J. Phys. Chem. A **1997,** *101,* 5551−5554

Characteristics of the Li_nC_{60} Complexes for $n = 1-6$ and 12: An *ab Initio* Study

Thammarat Aree and Supot Hannongbua*

Computational Chemistry Unit Cell, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

Received: January 10, 1997; In Final Form: May 28, 1997[⊗]

Ab initio calculations have been performed for Li_nC_{60} where $n = 1-6$ and 12 using STO-3G and 6-31G basis sets. The distance between Li and the center of C_{60} and geometrical parameters (bond lengths and bond angles) of C_{60} have been fully optimized. Electronic structures and the HOMO−LUMO energy gap of the complexes have been analyzed. It was found that both basis sets yield results lying with the same trend. Compared to those in a free C_{60} ligand, C−C and C═C bond lengths of C_{60} in the Li_nC_{60} complexes change slightly for increasing *n*. The complexes with more Li also have an increased of Li−C_{60} distance, except that for $n = 12$. In addition, the Li_3C_{60} complex was found to exhibit the lowest energy gap among the investigated clusters. This is in good agreement with experimental observations for K_nC_{60} and Rb_nC_{60} complexes and with the natural lattice structure of C_{60}, for which the unit cell contains two tetrahedral and one octahedral sites.

1. Introduction

It is generally agreed that the experimental discovery of fullerenes by Kroto and Smalley[1] is a scientific breakthrough. The outstanding characteristic of the buckminsterfullerene, C_{60}, is exohedral complexation with alkali metals yielding superconductivity at relatively high temperature for the K_3C_{60}[3−7] and Rb_3C_{60}[3,4] complexes. The great feature of these complexes is their conductivity, which depends strongly on their composition, so that some are conductors and some are insulators. Complexes of C_{60} with Na, K, and Cs have been synthesized, and related properties have been elucidated.[8−14] It is widely recognized that the K_3C_{60}[3−7] complex is a superconductor, whereas M_nC_{60} complexes where M denotes Li, Na, and Cs and $n = 1, 2, 3, ..., 6$, are insulators.[15] However, alloy metal fullerides of Na or Li are superconductors.[10] As there is a lack of both experimental and theoretical studies of Li−C_{60} complexes, the aim of this work is to investigate electronic and geometrical structures of the Li_nC_{60} complexes, where $n = 1-6$ and 12, based on *ab initio* calculations. The corresponding HOMO−LUMO energy gaps (E_g) have also been examined.

2. Calculation Methods

Ab initio self-consistent-field calculations were performed for the Li_nC_{60} complexes, where $n = 1-6$ and 12, using STO-3G, 6-31G, and DZP (double-ζ plus polarization function)[16−19] basis sets within the UHF method. An error due to an imbalance of the basis sets, known as basis set superposition error (BSSE), has also been examined. The calculations have been carried out using the Gaussian 92 program[20] on an IBM RISC 6000/530H workstation. Starting geometrical parameters for C_{60} where C−C = 1.448 Å and C═C = 1.375 Å have been taken from the literature.[21] The geometries of the complexes were then entirely optimized. The selected symmetry point groups of the complex were restricted to the following criteria:[22] (i) if possible, lithium atoms must lie on the normal vector at the center of a hexagon (six-membered ring); if not, that of a pentagon (five-membered ring) is the next priority (it is found[22] that the complexation energy when a lithium atom lies on the normal vector at the center of a hexagon is more negative than for a pentagon), (ii) lithium atoms must not be on the bridging sites (along a radial vector bisecting C−C or C═C bonds), and (iii) the complexes should exhibit as high a symmetry as possible. The point groups used for the Li_nC_{60} complexes where $n = 1-6$ and 12 are C_{3v}, D_{3d}, C_{3v}, C_{3v}, C_{3v}, C_{3v}, and I_h, respectively.

Each calculation required about 3−4 weeks (CPU time) depending on the symmetry point group and number of lithium atoms. Characteristics of the Li_nC_{60} complexes, for instance, stabilization energy per lithium atom ($\Delta E/n$), energy level diagram, and HOMO−LUMO energy gap, were then analyzed.

