on molecular-orbital (MO) calculations[4] discussing the bond energy and energy gap. Furthermore, some models[5–7] have been proposed in order to explain the magic numbers and the relative stabilities among isomers from the viewpoint of dynamical properties. We expect that a wide variety of higher fullerenes and their chemical derivations will bring a new field of study and application in addition to C_{60}.

Concerning the first higher fullerene of C_{70}, some conspicuous properties have been reported: C_{70} can act for electron transfer both as a photosensitizer from a donor molecule and as a mediator across a lipid bilayer membrane[8]. In spite of such wide fields of application for C_{70} as well as C_{60}, even the exact stable structure of C_{70} has been an open question, because of the disagreement between two experimental results on bond lengths.[9,10]

As for other higher fullerenes, the problem of the magic numbers is still challenging. Quite recently, C_{86} and C_{88}, which have been considered to be out of the magic numbers, were experimentally separated.[11] This result seems to suggest the possibility that other even-numbered higher fullerenes will appear in addition to the series of already isolated fullerenes. As a matter of fact, the mass spectrum of carbon clusters generated by laser vaporization of graphite[12,13] shows the existence of all even-numbered clusters greater than C_{32}. In particular, it is curious why C_{80} has not been isolated yet, i.e., the magic number jumps from 78 to 82 and skips 80, although as many as seven isomers are possible for C_{80} even under the isolated pentagon rule (IPR),[14,15] and, further, its neighboring C_{76}, C_{78}, C_{82}, and C_{84} fullerenes are abundantly isolated.

The purpose here is to present the *ab initio* MO calculations for C_{70} and some isomers of C_{80}. We first present the most stable structure of C_{70} and its electronic feature, and discuss the inconsistency of the experimentally deduced molecular structures. Further, we exhibit the optimized structures of seven C_{80} isomers satisfying IPR and their electronic properties. Some stable structures among them are proposed as a candidate for existence. Since there has been no systematic and *ab initio* MO calculations for C_{80}, to our knowledge, it is now urgently necessary to examine the relative stability of C_{80} to other isolated higher fullerenes. We should emphasize that there is no reason at present to exclude C_{80} from the stable fullerenes. In addition, we cannot overlook that the endohedral metal-fullerene $La_2@C_{80}$ is observed rather abundantly in the laser desorption mass spectrum.[16] Stable structures for C_{80} ions are also discussed, based on their electronic properties.

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The arrangement of this paper is as follows: the method of the *ab initio* MO calculation which we perform here is briefly explained in the next section. In Sec. III we present the most stable structure of C_{70} and also discuss the existence of a metastable structure. In Sec. IV we present the electronic properties of seven C_{80} isomers and examine their relative stability. The structures for C_{80} ions are discussed in Sec. V concerning the $La_2@C_{80}$ cage. The final section is devoted to the conclusion.

II. CALCULATIONAL METHOD

For the sake of obtaining stable structures of C_{70} and C_{80} theoretically, we perform a non-self-consistent-field (SCF) -MO calculation with Harris-functional approximation,[17] where the total electron density of the system is approximated by means of a superposition of electron densities for the isolated atoms with a first-order energy correction of the density error. This approximation has the advantage of more easily obtaining the procedures for calculating the electrostatic potential and Coulomb energy and, in particular, eliminates the SCF iteration. Through this non-SCF-MO calculation, we use the single Slater orbitals[18] as a basis set. The procedure of structure optimization is iteratively done until the maximum atomic force calculated from the energy gradients gets smaller than 0.01 hartree/a_0 where a_0 is the Bohr radius. The atomic force is evaluated based on the mesh points method, here we take as many as 1720 points per atom. We have already applied the above method to obtain a stable structure of C_{60}, and confirmed its applicability.[19]

