JCTC Journal of Chemical Theory and Computation

First-Principle Calculations of Large Fullerenes

Patrizia Calaminici,* Gerald Geudtner, and
Andreas M. Köster

*Departamento de Química, CINVESTAV, Avenida Instituto
Politecnico Nacional 2508, A.P. 14-740,
Mexico D.F. 07000, Mexico*

Abstract: State of-the-art density functional theory calculations have been performed for the large fullerenes C_{180}, C_{240}, C_{320}, and C_{540} using the linear combination of Gaussian-type orbitals density functional theory (LCGTO-DFT) approach. For the calculations all-electron basis sets were employed. All fullerene structures were fully optimized without symmetry constrains. The analysis of the obtained structures as well as a study on the evolution of the bond lengths and calculated binding energies are presented. The fullerene results are compared to diamond and graphene which were calculated at the same level of theory. This represents the first systematic study on these large fullerenes based on nonsymmetry adapted first-principle calculations, and it demonstrates the capability of DFT calculations for energy and structure computations of large scale structures without any symmetry constraint.

Introduction

Fullerenes are carbon clusters formed by the closing of a graphite sheet with the needed curvature supplied by intersecting, among a given number of graphitic hexagons, of twelve pentagons.[1,2] These carbon aggregates have been experimentally known for more than twenty years,[3] and, consequently, a large number of works, experimental as well as theoretical, focused on this subject (see, for example refs 4−7 and references therein). One main reason for the large interest in the study of fullerenes is certainly to be found in their particularly appealing geometrical form. The best known fullerene is the so-called buckminsterfullerene that contains sixty carbon atoms (C_{60}) and is composed of twelve pentagonal carbon rings located around the vertices of an icosahedron and twenty hexagonal carbon rings at the centers of icosahedral faces.[3] Larger fullerenes that have an icosahedral symmetry can be constructed[8,9] as well. These clusters, known as *giant fullerenes*, can be thought of as cut-out pieces of graphene that are folded into final shape (icosahedron). This kind of procedure generates twelve pentagonal carbon rings situated around vertices of an icosahedron, while all other carbon rings are hexagonal. Giant or large fullerenes have been the subject of different theoretical studies in the last years. For a more detailed overview we address the reader to refs 10−23 and references therein. Most of these studies were focused either to understand if the shape of these clusters is spherical or faceted,[10,11,15−19] to calculate their response properties,[12] or to test new algorithms developed for the investigation of large systems.[13,14] Most previous first-principle type theoretical studies of large fullerenes have been performed either at the Hartree−Fock level of theory using symmetry restrictions and relative small basis sets or employing analytic density-functional theory.[10−23] To the best of our knowledge, no systematic study on large fullerenes based on nonsymmetry adapted first-principle calculations has been performed so far. In this Letter we present the first all-electron density functional theory based study on the large fullerenes C_{180}, C_{240}, C_{320}, and C_{540}. The structures of these clusters were fully optimized without any symmetry constraint. This work provides insight into the structural changes, the evolution of the bond lengths, and binding energies with increasing fullerene size.

Computational Details

All calculations were performed using the density functional theory (DFT) deMon2k program.[24] The exchange-correlation potential was numerically integrated on an adaptive grid.[25] The grid accuracy was set to 10^{-5} in all calculations. The Coulomb energy was calculated by the variational fitting procedure proposed by Dunlap, Connolly, and Sabin.[26,27] The calculation of the exchange correlation energy was performed employing the auxiliary function density.[28] The structure optimizations were performed in the local density approximation (LDA) employing the Dirac exchange functional[29] in combination with the correlation functional from Vosko, Wilk, and Nusair (VWN).[30] DFT optimized double-ζ plus valence polarization (DZVP) all-electron basis sets optimized for local functionals[31] were employed. For the structure optimization a quasi-Newton method in internal redundant coordinates with analytic energy gradients was used.[32] The geometry optimizations were performed using the parallel version of the deMon2k code.[24] The convergence was based on the Cartesian gradient and displacement vectors with a threshold of 10^{-4} and 10^{-3} a.u., respectively. The diamond and graphene calculations were performed in the same