3. Results and Discussion

A. Optimized Geometry of the Li_nC_{60} Complexes. As shown in Table 1, the optimized bond lengths of C_{60} obtained from the STO-3G basis set are C═C = 1.375 Å and C−C = 1.448 Å. The corresponding values for the 6-31G basis set are 1.370 and 1.458 Å, respectively. They are in good agreement with the X-ray diffraction data[23] (C═C = 1.355 Å and C−C = 1.467 Å). Those values for the Li_nC_{60} complexes as well as the corresponding C_{60}−Li distances are also summarized in Table 1. Changes of the C_{60}−Li distances and the bond lengths are displayed in Figures 1 and 2, respectively. Stabilization energy per lithium atom as a function of *n* is plotted in Figure 3.

It is interesting to note here for all plots that the trends obtained from both the STO-3G and the 6-31G basis sets are in the same direction. An increase in the number of Li atoms causes an increase in the C_{60}−Li distance. The single point calculation takes 1.5, 13.5, and more than 150 h of CPU time for the STO-3G, 6-31G, and DZP basis sets, respectively. The use of the DZP basis set was given up afterward due to the requirement of a long computational time. As far as the optimal C_{60}−Li distance where the local minimum takes place and the corresponding interaction energy are concerned, a BSSE for the investigated clusters is not detected.[22]

It was found in our previous work[22] that the binding of Li to the hexagonal site leads to a longer C_{60}−Li distance than binding to the pentagon due to the higher electron density of the six-membered ring, and hence the higher C_{60}−Li repulsion. Consequently, the increase of *n* from 1 to 2 and from 3 to 5 (or

---

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

S1089-5639(97)00172-2 CCC: $14.00

TABLE 1: Characteristics of the Li_nC_{60} Complexes Calculated Using STO-3G (Normal Type) and 6-31G (Bold Type) Basis Sets: Ratio of *n*Li Situated at Centers of the Pentagons and at Centers of the Hexagons (C5:C6), Distance between the Center of C_{60} and Li (*r*); Total Energy (*E*); Stabilization Energy per Li Atom (Δ*E*/*n*); and HOMO−LUMO Energy Gap (E_g)

					characteristics					
molecule	C5:C6	symmetry	valence orbitals	spin state	*r* (Å)	C=C (Å)	C−C (Å)	*E* (hartrees)	Δ*E*/*n* (eV)	E_g (eV)
C_{60}		I_h	closed shell	singlet		1.375	1.458	−2244.2212		8.6518
						1.370	**1.448**	**−2270.9711**		**7.5562**
LiC_{60}	0:1	C_{3v}	a_1^1	doublet	5.24	1.376	1.463	−2251.5674	−0.8350	6.2417
					7.38	**1.375**	**1.452**	**−2278.4080**	**−0.4923**	**4.8512**
Li_2C_{60}	0:2	D_{3d}	e_u^2	triplet	5.47	1.377	1.462	−2258.9309	−1.0884	5.8412
					7.51	**1.376**	**1.452**	**−2285.8802**	**−0.8012**	**4.3624**
Li_3C_{60}	3:0	C_{3v}	$a_2^1e^2$	quartet	5.51	1.376	1.462	−2266.3199	−1.3914	5.3341
					7.55	**1.375**	**1.452**	**−2293.3654**	**−1.0254**	**4.1212**
Li_4C_{60}	3:1	C_{3v}	$a_2^2e^2$	triplet	5.60	1.379	1.461	−2273.7447	−1.7868	5.7278
					7.62	**1.374**	**1.452**	**−2300.8771**	**−1.3168**	**4.3007**
Li_5C_{60}	3:2	C_{3v}	$a_2^2e^2a_2^1$	quartet	5.73	1.378	1.463	−2281.1774	−2.0672	6.0778
					7.88	**1.375**	**1.452**	**−2308.1707**	**−1.5235**	**4.6518**
Li_6C_{60}	0:6	C_{3v}	$a_2^1e^2a_2^1e^2$	heptet	5.82	1.378	1.462	−2288.8652	−2.4450	6.3047
					7.95	**1.374**	**1.451**	**−2315.9434**	**−1.8019**	**4.7666**
$Li_{12}C_{60}$	12:0	I_h	closed shell	singlet	5.66	1.379	1.463	−2333.9345	−4.3714	5.4427
					7.64	**1.373**	**1.452**	**−2361.5544**	**−3.2216**	**4.2992**

