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Mechanistic Study of the Diels–Alder Reaction of Paramagnetic Endohedral Metallofullerene: Reaction of La@C_{82} with 1,2,3,4,5-Pentamethylcyclopentadiene

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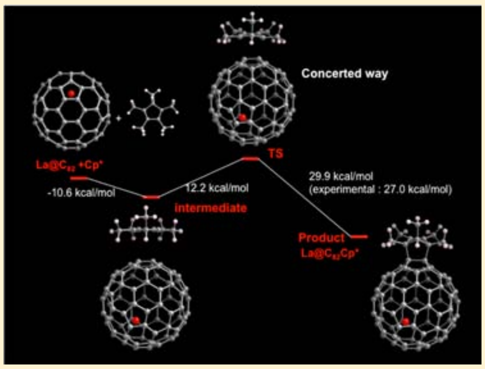
S *Supporting Information*

ABSTRACT: The reaction mechanism of the Diels–Alder reaction of paramagnetic endohedral metallofullerene, La@C_{82}, and 1,2,3,4,5-pentamethylcyclopentadiene was studied theoretically and experimentally. Theoretical calculations revealed that this reaction proceeds via a concerted mechanism that includes formation of a stable intermediate. The activation energy of a retro-Diels–Alder reaction was also studied experimentally, which is in good agreement with theoretical results.



INTRODUCTION

The Diels–Alder (DA) reaction is an extremely valuable type of cycloaddition in organic chemistry.[1] In recent years, much attention has been focused on the DA reaction of fullerenes because it can be a useful method for introducing functionality to fullerene cages. The fact that fullerenes such as C_{60} and C_{70} act as polyalkenes and possess a reactive dienophile character derived from their electron-deficient properties has prompted the development of numerous efficient DA reactions of fullerenes.[2] For example, C_{60} acts as a dienophile in the DA reaction with many types of reactive dienes, e.g., anthracene,[3] furan,[2a] cyclopentadiene,[4] and others.[5] Moreover, the reversible DA reaction of fullerenes is used for separation[6] and template synthesis.[7] The concerted reaction mechanism of C_{60} with dienes has been clarified theoretically.[4d,e]

Endohedral fullerene is a new type of carbon cluster that contains one or more atoms inside the hollow fullerene cage.[8] Especially, endohedral metallofullerenes have attracted broad attention because of their novel properties derived from an intramolecular metal–fullerene cage interaction.[9] A typical endohedral metallofullerene, La@C_{82}, possesses unique electronic properties such as a radical character and low redox potentials, induced by the electron transfer from La atom to C_{82} cage.[10] These aspects allow the new application of fullerenes.[11] Recently, we reported the reversible and highly regioselective DA reaction of paramagnetic endohedral metallofullerene, La@C_{82}, and cyclopentadiene (Cp)[12] or 1,2,3,4,5-pentamethylcyclopentadiene (Cp*).[13] The addition site of Cp* on La@C_{82} was revealed using X-ray crystallographic analysis (Figure 1). Theoretical studies using the B3LYP//LanL2DZ[La]/3-21G [C, H] showed that the addition site carbons have neither large β-LUMO coefficients nor large spin densities (see ref 13 and Supporting Information Figure S1), but they have high positive charge densities.[14] From these results, we speculated that one important factor for the regioselectivity is

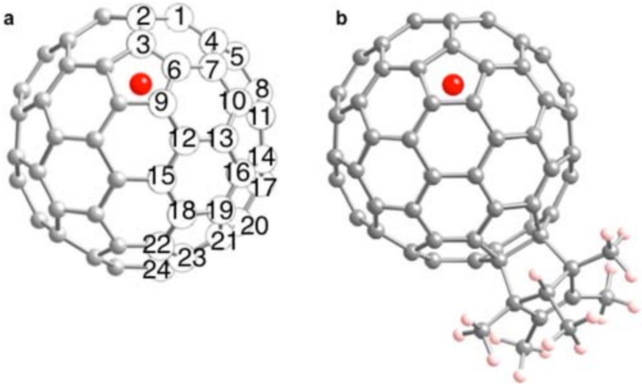


Figure 1. (a) La@C_{82} with 24 types of nonequivalent carbons and (b) La@C_{82}Cp*.