Once a stable structure is obtained, we calculate its electronic properties such as the bond energy, HOMO-LUMO (highest occupied MO– lowest unoccupied MO) energy gap, charge density, and so on, by means of the SCF-MO method[20] based on the non-local-density-functional formalism with generalized-gradient approximation (GGA).[21] It is well known that GGA reduces overestimated errors of the bond energy which arise from the local-density approximation. In the procedure, electrons are filled into the MO's according to the Fermi-Dirac statistic, where we take the Fermi distribution parameter as 100 hartree^{-1}. In the SCF-MO calculation we use a minimal basis set consisting of 1*s*, 2*s*, and 2*p* orbitals of a carbon atom. This basis set is insufficient for evaluating quantitative bond energies for fullerenes, however, we can discuss at least their relative stability based on it. In our previous study,[22] we performed the calculations utilizing the minimal basis set and the double basis plus one *d* orbital (DBd) basis set, which consists of minimal plus 2*s* and 2*p* orbitals of C^{2+} ion and one *d* orbital, and we confirmed that the relative difference of bond energies between two basis sets is almost the same for C_{60}, C_{36}, and C_{24}.

III. STABLE STRUCTURE OF C_{70}

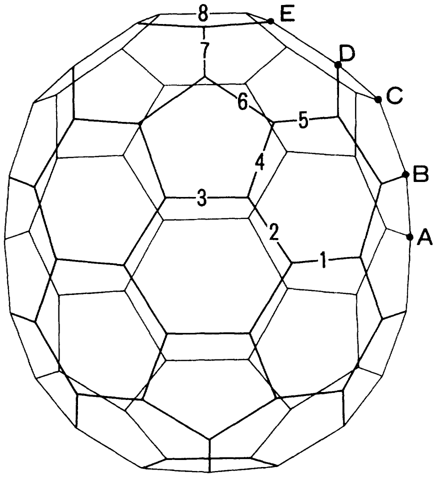

FIG. 1. The optimized structure of C_{70} with D_{5h} symmetry. The numbering of eight inequivalent bonds is the same as that in Ref. 10.

TABLE I. Calculated bond lengths (Å) for C_{70} by the present (Present) and Hartree-Fock (HF) method (Ref. 23). The experimental results [Expt. I (Ref. 10) and Expt. II (Ref. 9)] are also listed for comparison. Each bond type is shown in Fig. 1.

	Expt. I	Expt. II	HF	Present
Bond 1	1.41	1.46	1.475	1.48
Bond 2	1.39	1.42	1.407	1.44
Bond 3	1.47	1.44	1.415	1.45
Bond 4	1.46	1.43	1.457	1.46
Bond 5	1.37	1.37	1.361	1.41
Bond 6	1.47	1.45	1.446	1.46
Bond 7	1.37	1.38	1.375	1.41
Bond 8	1.464	1.46	1.451	1.47

We first show the optimized structure of C_{70} with D_{5h} symmetry in Fig. 1. Since it keeps topological symmetry D_{5h} even after the structure optimization, each bond in C_{70} is grouped into eight types of bonding, according to its environment. Each bond length is listed in Table I, where we tabulate in parallel the experimental results,[9,10] and the theoretical results by the Hartree-Fock (HF) method[23] for comparison. The difference in structure between experiments I and II is notably seen on the bond lengths around an equatorial zone of C_{70}, i.e., from bonds 1 to 4. The former is considered to suggest a waist-pinched ellipsoidal structure, in which the atoms on the equator are slightly pinched to the center of C_{70}, while the latter is a waist-swollen structure, as seen from the large difference of bond 1. In the latter, bond 1 has the longest bond length. Both the HF and our results support experiment II.[9]

On the other hand, to inspect the possibility for a waist-pinched shape, we attempt the structure optimization starting with the initial atomic configuration where we pinch the atoms on bond 1 by 5% inward. As a result, we obtain a waist-pinched structure, although it is metastable and has a 0.02 eV/atom smaller bond energy than the waist-swollen structure. Since this difference in

TABLE II. Bonding and electronic properties for C_{70} and seven isomers of C_{80}. Symmetry indicates the topological symmetry before structure optimization.