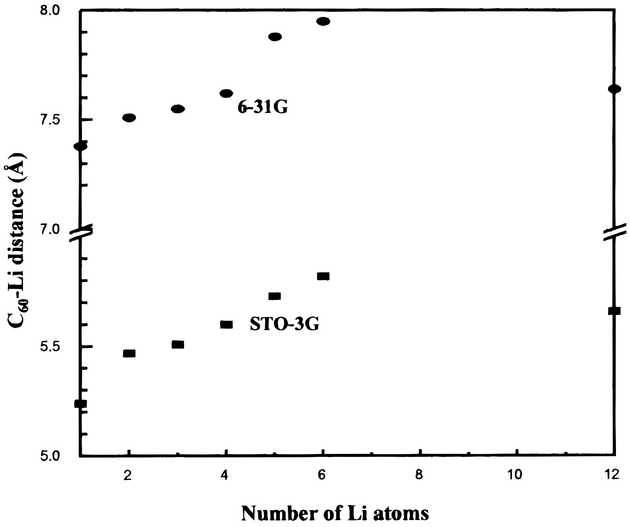


Figure 1. C_{60}−Li distance (from the center of C_{60} cage) as a function of *n* for the Li_nC_{60} complexes.

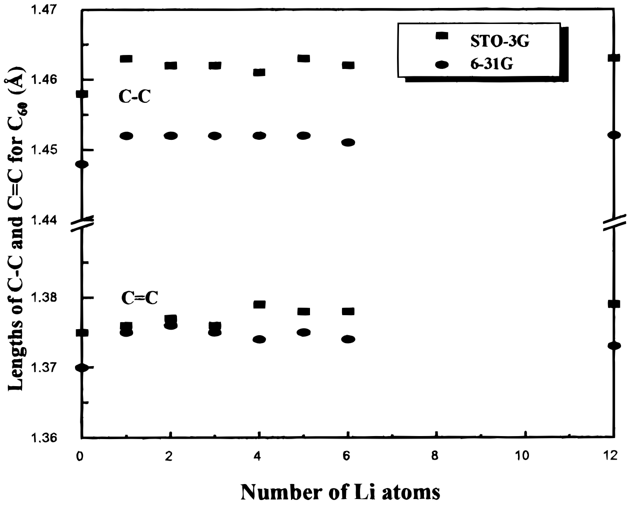


Figure 2. Calculated C−C and C=C bond lengths of the C_{60} as a function of *n* for the Li_nC_{60} complexes.

even to 6) when one more Li is added to a hexagonal site (see the ratio C5:C6 in Table 1) yields a higher slope of the plot (Figure 1) than those of the other ranges. Decrease of the C_{60}−Li separation for $n = 12$ where all lithium atoms are at the center of pentagons can be also understood by this fact.