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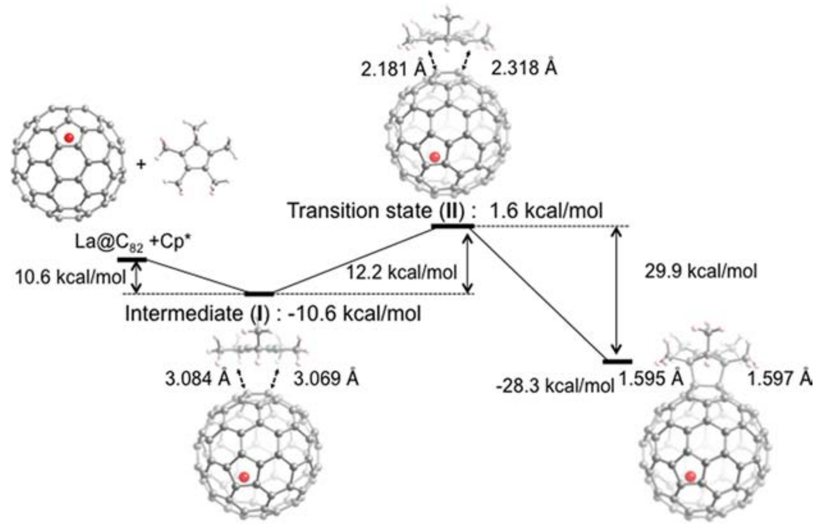

Figure 2. Reaction profile for the cycloaddition reaction of La@C_{82} and Cp*.

positive charge densities on the fullerene cage carbon because Cp* is an electron-rich diene.

Closed shell pericyclic reactions are quite well understood through the Woodward–Hoffmann rule[15] and the frontier orbital concept.[16] However, the electron-transfer catalyzed DA reaction, where the diene or dienophile units possess radical cation character, has also been studied.[17] Recently, density functional theory (DFT) calculation predicted that the reaction between 1,3-butadiene radical cation with ethylene proceeds via a stepwise path involving an open chain intermediate.[18] Nevertheless, even qualitative concepts are lacking for the DA reaction using paramagnetic molecules in the ground state. More detailed insight into the mechanisms of the reaction related to the paramagnetic molecule is desirable because it is important to clarify the nature of transition states and intermediates for understanding the critical steps and possibilities for manipulating the reaction. Recently, Morokuma, Solà, and co-workers reported the performance of the ONIOM method to study the chemical reactivity of fullerene by computing the reaction energy and energy barrier of the DA reaction between C_{60} and Cp.[4d] Their results indicate that both the ONIOM2(M06-2X/6-31G(d):SVWN/STO-3G) and the M06-2X/6-31G(d)//ONIOM2-(B3LYP/6-31G(d):SVWN/STO-3G) approaches are among the most reliable and computationally efficient methods to be exploited for studying the chemical reactivity of the [6,6]-bonds in fullerenes.

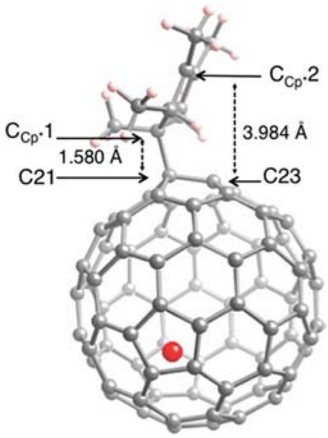

Figure 3. Singly linked intermediate (**III**) for the stepwise cycloaddition reaction between La@C_{82} and Cp*.

In this article, we studied the mechanism of DA reaction of paramagnetic metallofullerene, La@C_{82}, with Cp*, using the M06-2X method. Furthermore, the reason for its energy barrier and high regioselectivity was discussed, not only theoretically but also experimentally.

■ COMPUTATIONAL METHOD

Calculations were carried out using the Gaussian 09 program.[19] Geometries were optimized using density functional theory at the spin-unrestricted

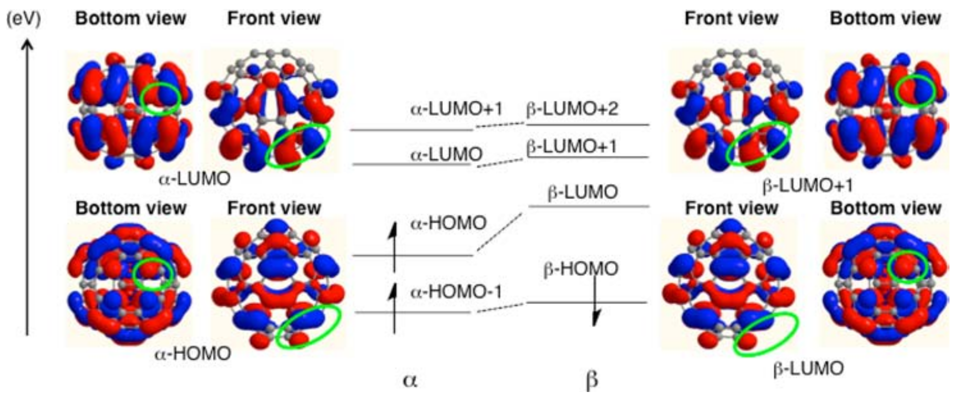

Figure 4. Molecular orbitals of La@C_{82}. Green circles show the addition site.