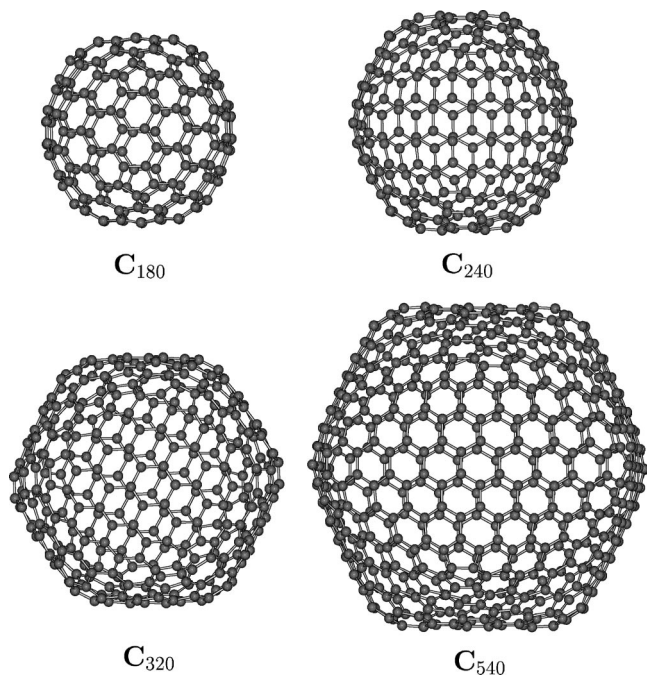* Corresponding author e-mail: pcalamin@cinvestav.mx.

30 *J. Chem. Theory Comput., Vol. 5, No. 1, 2009*

Letter

Figure 1. Optimized structure of C_{180}, C_{240}, C_{320}, and C_{540} fullerenes. The calculations have been performed with the VWN functional in combination with DZVP basis sets.

theoretical framework employing the cyclic cluster model (CCM).[33] For this reason the here reported relative energy differences between the fullerene binding energies and the cohesive energies in diamond and graphene should be quite reliable.

Results and Discussion

In Figure 1 the DFT optimized singlet structures of C_{180}, C_{240}, C_{320}, and C_{540} are depicted. These structures have been fully optimized at the all-electron level using DZVP basis sets in combination with the VWN functional. A long standing discussion in the literature addresses the question if giant fullerenes prefer a faceted or a spherical shape. This question was raised by transmission electron microscopy (TEM) images that have shown evidence of possible spheroidal structures in concentric carbon particles.[34−36] Using a divide-and-conquer method for density functional calculations the structure and stability of C_{240} were studied, and the most stable structure was claimed to be highly spherical.[15] However, this result was not confirmed by any successive theoretical work. Instead, all other calculations indicated strong evidence of a faceted shape for this fullerene.[10,11,16−20] It has been clearly explained in the literature that depending on the view axis, simulated TEM of icosahedral fullerenes can provide either images with spherical or with polyhedral shapes.[18] In addition, an explanation of why experimental results showed rounder shapes for large fullerenes was also given.[18] As Figure 1 shows our first-principle based structure optimizations predict that larger fullerenes, C_{240}, C_{320}, and C_{540}, prefer a faceted shape. Moreover, as Figure 1 shows, even for the smallest fullerene studied here, C_{180}, there is clear evidence that the faceted shape is preferred over a spherical shape if first-principle all-electron optimizations without any symmetry restriction are performed. Details about the timing of these calculations are reported in ref 14. We notice that our
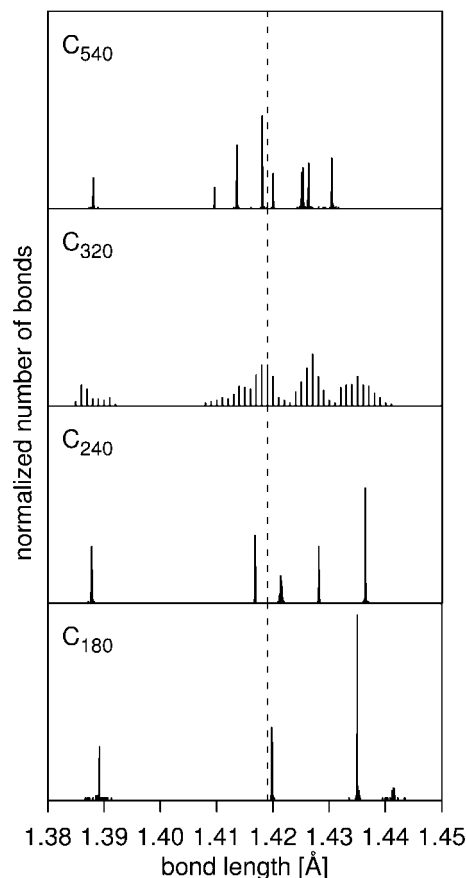