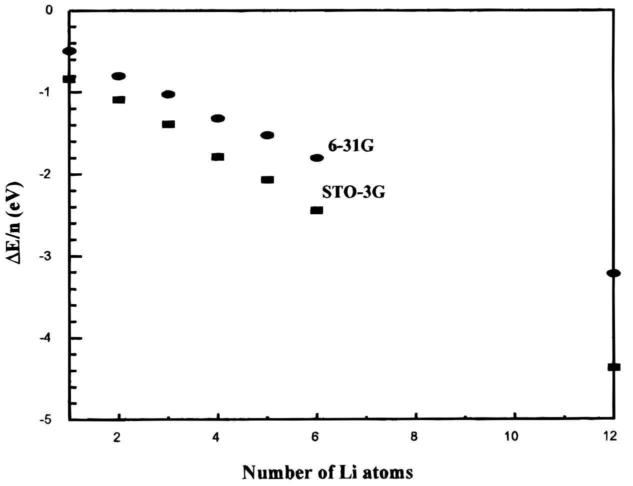
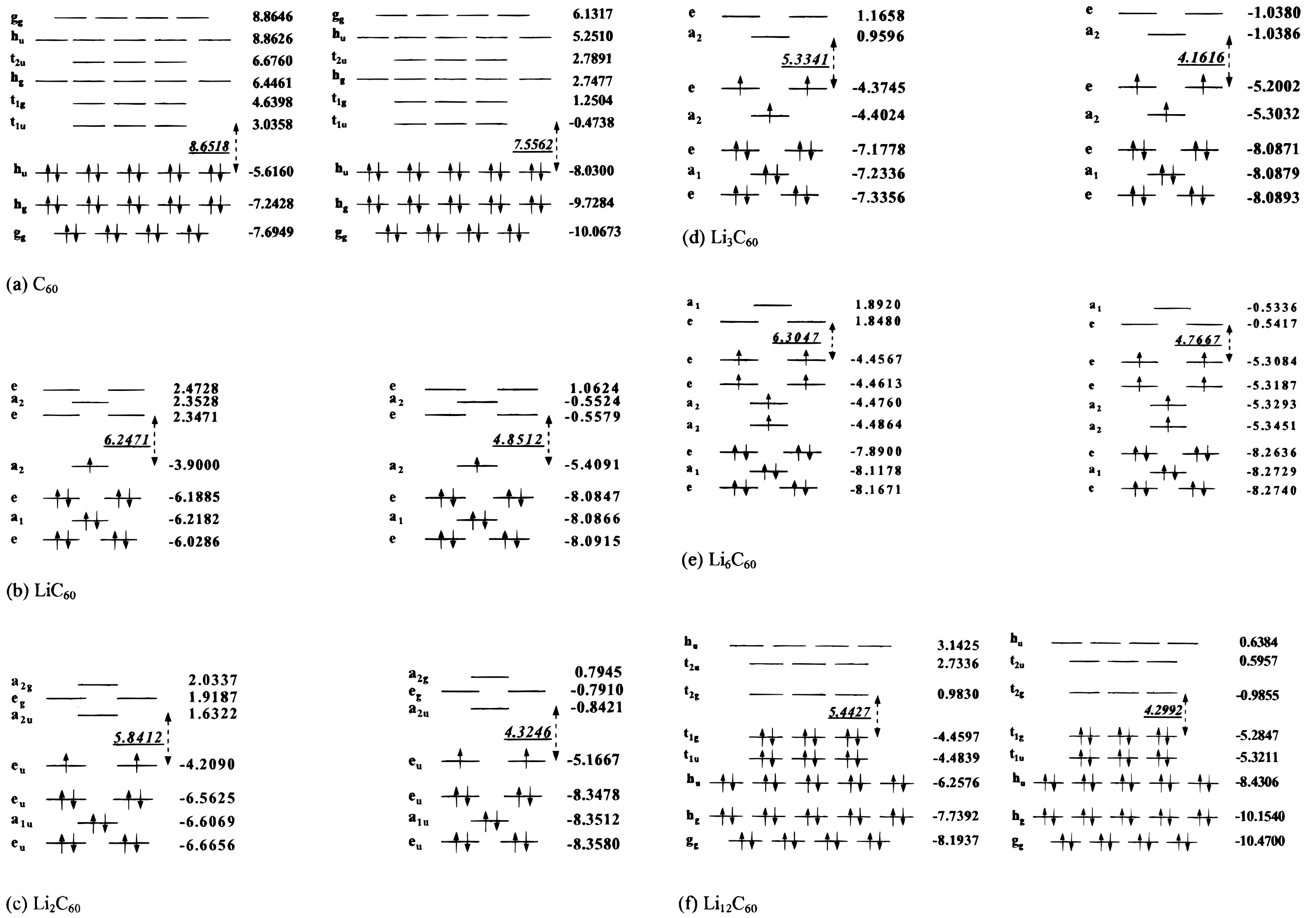


Figure 3. Binding energy per Li (Δ*E*/*n*) as a function of *n* for the Li_nC_{60} complexes.