M06-2X[20] level: the double-zeta basis set (Lanl2dz) and effective core potential (Lanl2 ECP)[21] were used for La and the 6-31G(d) basis set was used for C and H. Energies were improved by single-point calculations with the larger 6-311+G(d,p) basis set for C and H. In an attempt to evaluate dispersion interactions considered in the M06-2X functional, single point calculations were performed using standard B3LYP[22] and dispersion-corrected B3LYP-D3[23] methods with Lanl2dz and Lanl2 ECP for La and 6-31G(d) for C and H. These B3LYP and B3LYP-D3 calculations were performed using the GAMESS package.[24]

General Experiment. Toluene was distilled over benzophenone sodium ketyl. Maleic anhydride was purchased from Wako Pure Chemical Industries, Ltd., and used as received. HPLC isolation was performed on an LC-908 (Japan Analytical Industry Co. Ltd.) monitored by UV absorption at 330 nm. The ESR measurements were performed using a spectrometer (Bruker EMX-T), equipped with Bruker N_2 temperature controller. The spectra were simulated using the NIEHS WinSim software.[25]

Materials. Soot containing lanthanide metallofullerenes was prepared according to the reported procedure[26] using a composite anode that contains graphite and the metal oxide with the atomic ratio of La/C equal to 2.0%. The composite rod was subjected to an arc discharge as an anode under 150 Torr helium pressure. Raw soot containing lanthanide metallofullerenes was collected and extracted using 1,2,4-trichlorobenzene. To isolate La@C_{82}, the soluble fraction was injected into the HPLC; a 5PYE column (ϕ20 mm × 250 mm, Cosmosil; Nacalai Tesque Inc.) was used in the first step and a Buckyprep column (ϕ20 mm × 250 mm, Cosmosil; Nacalai Tesque, Inc.) in the second step to give pure La@C_{82}. For the determination of kinetics, La@C_{82}Cp* was synthesized according to a reported procedure.[13]

■ RESULTS AND DISCUSSION

Theoretical studies of the DA reaction of La@C_{82} with Cp* were conducted using the M06-2X methods. The energy profile calculated for the reaction is presented in Figure 2. In the initial step for the cycloaddition reaction, a complex of La@C_{82} and Cp* (intermediate **I**) was formed, which is more stable by 10.6 kcal/mol than the reactants (La@C_{82} + Cp*). The shortest atomic distances between La@C_{82} and Cp* for **I** with addition carbon sites (C21 and C23 in Figure 1a) are 3.069 and 3.084 Å. The slight differences of these two distances are derived from the asymmetric structure of **I**. The energy barrier from **I** to the final adduct via a transition state (**II**) is 12.2 kcal/mol. The geometry of **II** closely resembles the reported transition structure for the DA reaction of C_{60} with Cp.[4d] The closest carbon−carbon distances between La@C_{82} and Cp* are 2.318 and 2.181 Å, which are similar to the distances reported for the transition states of C_{60}−Cp[4d] and C_{60}−quinodimethane reactions.[27] As is clear from Figure 2, the DA reaction of La@C_{82} with Cp* proceeds in a concerted way.

To validate the concerted mechanism, calculations were conducted for the case of the stepwise addition, which proceeds via the formation of a singly linked intermediate between La@C_{82} and Cp* at C21 or C23. The singly linked intermediate was searched in detail. As a result, the formation of one singly linked intermediate (**III**) shown in Figure 3 was found. It is notable that the Intermediate is 19.3 kcal/mol higher in energy than reactants. This result suggests that the energy barrier for the stepwise path is considerably larger than that for the concerted path in the reaction of La@C_{82} and Cp*.