Figure 2. Normalized number of bonds for C_{180}, C_{240} C_{320}, and C_{540} versus the bond lengths (in Å).

results are in agreement with most of the previous reported theoretical studies.[10,11,16−20] In order to gain more insight into the structural changes of these systems as the number of carbon atoms increases we performed a detailed analysis of the bond length evolution. In Figure 2 the normalized number of bonds for C_{180}, C_{240} C_{320}, and C_{540} are plotted versus the bond length. The dashed line at 1.419 Angstrom represents the graphene bond length obtained from the periodic deMon2k calculation.[33] Most obvious from this figure is the difference of C_{320} to all other fullerenes. In fact, whereas usually a discrete distribution of bond lengths is found, in C_{320}, a wide, in some ranges almost continuous, bond length distribution is observed. This clearly indicates a break in the expected high symmetry of the system. Our studies show that the C_{320} fullerene possesses a ground-state potential energy surface (PES) of higher multiplicity, most likely either triplet or quintet. This observation is in agreement with the conclusions given by Fowler.[37] Further test calculations revealed that for this fullerene also in the cases of triplet and quintet PESs the continuous bond length distribution observed for the singlet PES persists. Of course, only nonsymmetry adapted optimizations can lead to such a result. To the best of our knowledge this symmetry breaking in larger fullerenes due to their electronic structure has never been observed in previous calculations. As Figure 1 shows the observed symmetry breaking does not alter the global shape of the giant fullerene. For the other systems, C_{180}, C_{240}, and C_{540}, the expected discrete bond length distribution is obtained, indicating that the symmetry of the electronic structures matches with the expected geometrical symmetry. In these systems the number of different bond lengths
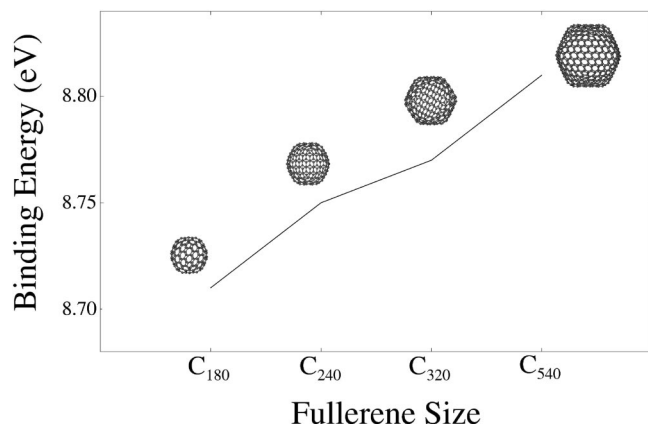
Letter

J. Chem. Theory Comput., Vol. 5, No. 1, 2009 **31**

Figure 3. Binding energy (in eV) for C_{180}, C_{240}, C_{320}, and C_{540} fullerenes. The calculations have been performed with the VWN functional in combination with DZVP basis sets.

increases with system size, and an accumulation of bond lengths around the graphene bond length is observed. More surprising is the trend that the longest bond length in the cluster shortens with increasing cluster size. This indicates that delocalization increases with cluster size despite the global building pattern, i.e. the appearance of twelve pentagons. With the aim to guide future desirable experiments on large fullerenes and to gain more information about their stability we have also explored the behavior of the binding energy of the studied fullerenes with increasing fullerene size. The results of the uncorrected binding energy (in eV) per carbon atom obtained with the VWN functional are illustrated in Figure 3. The inclusion of the basis set superposition error (BSSE) decreases the calculated binding energies to 8.64 eV (C_{180}), 8.68 eV (C_{240}), 8.69 eV (C_{320}), and 8.75 eV (C_{540}), respectively. The depicted trend in Figure 3 is not altered by the BSSE correction. In fact the BSSE is in giant fullerenes much smaller than for the equivalent graphene calculation. As can be seen from Figure 3 the binding energy increases monotonically with the number of carbon atoms increases. This indicates that the large fullerenes become more and more stable with increasing size. However, the increase is very moderate. From the comparison of the CCM calculations we find that the binding energy of C_{540} is very close to the cohesive energy of diamond (8.78 eV). This indicates that C_{540} has a similar binding energy to diamond which fuels the hope that such giant fullerenes could indeed be prepared. However, the binding energy of even the largest fullerene, C_{540}, studied here is still far away from the corresponding value in graphene which was calculated to be 8.91 eV.[33] This is in the range of other calculated cohesive energies for graphene.[38,39] Because the fullerenes and graphene calculations are performed within the same theoretical framework, the relative energy differences found here, are reliable.