In Figure 2, a slight change in the C−C and C=C bond lengths in the Li_nC_{60} complexes can be detected, relative to those of free ligands. Swell of the C_{60} structures for all cases can be understood by the Jahn−Teller distortion.[24] Here, the LUMO (t_{1u} orbital) of C_{60} is filled since each lithium atom brings one electron to the complex, leading to a lower symmetry and a higher stability of the C_{60}. This molecular orientational disorder[25] is known to exist in solid state crystals and plays an important role in controlling the electronic properties of the molecules.[26] In terms of the interaction energy (Δ*E*), a linear decrease of Δ*E*/*n* for the Li_nC_{60} complexes has been found (Figure 3).

B. Electronic Structure of the Li_nC60 Complexes. The electronic structures, resulting from the calculations using both STO-3G and 6-31G basis sets, have been analyzed and displayed in terms of energy level diagram (Figure 4). Changes of HOMO−LUMO energy gaps as a function of the number of lithium atoms have been plotted in Figure 5.

In Figure 4a, MO diagrams from the STO-3G and the 6-31G basis sets for C_{60} in its optimal form display energy gaps of 8.65 and 7.56 eV, respectively. These are about 2 times higher than that of 4.91 eV obtained experimentally.[27] When one lithium atom is added to form the LiC_{60} complex, a 2s electron of the lithium atom is transferred to t_{1u} of the C_{60}, splitting t_{1u} into a_2 and e orbitals. In addition, the energy gap per lithium atom decreases to 6.24 and 4.85 eV for the STO-3G and the



(a) C_{60}

(b) LiC_{60}

(c) Li_2C_{60}

(d) Li_3C_{60}

(e) Li_6C_{60}

(f) $Li_{12}C_{60}$

Figure 4. Molecular orbital diagram near the frontier of the C_{60} and the Li_nC_{60} complexes where n = 1, 2, 3, 6, and 12, calculated using the STO-3G (left) and the 6-31G (right) basis sets.

6-31G basis sets, respectively. For the Li_2C_{60} complex, the two electrons from the two lithium atoms occupy an e_u orbital, and the spin state of the complex is a triplet state. The energy gap per lithium atom for the STO-3G is 5.84 eV and for the 6-31G is 4.32 eV. In the case of Li_3C_{60}, the symmetry of the complex is still C_{3v} and the valence-electron configuration of $a_2^1e^2$ is in a quartet state. Furthermore, the energy gap of this complex was reduced to 5.33 eV (STO-3G) or 4.16 eV (6-31G). When one more Li is added, the Li_4C_{60} complex (C_{3v} symmetry) displays an electron configuration of $a_2^2e^2$ in a triplet state. Its energy gap of 6.08 eV by the STO-3G and 4.65 eV by the 6-31G are higher than those of Li_3C_{60}. Including one more Li, the Li_5C_{60} complex retains C_{3v} symmetry and the energy gap increases. In the Li_6C_{60} complex, the six electrons of lithium atoms split the t_{1u} and t_{1g} orbitals of the C_{60} to 2(a+e) and fill up these orbitals. This complex shows a higher HOMO−LUMO energy gap than those for $n = 1-5$. The last composition that is considered in this study is $Li_{12}C_{60}$. Its symmetry remains that of the original symmetry of the C_{60}, i.e., I_h. All electrons from lithium atoms fully occupy the t_{1u} and t_{1g} orbitals, leading to a decrease of the energy gap (Figure 4f).