It has been widely accepted that the addition pattern of DA reaction is explainable by the Woodward−Hoffmann rule[15] and Frontier Molecular Orbital theory.[16] In this context, the LUMO of La@C_{82} is expected to play a key role in the interaction with the HOMO of Cp* because the smaller HOMO−LUMO gap between the HOMO of diene and the LUMO of dienophile results in the decreasing of the energy barrier. Furthermore, it is required that the addition site for La@C_{82} possesses suitable orbitals to interact with Cp*. However, molecular orbital (MO) calculations showed that the β-LUMO of La@C_{82} has no large coefficients on the addition site carbons (C21 and C23) (Figure 4). Hence, to provide further insight regarding this reaction system, the MOs of **I** are illustrated in Figure 5. In the initial step for this reaction, we found that while the β-LUMO of La@C_{82} has no suitable orbital coefficients on the addition site carbons, the α-LUMO and β-LUMO+1 of La@C_{82} have large orbital coefficients. This indicates that the α-LUMO and β-LUMO+1 of La@C_{82} can play a main role in interaction with the HOMO of Cp*. The fact that the α-LUMO and β-LUMO+1 of La@C_{82}

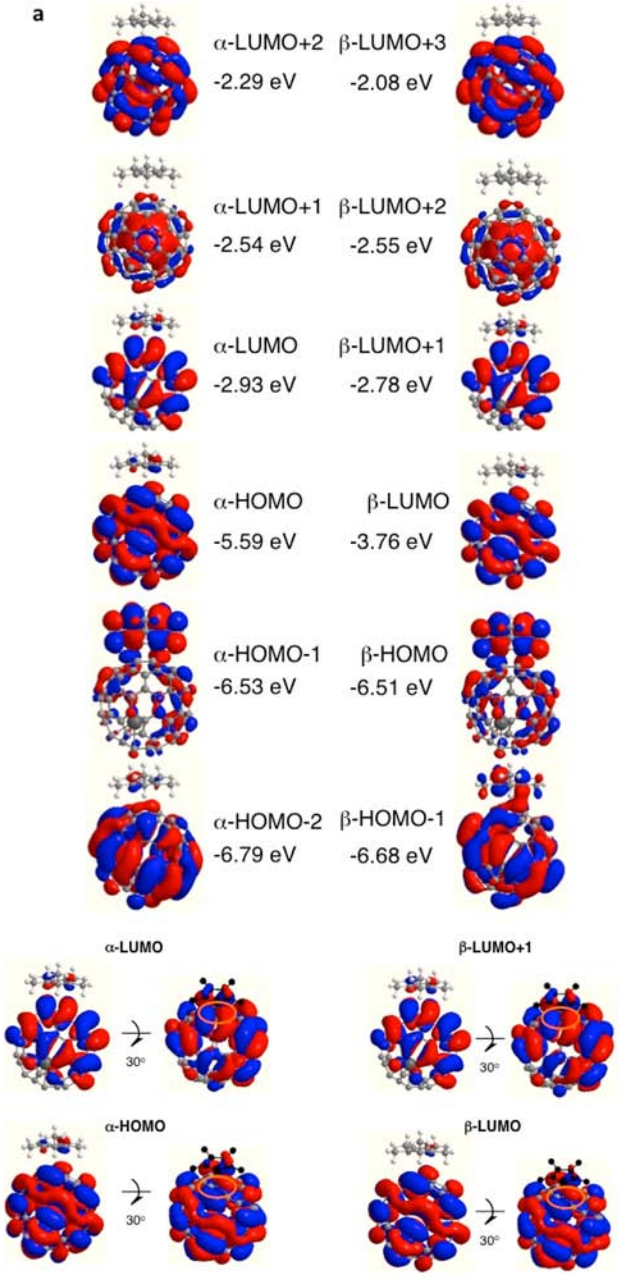

Figure 5. (a) Molecular orbitals of intermediate **I** in the cycloaddition reaction of La@C_{82} and Cp*. (b) The α-HOMO, β-LUMO, α-LUMO, and β-LUMO+1 of **I** are expanded for clarity. Orange circles show the addition site.