	Symmetry	Bond lengths (Å)	Distance from center (Å)	Bond energy (eV/atom)	HOMO-LUMO gap (eV)
C_{70}	D_{5h}	1.41–1.48	3.59–4.17	5.50	1.55
$C_{80}(1)$	D_2	1.39–1.46	3.55–4.66	5.50	0.55
$C_{80}(2)$	I_h	1.43–1.47	4.11–4.15	5.52	0.12
$C_{80}(3)$	D_{5d}	1.40–1.46	3.58–4.73	5.46	0.25
$C_{80}(4)$	D_{5h}	1.39–1.49	4.07–4.19	5.50	0.12
$C_{80}(5)$	C_{2v}	1.39–1.47	3.85–4.55	5.51	0.11
$C_{80}(6)$	D_3	1.39–1.46	3.38–4.53	5.48	0.20
$C_{80}(7)$	C_{2v}	1.39–1.48	3.87–4.38	5.50	0.11

bond energy corresponds to just about 200 K in temperature, we predict that besides the most abundant cage with the waist-swollen shape, the waist-pinched C_{70} is contained in a small portion of C_{70} soot, which should be detected in experiment I.[10]

The bond energy and the HOMO-LUMO energy gap of the most stable C_{70} are calculated by the SCF-MO method and shown in Table II. We note that because of the basis set incompleteness which we mentioned in the last section, the bond energy is 1.7 eV/atom smaller than that of C_{60} reported in our previous paper.[19] We can see that the 1.55 eV HOMO-LUMO energy gap is comparable to 1.63 eV of C_{60}.[19] The distribution of the energy levels near the Fermi level is displayed in Fig. 2, where the energies that agree with each other within a difference of 0.02 eV are regarded as degenerated.

In the D_{5h}-C_{70} cage, there are five types of topologically distinctive sites. To clarify the reactive sites among them for acceptor or donor type of reactants, we evaluate the Mulliken's charges for each atom and further the distributions of the HOMO and LUMO. The Mulliken's charges vary from 5.96 to 6.03 indicating the uniform distribution of charge density on each atom. On the other hand, the HOMO and LUMO are found to inhomogeneously distribute; the HOMO with nearly threefold degeneracy distributes as much as 50% on *B*-type atoms near the equator and 35% on *C*-type atoms, while the distribution of the LUMO with also threefold degeneracy is assigned 19% on *E* atoms on both poles, 39% on *B* and 32% on *C* atoms. The MO lying about 0.6 eV higher than the LUMO has the main distribution on *A*-type atoms just along the equatorial line. These results lead to the prediction that an electron-acceptable molecule with larger electronegativity than C_{70} should react on either *B*- or *C*-type atoms, while an electron-donatable molecule can be reactive on E atoms as well as *B* and *C*.

IV. STABILITY OF SEVEN C_{80} ISOMERS

It is known that C_{80} has seven types of topologically different isomers under IPR,[14,15] as shown in Fig. 3, along with their topological symmetry. Here we perform our *ab initio* calculation for these isomers. In the procedure, the structure optimizations are started with the structures whose topological Cartesian coordinates are generated in the use of the program FULLER by Yoshida and Osawa.[24] The bond energy, the energy gap, and the atomic configuration for each isomer are tabulated in Table II. We note that symmetry in it does not indicate the geometrical symmetry after the structure optimization, but just the topological symmetry before it. For some isomers with a small HOMO-LUMO energy gap, the Jahn-Teller distortion causes the lowering of their symmetry. For example, the symmetry of the $C_{80}(2)$ and $C_{80}(4)$ isomers, which have no energy gap between HOMO and LUMO within a simple Hückel MO approxi-

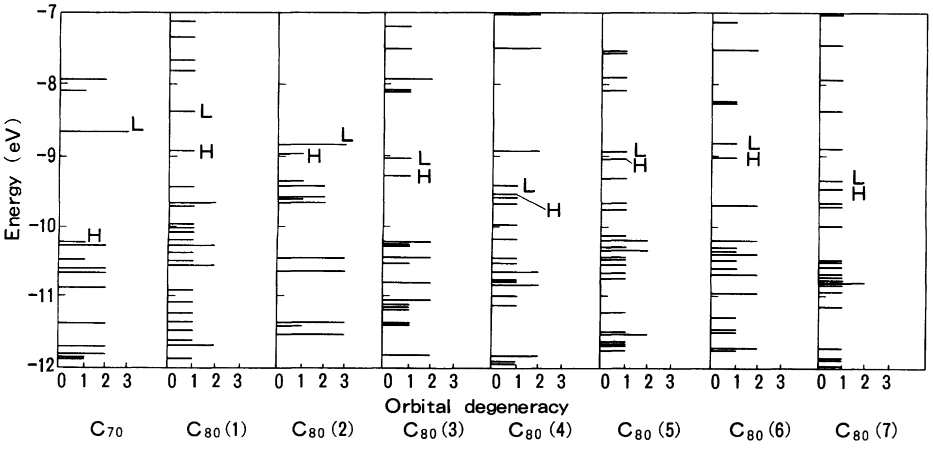

FIG. 2. The energy levels near the Fermi level of C_{70} and seven isomers for C_{80}. The molecular orbitals whose energies agree with each other within a difference of 0.02 eV are regarded as degenerated, and the length of the horizontal bars shows the orbital degeneracy. The HOMO and LUMO are marked with *H* and *L*, respectively.