Conclusions

In conclusion, state of-the-art density functional theory calculations have been performed for the large fullerenes C_{180}, C_{240}, C_{320}, and C_{540} using the linear combination of Gaussian-type orbitals density functional theory. The calculations were of all electron types. All structures have been fully optimized without any symmetry restriction. This work confirms that for all large fullerenes studied here a faceted shape is preferred over the

spherical shape. The analysis of the bond length evolution shows for the C_{320} a qualitative different pattern than for the other fullerenes. The most likely explanation for this difference is a symmetry breaking in the electron structure of C_{320}. The shortening of the longest bond length with increasing cluster size indicates that delocalization increases with cluster size. The calculated binding energies are in the range of diamond but considerably below the graphene value. Thus, even giant fullerenes like the ones studied here are only meta-stable.

References

(1) Kadish, K. M.; Ruoff, R. S. In *Fullerenes: Chemistry, Physics, and Technology*; John Wiley & Sons Inc.: New York, 2007.

(2) Andreoni W. In *The Physics of Fullerene-Based and Fullerene-Related Materials;* Kluwer Academic Publishers: Dordrecht, Netherlands, 2007.

(3) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. C_{60}-Buckminsterfullerene. *Nature (London)* **1985**, *318*, 162–163.

(4) Seifert, G.; Vietze, K.; Schmidt, R. Ionization Energies of fullerenes - Size and charge dependence. *J. Phys. B* **1996**, *29*, 5183–5192.

(5) Boltalina, O. V.; Ioffe, I. N.; Sidorov, L. N.; Seifert, G.; Vietze, K. Ionization energy of fullerenes. *J. Am. Chem. Soc.* **2000**, *122*, 9745–9749.

(6) Cioslowski, J. In *Electronic Structure Calculations on Fullerenes and Their Derivatives;* Oxford University Press: New York, 1995.

(7) Bülh, M.; Hirsch, A. Spherical aromaticity of fullerenes. *Chem. Rev.* **2001**, *101*, 1153–1183.

(8) Kroto, H. W.; McKay, K. The formation of quasi-icosahedral spiral shell carbon particles. *Nature* **1988**, *331*, 328–331.

(9) Itoh, S.; Ordejón, P.; Drabold, D. A.; Martin, R. M. Structure and energetics of giant fullerenes: An order-N molecular dynamics study. *Phys. Rev. B* **1996**, *53*, 2132–2140.

(10) Bakowies, D.; Bülh, M.; Thiel, W. Can large fullerenes be spherical. *J. Am. Chem. Soc.* **1995**, *117*, 10113–10118.

(11) Scuseria, G. E. The equilibrium structures of giant fullerenes - faceted or spherical shape - An ab-initio Hartree-Fock study of icosahedral. C_{240} and C_{540}. *Chem. Phys. Lett.* **1995**, *243*, 193–198.

(12) Zope, R. R.; Baruah, T.; Pederson, M. R.; Dunlap, B. I. Static dielectric response of icosahedral fullerenes from C_{60} to C_{2160} characterized by an all-electron density functional theory. *Phys. Rev. B* **2008**, *77*, 115452.

(13) Dunlap, B. I.; Zope, R. R. Efficient quantum-chemical geometry optimization and the structure of large icosahedral fullerenes. *Chem. Phys. Lett.* **2006**, *422*, 451–454.

(14) Geudtner, G.; Janetzko, F.; Köster, A. M.; Vela, A.; Calaminici, P. Parallelization of the deMon2k code. *J. Comput. Chem.* **2006**, *27*, 483–490.

(15) York, D.; Lu, J. P.; Yang, W. Density-functional calculations of the structure and stability of C_{240}. *Phys. Rev. B* **1994**, *49*, 8526–8528.

(16) Haddon, R. C.; Scuseria, G. E.; Smalley, R. E. C_{240} - The most chemically inert fullerene. *Chem. Phys. Lett.* **1997**, *272*, 38–42.

(17) Bates, K. R.; Scuseria, G. E. Why are buckyonions round. *Theor. Chem. Acc.* **1998**, *99*, 29–33.

(18) Scuseria, G. E. Ab initio calculations of Fullerenes. *Science* **1996**, *271*, 942–945.