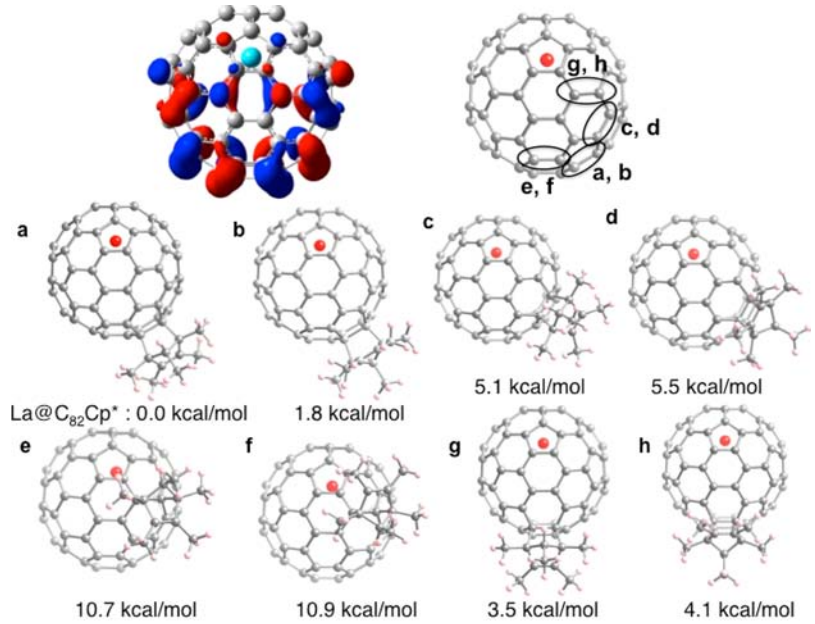

Figure 6. Relative energies calculated for La@C$_{82}$Cp* isomers. Addition sites of each isomer were selected from those which possess large orbital coefficients in β-LUMO+1.

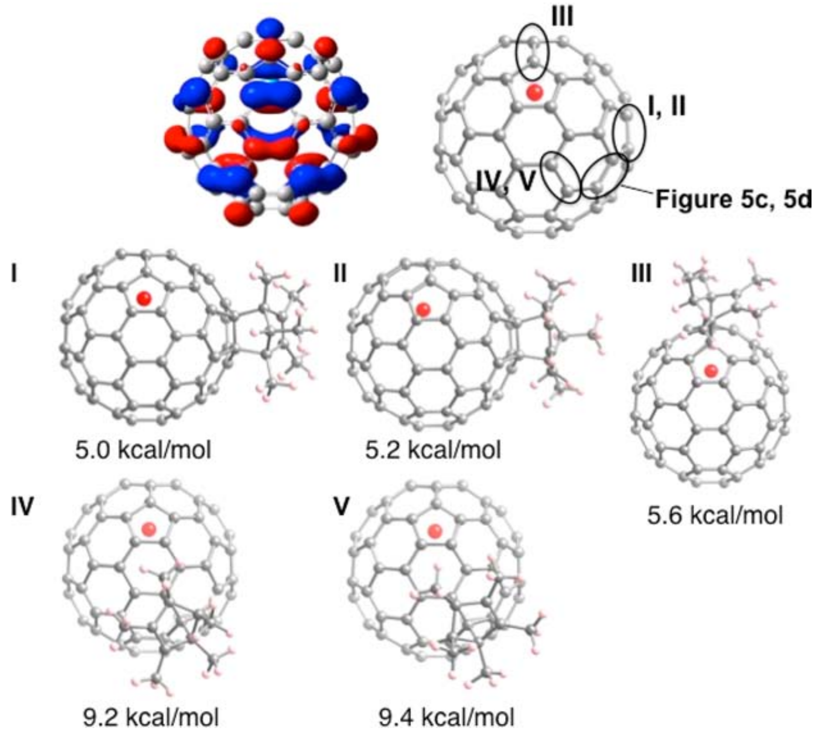

Figure 7. Relative energies calculated for La@C$_{82}$Cp* isomers. Addition sites of each isomer were selected from those which possess large orbital coefficients in β-LUMO.

present a favorable orbital at the addition site to react with Cp* suggests that the DA reaction proceeds via a concerted mechanism.

Experimentally, the DA reaction between La@C$_{82}$ and Cp* afforded only one isomer.[13] To analyze the reason for this regiospecific manner, the optimized structure and relative stability of regioisomers and their stereoisomers were calculated, respectively. The addition site of 13 isomers was selected by the orbital coefficients in the LUMO of La@C$_{82}$. Figures 6 and 7 portray the optimized structures and relative energy of La@C$_{82}$Cp* isomers. It should be noted that isomer **a** (addition site carbons are C21 and C23), which is determined using X-ray crystallographic analysis, is the most stable one. These results confirm that isomer **a** is not only kinetically but also thermodynamically the most conceivable monoadduct.