mation, is to be broken through the distortions, thus they have a small HOMO-LUMO energy gap about 0.1 eV.

Let us first discuss the stability of seven C_{80} isomers, especially based on their bond energies and HOMO-LUMO energy gaps in Table II. As for bond energy, $C_{80}(2)$ has the largest bond energy, so that it seems to have the largest static stability among the isomers. This large bond energy comes mainly from the almost spherical and equally bonded structure of $C_{80}(2)$ with nearly I_h symmetry, which gives a uniform distribution of strain. However, the small HOMO-LUMO gap 0.12 eV of $C_{80}(2)$ indicates its high reactivity, and it is thus expected that $C_{80}(2)$ is electronically unstable. The same argument can be applied to $C_{80}(4)$, $C_{80}(5)$, and $C_{80}(7)$ with a comparable bond energy to C_{70}, but with only about a 0.1 eV energy gap. On the other hand, it is found that $C_{80}(3)$ and $C_{80}(6)$ have rather large HOMO-LUMO gaps. It is noted that although the $C_{80}(3)$ isomer with D_{5d} symmetry has an open-shell electronic structure under the assumption of equal bond length,[22,25] the Jahn-Teller distortion causes this large energy gap. However, the small bond energies of $C_{80}(3)$ and $C_{80}(6)$ suggest that these isomers are less stable. The rest isomer is $C_{80}(1)$. It has the largest HOMO-LUMO energy gap of 0.55 eV, which is almost one-third of that for C_{70} and comparable to those for other isolated higher fullerenes.[26] It has also the same bond energy as C_{70}. Consequently, we predict that the $C_{80}(1)$ isomer with nearly D_2 symmetry is the best candidate for a stable C_{80} isomer. It should be emphasized that its relative stability is by no means inferior to those of other isolated higher fullerenes. The possibility of existence of a stable C_{80} fullerene does not contradict the experimental observation of the all even-numbered carbon clusters greater than C_{32} in mass spectrum.[12,13]