(19) Xu, C. H.; Scuseria, G. E. An O(N) tight-binding study of carbon clusters up to C_{8640}: the geometrical shape of the giant icosahedral fullerenes. *Chem. Phys. Lett.* **1996**, *262*, 219–226.

(20) Dunlap, B. I.; Brenner, D. W.; Mintmire, J. W.; Mowrey, R. C.; White, C. T. Local density functional electronic structures of three stable icosahedral fullerenes. *J. Phys. Chem.* **1991**, *95*, 8737–8741.

(21) Heggie, M. I.; Terrones, M.; Eggen, B. R.; Jungnickel, G.; Jones, R.; Latham, C. D.; Briddon, P. R.; Terrones, H. Quantitative density-functional study of nested fullerenes. *Phys. Rev. B* **1998**, *57*, 13339–13342.

(22) Shao, N.; Gao, Y.; Yoo, S.; An, W.; Zeng, X. C. Search for lowest-energy fullerenes: C_{98} to C_{110}. *J. Phys. Chem. A* **2006**, *110*, 7672–7676.

(23) Shao, N.; Gao, Y.; Zeng, X. C. Search for lowest-energy fullerenes 2: C_{38} to C_{80} and C_{112} to C_{120}. *J. Phys. Chem. C* **2007**, *111*, 17671–17677.

(24) Köster A. M.; Calaminici P.; Flores-Moreno P.; Geudtner G.; Goursot A.; Heine T.; Janetzko F.; Patchkovskii S.; Reveles J. U.; Vela A.; Salahub D. R. deMon2k; The deMon developers: 2004.

(25) Köster, A. M.; Flores-Moreno, R.; Reveles, J. U. Efficient and reliable numerical integration of exchange-correlation energies and potentials. *J. Chem. Phys.* **2004**, *121*, 681–690.

(26) Dunlap, B. I.; Connolly, J. W. D.; Sabin, R. J. 1st-row diatomic molecules and local density models. *J. Chem. Phys.* **1979**, *71*, 4993–4999.

(27) Mintmire, W.; Dunlap, B. I. Fitting the Coulomb potential variationally in linear combination of atomic orbitals density functional calculations. *Phys. Rev. A* **1982**, *25*, 88–95.

(28) Köster, A. M.; Reveles, J. U.; M. del Campo, J. Calculations of exchange-correlation potentials with auxiliary function densities. *J. Chem. Phys.* **2004**, *121*, 3417–3424.

(29) Dirac, P. A. M. Note on exchange phenomena in the Thomas atom. *Proc. Cambridge Philos. Soc.* **1930**, *26*, 376–385.

(30) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate spin-depentent electron liquid correlation energies for local spin-density calculations - a critical analysis. *Can. J. Phys.* **1980**, *58*, 1200–1211.

(31) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. Optimization of gaussian-type basis-sets for local spin-density functional calculations. 1. boron through neon, optimization technique and validation. *Can. J. Phys.* **1992**, *70*, 560–571.

(32) Reveles, J. U.; Köster, A. M. Geometry optimization in density functional methods. *J. Comput. Chem.* **2004**, *25*, 1109–1116.

(33) Janetzko, F.; Köster, A. M.; Salahub, D. R. Development of the cyclic cluster model formalism for Kohn-Sham auxiliary density functional theory methods. *J. Chem. Phys.* **2008**, *128*, 024102.

(34) Iijima, S. Direct observation of the tetrahedral bonding in graphitized carbon-black by high-resolution electron-microscopy. *J. Cryst. Growth* **1980**, *50*, 675–683.

(35) Ugarte, D. Curling and closure of graphitic networks under electron-beam irradiation. *Nature* **1992**, *359*, 707–709.

(36) Ugarte, D. Onion-like graphitic particles. *Carbon* **1995**, *33*, 989–993.

(37) Fowler, P. W. How unusual is C_{60}? Magic numbers for carbon clusters. *Chem. Phys. Lett.* **1986**, *131*, 444–450.

(38) Trickey, S. B.; Müller-Plate, F.; Diercksen, G. H. F.; Boettger, J. C. Interplanar binding and lattice relaxation in a graphite dilayer. *Phys. Rev. B* **1992**, *45*, 4460–4468.

(39) Dunlap, B. I.; Boettger, J. C. Local-density-functional study of the fullerenes, graphene and graphite. *J. Phys. B* **1996**, *29*, 4907–4913.