It is interesting to note that the E_g, which plays a direct role in determination of metallic behavior of the Li_nC_{60} complex, depends on the number of lithium atoms. Although the E_g for the C_{60} free ligand obtained from this study is about 2 times higher than that from experimental data,[27] the size of the system under consideration obviously did not allow the use of a more extended basis set because of the unreasonable computational time that would have been required. However, basis set dependence of the E_g in relative terms should be only a minor methodological problem and should not alter the trend of the E_g plot shown in Figure 5. In addition, a bigger basis set would lead to a slight decrease in the energy gap, as it is known that the energy difference between the conduction and the valence bands of an insulator is higher than 1 eV.[28] Therefore, the lack of metallic character in the Li-doped C_{60}[3,15] can be understood clearly from this fact, as the corresponding E_g for all cases (Figure 5) is above 4 eV.

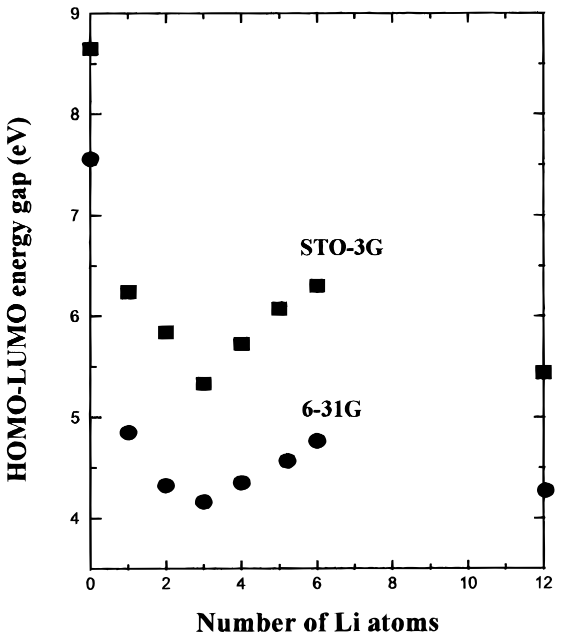


Figure 5. Calculated HOMO−LUMO energy gaps of C_{60} and Li_nC_{60} complexes, plotted versus n.

Comprehensive investigations have been made by Gupta et al.[26] on the electronic structure of the Li_2C_{60} complex using a Hueckel-like Hamiltonian. In their calculations, the geometry of C_{60} is assumed to be rigid and metal−metal and metal−C_{60} distances are kept constant. The result shows that Li_2C_{60} is metallic. Orientational disorder of the molecule, which is normally found in the crystal lattice, has been afterward taken into account. Then, separation between valence and conduction bands was yielded, rendering Li_2C_{60} nonmetallic. This confirms our conclusion on the lack of metallic behavior of the Li_nC_{60} complexes as well as the role of molecular distortion on the prediction of electronic properties of the molecules. Note that the energy gap for Li_2C_{60} obtained from our *ab initio* calculations with both STO-3G and 6-31G basis sets is about 2 times higher than that of Gupta's value. The only possibility to understand this discrepancy is due to error cancellations in their tight-binding electronic structure calculations, leading accidentally to the better E_g (in comparison to experimental prediction).[27]

As a function of n, the E_g plot (Figure 5) shows a minimum at $n = 3$, for the Li_3C_{60} complex. This result confirms the natural occurrence of the lattice structure of C_{60}, for which the unit cell contains one octahedral and two tetrahedral sites. With this composition, encapsulation of three lithium atoms leads to delocalization of the their valence electrons. The electrons are also able to distribute over the whole lattice. The observed composition is the same as those of the K_3C_{60}[3−7] and the Rb_3C_{60}[3,4] complexes, where the superconductivity is detected.

An increase in E_g for the Li_nC_{60} complexes with $3 < n \leq 6$ (Figure 5) is a consequence of the excess number of lithium atoms, as only three holes per unit cell are available in its crystal lattice. This leads also to the decreased degree of delocalization of the electrons. For the $Li_{12}C_{60}$ complex, the calculated E_g as well as the C_{60}−Li distance are very similar to those of Li_4C_{60}; that is, cluster size is smaller and E_g is lower compared to those of Li_5C_{60} and Li_6C_{60}. This fact supports the result obtained by a molecular dynamics study,[28] which signals the possibility that a cluster of type $Li_{12}C_{60}$ may be stable.