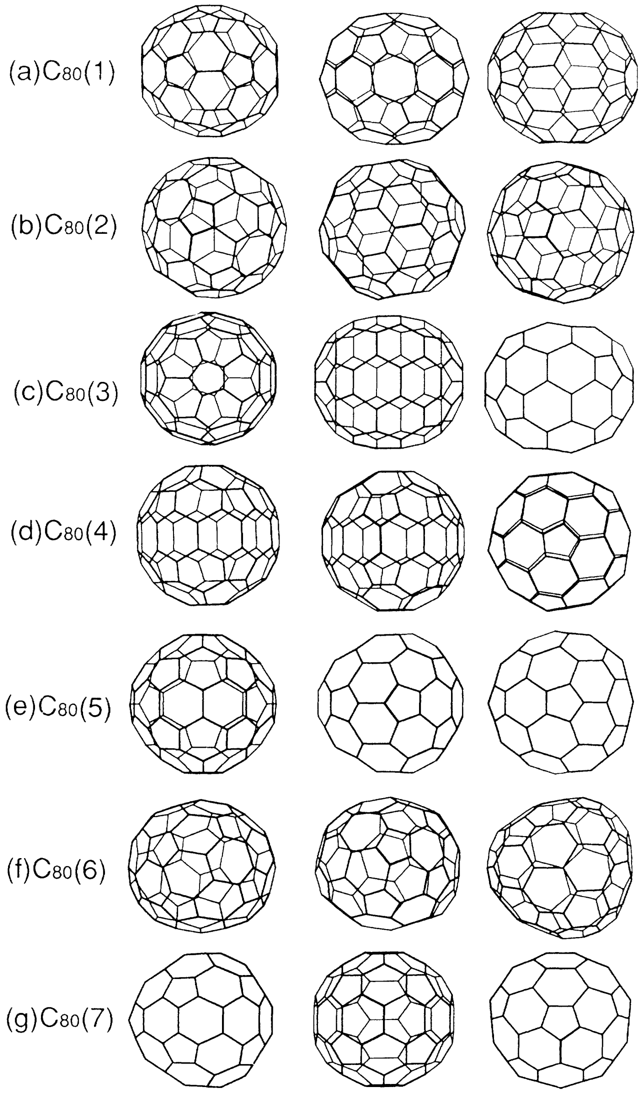

FIG. 3. Three orthogonal views for seven types of C_{80} isomers. These structures are generated by M. Yoshida, by using the package program (Ref. 24). Starting with these structures, the stable structures of C_{80} isomers are obtained, whose bonding and electronic properties are listed in Table II.

Manolopoulos and Fowler[27] showed by a simple Hückel calculation that the I_h-C_{80} isomer has an open-shell electronic structure and that the other six types of C_{80} isomers have pseudo-closed-shells indicating small HOMO-LUMO gaps. However, we have to pay attention to the fact that the electronic structure is sometimes drastically changed through the structure optimization. In Fig. 2 we show the distribution of energy levels near the Fermi level for each optimized structure. We can see many high-degenerated levels in $C_{80}(2)$ because of its high symmetry nearly I_h. If we keep the I_h symmetry of $C_{80}(2)$, the HOMO is fourfold degenerated and occupied with only two electrons. The Jahn-Teller distortion causes 0.12 eV energy gap between the nondegenerated closed HOMO and the threefold degenerated LUMO, as shown in Fig. 2. This result contrasts sharply with that by the simple Hückel calculation,[27] and shows that an *ab initio* MO method considering the change in bond lengths is indispensable even for qualitative discussion on the electronic properties near the Fermi level.

In order to clarify the qualitative difference of electronic properties between C_{70} and C_{80}, we also evaluate the Mulliken's charges of each atoms and the distributions of HOMO and LUMO for the predictably stable $C_{80}(1)$ isomer. The Mulliken's charges vary from 5.95 to 6.04, which means the uniform charge distribution and is equivalent to C_{70} shown in the last section. However, concerning the HOMO and LUMO distributions, in contrast with C_{70} where the HOMO and LUMO are localized on some specific sites, in C_{80} they are rather uniformly extended, indicating that C_{80} has no specific reactive site. Therefore we expect that reactivity or solubility of the $C_{80}(1)$ cage may be significantly smaller than that of C_{70}, because the HOMO and LUMO of C_{70} are more localized on some specific sites as mentioned in the preceding section. This qualitative difference of HOMO and LUMO distributions between C_{70} and C_{80} may be due to the fact that statically stable C_{80} isomers have not been isolated in the same way as C_{60} and C_{70} isolations. For more quantitative discussion on the solubility of fullerene, not only a MO calculation but a dynamical calculation considering the reaction between fullerene and solvent molecules may be indispensable.

V. STRUCTURE OF C_{80} IONS

We show the estimated HOMO-LUMO energy gaps for C_{80} anions and cations in Table III, under the assumption that the energy levels of ions are not affected by those of a neutral C_{80} isomer. The following features on the electronic property of C_{80} ions can be seen from Table III. All ${C_{80}}^{2-}$ cations except ${C_{80}}^{2-}(2)$ have large HOMO-LUMO gaps, and in particular, ${C_{80}}^{2-}(3)$ has a larger HOMO-LUMO gap than the ${C_{80}}^{2-}(5)$ proposed by Manolopolous and Fowler.[27] As for ${C_{80}}^{2+}$ anions, ${C_{80}}^{2+}(3)$ has a larger HOMO-LUMO gap than ${C_{80}}^{2+}(2)$, consistent with the results based on the simple Hückel calculation.[28] However, the difference in HOMO-LUMO gaps between ${C_{80}}^{2+}(3)$ and ${C_{80}}^{2+}(2)$ is much larger in our *ab initio* calculation. Here we have to recall that the neutral $C_{80}(3)$ and $C_{80}(6)$ have rather small bond energies, therefore both their ions are likely to be less stable than the other isomers from the viewpoint of static stability. Consequently, we expect from Table III that the ${C_{80}}^{2-}(5)$ cation and the ${C_{80}}^{2+}(1)$ and ${C_{80}}^{2+}(2)$ anions will be stable.