To disclose kinetic parameters for the retro-DA reaction of La@C$_{82}$Cp* to La@C$_{82}$ and Cp*, the rates of decomposition were experimentally determined (see Supporting Information Figure S2) in the temperature range at 283–303 K (Table 1).[28] A toluene solution of isolated La@C$_{82}$Cp* (1.8×10^{-5} M) and excess molar amount of maleic anhydride were prepared, for

Table 1. Rates and Activation Energies of the Cycloreversion of $La@C_{82}Cp^*$

T (K)	k^{-1} (s^{-1})	$t_{1/2}$ (h)
283	8.17×10^{-6}	23.5
288	2.23×10^{-5}	8.63
293	5.60×10^{-5}	3.42
298	9.79×10^{-5}	1.97
303	1.92×10^{-4}	1.00
		E_a (kcal/mol)
$La@C_{82}Cp^*$		27.0
$La@C_{82}Cp$[a]		23.9

[a] Reference 12.

which maleic anhydride was used as a scavenger of Cp* to prevent recombination between $La@C_{82}$ and Cp*. The ESR spectrum of the tracing retro-DA reaction exhibited a set of octet signals for $La@C_{82}Cp^*$ and $La@C_{82}$ (see Supporting Information Figure S3). The rate constants at 283, 288, 293, 298, and 303 K were determined based on the ratio of the ESR signals of $La@C_{82}Cp^*$ and $La@C_{82}$ estimated by simulation of their ESR spectra. Furthermore, to obtain kinetic parameters for the decomposition of $La@C_{82}Cp^*$, the data of rate constants in Table 1 were applied to the Arrhenius form of the rate expression: $k = Ae^{-E_a/RT}$ (see Supporting Information Figure S4). Consequently, the activation energy for this retro-DA reaction was determined as 27.0 kcal/mol, which is 3.1 kcal/mol higher in energy than the retro-DA reaction of $La@C_{82}Cp$. This higher activation energy is mainly attributable to the substituent effect of electron donation derived from five methyl groups of Cp*, increasing the stability of $La@C_{82}Cp^*$ similarly in the case of $C_{60}Cp^*$.[4b] In addition, the experimental value of 27.0 kcal/mol agrees reasonably well with the calculated values of 29.9 kcal/mol.

CONCLUSION

In conclusion, results of this study show that the DA cycloaddition reaction of Cp* and paramagnetic $La@C_{82}$ proceed via a concerted bond formation mechanism, through an intermediate formation of $La@C_{82}$ and Cp*. The experimentally obtained results related to the retro-DA reaction of $La@C_{82}Cp^*$ exhibit the activation energy, which is in good agreement with the theoretical predicted one. Using the M06-2X method[29] therefore enables the analysis of endohedral metallofullerene DA cycloaddition reactions, in spite of the fact that $La@C_{82}$ has a radical character. This approach is therefore also promising for further investigation of the reaction mechanism of functionalization of endohedral metallofullerenes.[30]

ASSOCIATED CONTENT

Supporting Information

Charge density, p-orbital axis vector (POAV) angles, and SOMO spin density of carbon atoms in $La@C_{82}$ and the experimental results of kinetics studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 16−31. (b) Sauer, J.; Sustman, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779−807. (c) Houk, K. N.; Evanseck, J. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 682−708. (d) Houk, K. N.; Gonzalez, J.; Li, Y. *Acc. Chem. Res.* **1995**, *28*, 81−90. (e) Horn, B. A.; Herek, J. L.; Zewail, A. H. *J. Am. Chem. Soc.* **1996**, *118*, 8755−8756. (f) Sustmann, R.; Tappanchai, S.; Bandmann, H. *J. Am. Chem. Soc.* **1996**, *118*, 12555−12561. (g) Dewar, M. J. S.; Jie, C. *Acc. Chem. Res.* **1992**, *25*, 537−543. (h) Nicolaou, N. C.; Snyder, S. A.; Montagnon, T.; Vassilikogiannakis, G. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 1668−1698.

(2) (a) Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157−161. (b) Haddon, R. C. *Science* **1993**, *261*, 1545−1550. (c) Chaur, M. N.; Melin, F.; Ortiz, A. L.; Echegoyen, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 7514−7538. (d) Osuna, S.; Swart, M.; Solà, M. *Phys. Chem. Chem. Phys.* **2011**, *13*, 3585−3603.