Acknowledgment. We are grateful to the Austrian-Thai Center (ATC) for Computer-Assisted Chemical Education and Research, in Bangkok, for computer resource supplements and other facilities. We thank Dr. T. Kerdcharoen for helpful discussions and Dr. D. Ruffolo for proofreading the manuscript.

References and Notes

(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *162*, 318.

(2) Weaver, J. H. *Acc. Chem. Res.* **1992**, *25*, 143.

(3) Holczer, K.; Klein, O.; Huang, S. M.; Kaner, R. B.; Fu, K. J.; Whetten, R. L.; Diederich, F. *Science* **1991**, *252*, 1154.

(4) Stephens, P. W.; Mihaly, L.; Lee, P. L.; Whetten, R. L.; Huang, S. M.; Kaner, R. B.; Diederich, F.; Holczer, K. *Nature (London)* **1991**, *351*, 632.

(5) Herbard, A. F.; Rosseinsky, M. J.; Hoddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Raminez, A. P.; Kortan, A. R. *Nature (London)* **1991**, *350*, 600.

(6) Tycko, R.; Dabbagh, G.; Rosseinsky, M. J.; Murphy, D. W.; Fleming, R. M.; Raminez, A. P.; Tully, J. C. *Science* **1991**, *253*, 884.

(7) Cioslowski, J.; Fleischmann, E. D. *J. Chem. Phys.* **1991**, *94*, 3730.

(8) Östling, D.; Rosen, A. *Chem. Phys. Lett.* **1993**, *202*, 389.

(9) Turek, I.; Hafner, J. *Phys. Rev. B* **1993**, *48*, 14925.

(10) Tanigaki, K.; Hirosawa, I.; Ebbesen, T. W.; Mizuki, J.; Shimakawa, Y.; Kubo, Y.; Tsai, J. S.; Kuroshima, S. *Nature* **1992**, *356*, 419.

(11) Duclos, S. J.; Haddon, R. C.; Glarum, S. H.; Hebard, A. F.; Lyons, K. B. *Science* **1991**, *254*, 1625.

(12) Rosseinsky, M. J.; Murphy, D. W.; Fleming, R. M.; Tycko, R.; Raminez, R. P.; Siegrist, T.; Dabbagh, G.; Barrett, S. E. *Nature* **1992**, *356*, 416.

(13) Benning, P. J.; Martins, J. L.; Weaver, J. H.; Chibante, L. P. F.; Smalley, R. E. *Science* **1991**, *257*, 1417.

(14) Hoddon, R. C. *Acc. Chem. Res.* **1992**, *25*, 127.

(15) Fleming, R. M.; Ramirez, A. P.; Rosseinsky, M. J.; Murphy, D. W.; Haddon, R. C.; Zahurak, S. M.; Makhija, A. V. *Nature* **1991**, *352*, 787.

(16) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(17) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(18) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(19) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

(20) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Beker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92, Revision A*; Gaussian, Inc.: Pittsburgh, PA, 1992.

(21) Scuseria, G. E. *Chem. Phys. Lett.* **1991**, *176*, 423.

(22) Aree, T.; Hannongbua, S. *Chem. Phys. Lett.* **1997**, *226*, 427.

(23) Liu, S.; Lu, Y. J.; Kappes, M. M.; Ibers, J. A. *Nature* **1991**, *254*, 408.

(24) Liehr, A. D. *Annu. Rev. Phys. Chem.* **1962**, *13*, 47.

(25) Barret, S. E.; Tycko, R. *Phys. Rev. Lett.* **1992**, *69*, 3754.

(26) Gupta, R. P.; Gupta. M. *Physica C* **1994,** *219*, 21.

(27) Haufler, R. E.; Wang, L. S.; Chibante, L. P. F.; Jin, C.; Conceicao, J. J.; Chai, Y.; Smalley, R. E. *Chem. Phys. Lett.* **1991**, *179*, 449.

(28) Kohanoff, J.; Andreoni, W.; Parrinello, M. *Chem. Phys. Lett.* **1992**, *198*, 472.

(29) Ohanian, H. C *Modern Physics*; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1987; p 329.