Special emphasis should be put on the ${C_{80}}^{6-}(2)$ cation with nearly I_h symmetry and the ${C_{80}}^{6-}(4)$ one with nearly D_{5h} symmetry, which have as much as 2.19 and 1.44 eV of HOMO-LUMO gaps, respectively. These sizes are comparable to or larger than those for 1.63 eV of neutral C_{60} (Ref. 19) and 1.55 eV of C_{70}. As mentioned in the preceding section, $C_{80}(2)$ has the largest bond energy among the seven isomers. We, therefore, conclude from the viewpoints of static stability and electronic properties that the ${C_{80}}^{6-}(2)$ cation is expected to possibly exist, if such a highly ionized state can be obtained without much change in structure. There is also a possibility that the ${C_{80}}^{6-}(4)$ cation will be present.

Two ways can be proposed for obtaining such high ionized cages. One way is substitution of carbon atoms by other similar atomic-sized atoms like boron or nitrogen atoms, and another is encapsulation of atoms or molecules in the cage. As for substitution, $C_{74}N_6$ with the same total number of electrons as ${C_{80}}^{6-}$ is unlikely to be stable, because the multisubstituted $C_{58}N_2$ fullerene already has a 0.14 eV/atom smaller bond energy than C_{60}.[29] While for encapsulation, an extractable $La_2@C_{80}$ was produced[16] by means of the Krätschmer-Huffman method using lanthanum-graphite rods, and suggested that the La atoms are encapsulated in a C_{80} cage with I_h symmetry and in the oxidation state $(La_2)^{6+}{C_{80}}^{6-}$. This experimental result agrees well with our calculated result. The *ab initio* MO calculation on $La_2@C_{80}$ for determining its stable structure and estimating the amount of charge transfer between La atoms and the C_{80} cage is a future problem.

TABLE III. Estimated HOMO-LUMO energy gaps (eV) of anions and cations for C_{80} isomers.

Valency	$C_{80}(1)$	$C_{80}(2)$	$C_{80}(3)$	$C_{80}(4)$	$C_{80}(5)$	$C_{80}(6)$	$C_{80}(7)$
+2	0.50	0.38	0.95	0.05	0.26	0.65	0.20
−2	0.57	0	0.92	0.48	0.86	0.56	0.44
−6	0.33	2.19	0.16	1.44	0.35	0.73	0.43

VI. CONCLUSION

In order to provide the stable structure of C_{70} and clarify the stability of C_{80} isomers, we performed the *ab initio* MO calculation for C_{70} and seven C_{80} isomers satisfying IPR, utilizing the SCF-MO method based on the non-local-density-functional formalism. Their molecular structures were optimized by the non-SCF-MO method with the Harris-functional approximation. We found that the most stable structure of C_{70} is a waist-swollen ellipsoid shape, and that the waist-pinched C_{70} can exist as a metastable structure. Among C_{80} isomers, the isomer with nearly D_2 symmetry (D_2-C_{80}) was found to have a 0.55 eV of HOMO-LUMO energy gap, which is almost one-third of that for C_{70} and comparable to those for other isolated higher fullerenes. However, the HOMO and LUMO are extendedly distributed in $C_{80}(1)$, while they are localized on some specific sites in C_{70}. The D_2-C_{80} has also a comparable bond energy to C_{70}. Therefore, based on the electronic properties we conclude that D_2-C_{80} is the best candidate for a stable C_{80} isomer and as stable as other higher fullerenes, while its solubility may be less than that of C_{70}. Furthermore, it was found that the ${C_{80}}^{6-}$ cation with nearly I_h symmetry (I_h-${C_{80}}^{6-}$) has a larger HOMO-LUMO energy gap than C_{60} and C_{70}. This fact suggests the possibility that the I_h-${C_{80}}^{6-}$ cation will abundantly appear like C_{60} and C_{70}, which is consistent with the experimental observation of an encapsulated $La_2@C_{80}$ fullerene.

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