(3) (a) Sarova, G. H.; Berberan-Santos, M. N. *Chem. Phys. Lett.* **2004**, *397*, 402−407. (b) Tsuda, T.; Ishida, T.; Nogami, T.; Kurono, S.; Ohashi, M. *J. Chem. Soc., Chem. Commun.* **1993**, 1296−1298. (c) Rubin, Y.; Khan, S.; Freedberg, D. I.; Yeretzian, C. *J. Am. Chem. Soc.* **1993**, *115*, 344−345.

(4) (a) Rotello, V. M.; Howard, J. B.; Yadav, T.; Conn, M. M.; Viani, E.; Giovane, L. M.; Lafleur, A. L. *Tetrahedron Lett.* **1993**, *34*, 1561−1562. (b) Meidine, M. F.; Avent, A. G.; Darwish, A. D.; Kroto, H. W.; Ohashi, O.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1189−1193. (c) Pang, L. S. K.; Wilson, M. A. *J. Phys. Chem.* **1993**, *97*, 6761−6763. (d) Osuna, S.; Morera, J.; Cases, M.; Morokuma, K.; Solà, M. *J. Phys. Chem. A* **2009**, *113*, 9721−9726. (e) Osuna, S.; Swart, M.; Solà, M. *J. Phys. Chem. A* **2011**, *115*, 3491−3496.

(5) (a) Yurovskaya, M. A.; Trushkov, I. V. *Russ. Chem. Bull. Int. Ed.* **2002**, *51*, 367−443. (b) Osuna, S.; Swart, M.; Solà, M. *Phys. Chem. Chem. Phys.* **2011**, *13*, 3585−3603. (c) Garcia-Borràs, M.; Osuna, S.; Luis, J. M.; Swart, M.; Solà, M. *Chem.−Eur. J.* **2012**, *18*, 7141−7154.

(6) (a) Nie, B.; Rotello, V. M. *J. Org. Chem.* **1996**, *61*, 1870. (b) Ge, Z.; Duchamp, J. C.; Cai, T.; Gibson, H. W.; Dorn, H. C. *J. Am. Chem. Soc.* **2005**, *127*, 16292−16298.

(7) Lamparth, I.; Maichle-Mössmer, C.; Hirsh, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1607−1609.

(8) *Endofullerenes: A New Family of Carbon Clusters*; Akasaka, T., Nagase, S., Eds.; Kluwer: Dordrecht, The Netherlands, 2002.

(9) *Chemistry of Nanocarbons*; Akasaka, T., Wudl, F., Nagase, S., Eds.; Wiley:: London, U.K., 2010.

(10) (a) Maeda, Y.; Tsuchiya, T.; Lu, X.; Takano, Y.; Akasaka, T.; Nagase, S. *Nanoscale* **2011**, *3*, 2421−2429. (b) Lu, X.; Akasaka, T.; Nagase, S. *Chem. Commun.* **2011**, *47*, 5942−5957. (c) Tsuchiya, T.; Akasaka, T.; Nagase, S. *Pure Appl. Chem.* **2010**, *82*, 505−521. (d) Chaur, M. N.; Melin, F.; Ortiz, A. L.; Echegoyen, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 7514−7538.

(11) (a) Tsuchiya, T.; Kumashiro, R.; Tanigaki, K.; Matsunaga, Y.; Ishitsuka, M. O.; Wakahara, T.; Maeda, Y.; Takano, Y.; Aoyagi, M.; Akasaka, T.; Liu, M. T. H.; Kato, T.; Suenaga, K.; Jeong, J. S.; Iijima, S.; Kimura, F.; Kimura, T.; Nagase, S. *J. Am. Chem. Soc.* **2008**, *130*, 450−451. (b) Sato, S.; Seki, S.; Honsho, Y.; Wang, L.; Nikawa, H.;

Luo, G.; Lu, J.; Haranaka, M.; Tsuchiya, T.; Nagase, S.; Akasaka, T. *J. Am. Chem. Soc.* **2011**, *133*, 2766−2771. (c) Sato, S.; Nikawa, H.; Seki, S.; Wang, L.; Luo, G.; Lu, J.; Haranaka, M.; Tsuchiya, T.; Nagase, S.; Akasaka, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 1589−1591.

(12) Maeda, Y.; Miyashita, J.; Hasegawa, T.; Wakahara, T.; Tsuchiya, T.; Nakahodo, T.; Akasaka, T.; Mizorogi, N.; Kobayashi, K.; Nagase, S.; Kato, T.; Ban, N.; Nakajima, H.; Watanabe, Y. *J. Am. Chem. Soc.* **2005**, *127*, 12190−12191.

(13) Maeda, Y.; Sato, S.; Inada, K.; Nikawa, H.; Yamada, M.; Mizorogi, M.; Hasegawa, T.; Tsuchiya, T.; Akasaka, T.; Kato, T.; Slanina, Z.; Nagase, S. *Chem.−Eur. J.* **2010**, *16*, 2193−2197.

(14) (a) Feng, L.; Nakahodo, T.; Wakahara, T.; Tsuchiya, T.; Maeda, Y.; Akasaka, T.; Kato, T.; Horn, E.; Yoza, K.; Mizorogi, N.; Nagase, S. *J. Am. Chem. Soc.* **2005**, *127*, 17136−17137. (b) Feng, L.; Wakahara, T.; Nakahodo, T.; Tsuchiya, T.; Piao, Q.; Maeda, Y.; Lian, Y.; Akasaka, T.; Horn, E.; Yoza, K.; Kato, T.; Mizorogi, N.; Nagase, S. *Chem.−Eur. J.* **2006**, *12*, 5578−5586. (c) Feng, L.; Tsuchiya, T.; Wakahara, T.; Nakahodo, T.; Piao, Q.; Maeda, Y.; Akasaka, T.; Kato, T.; Yoza, K.; Horn, E.; Mizorogi, N.; Nagase, S. *J. Am. Chem. Soc.* **2006**, *128*, 5990−5991.

(15) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781−853.

(16) (a) Fukui, K.; Yonezawa, T.; Shingu, H. *J. Chem. Phys.* **1952**, *20*, 722−725. (b) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57−64.

(17) (a) Bauld, N. L.; Bellville, D. J.; Harirchian, B.; Lorenz, K. T.; Pabon, R. A.; Reynolds, D. W.; Wirth, D. D.; Chiou, H. −S.; Marsh, B. K. *Acc. Chem. Res.* **1987**, *20*, 371−378. (b) Bauld, N. L. *Tetrahedron* **1989**, *45*, 5307−5363. (c) Pandey, G. *Top. Curr. Chem.* **1993**, *168*, 175−221. (d) Schmittel, M.; Burghart, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2551−2589. (e) Schmittel, M.; Wöhrle, C.; Bohn, L. *Acta Chem. Scand.* **1997**, *51*, 151−157. (f) Mattay, J. *Synthesis* **1989**, 233−252.

(18) (a) Hofmann, M.; Schaefer, H. F. *J. Am. Chem. Soc.* **1999**, *121*, 6719−6729. (b) Haberl, U.; Wiest, O.; Steckhan, E. *J. Am. Chem. Soc.* **1999**, *121*, 6730−6736. (c) Hofmann, M.; Schaefer, H. F. *J. Phys. Chem. A* **1999**, *103*, 8895−8905. (d) Hintz, S.; Heidbreder, A.; Mattay, J. *Top. Curr. Chem.* **1996**, *177*, 77−124.

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision A.01; Gaussian, Inc.: Wallingford, CT, 2009.

(20) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215−241.

(21) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284−298.

(22) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(23) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

(24) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347−1363.

(25) Duling, D. R. *J. Magn. Reson. Ser. B* **1994**, *104*, 105−110.

(26) Yamamoto, K.; Funasaka, T.; Takahashi, T.; Akasaka, T.; Suzuki, T.; Maruyama, Y. *J. Phys. Chem.* **1994**, *98*, 12831−12833.

(27) Manoharan, M.; Proft, F. D.; Geerlings, P. *J. Org. Chem.* **2000**, *65*, 6132−6137.

(28) Because, unfortunately, multiple adducts are formed in the reaction between La@C_{82} and Cp*, it is difficult to estimate the rate constants of the cycloaddition reaction.

(29) We have checked other DFT functional methods, B3LYP and B3LYP+D3. The DA reaction of La@C_{82} and Cp* was calculated to be only 2.0 kcal/mol exothermic at the B3LYP level, while it was 19.0 and 28.3 kcal/mol at B3LYP+D3 and M0-2X levels, respectively. These results show that dispersion attractions, which are taken into account for B3LYP+D3 and M06-2X, play an important role in the binding of La@C_{82} and Cp*. Because the M06-2X method showed good agreement with experimental results, it was employed in this work.

(30) Very recently, the regioselectivity and product stability of the reactions of La@C_{82} with Cp or Cp* were theoretically investigated by Garcia-Borràs, M.; Luis, J. M.; Swart, M.; Solà, M. *Chem.—Eur. J.* **2013**, *19*, 4468−4479.