PHYSICAL REVIEW B VOLUME 60, NUMBER 19 15 NOVEMBER 1999-I

Structure and stability of solid C_{36}

Madhu Menon* and Ernst Richter
Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506-0055
and Center for Computational Sciences, University of Kentucky, Lexington, Kentucky 40506-0045

(Received 11 May 1999)

Structure and stability of synthesized C_{36} solid [C. Piskoti, J. Yarger, and A. Zettl, Nature (London) **393**, 771 (1998)] is investigated using a generalized tight-binding molecular-dynamics method. Out of the many solid forms considered, the most stable structure consists of a polymeric phase of C_{36} with mixed sp^2 and sp^3 bonding for the atoms. The cross-linking is found to be across the hexagonal faces with strong covalent intermolecular coupling. Furthermore, formation of this polymer is found to be an exothermic process. The structural properties are consistent with experiment. [S0163-1829(99)06143-3]

The discovery of caged forms of carbon clusters[1,2] has sparked a tremendous interest in pure carbon clusters. The experimentally abundant yields of C_{60} cages with perfect icosahedral (I_h) symmetry have confirmed its remarkable stability beyond any reasonable doubt. Also, studies of fullerene based carbon solids have revealed that C_{60} molecules form a face-centered-cubic (fcc) crystal lattice at room temperature with weak van der Waals–type bonding between the molecules.[3] Furthermore, Raman scattering investigations of visible or ultraviolet irradiated solid C_{60} film has revealed yet another solid form in which photopolymerized fullerene molecules were observed with covalent intermolecular bonding in contrast to the weak van der Waals–type bonding found in the crystal.[4] Interestingly, the pristine van der Waals bonded solid was recovered by heating the photopolymerized C_{60} film under vacuum suggesting that the polymerization does not involve breaking of the icosahedral cage. This discovery was immediately followed by theoretical investigations of various covalent bonding configurations of the C_{60} dimer to determine the most stable bonding geometry.[5] It was found that the most stable dimer configuration involved the photochemical 2+2 cycloaddition where parallel double bonds on adjacent C_{60} molecules break and reform into a four-membered ring cross-linking the molecules. The most stable dimer bonding configurations for other fullerenes were also investigated.[6]

Subsequently, other theoretical[7–9] and experimental[10–15] works substantiated this finding. Our theoretical calculations also showed the most stable dimer configuration to be slightly less stable than two isolated C_{60} monomers (≈ 0.4 eV) with a barrier for the dimer formation.[5] This was consistent with the experimental finding that polymerization can proceed only when assisted by visible or ultraviolet irradiation.

This raises the important and provocative issue of synthesizing carbon solids from fullerene molecules with less than the perfect icosahedral symmetry of C_{60} (I_h). Indeed, very recently, successful synthesis of the C_{36} solid has been reported using the arc-discharge method.[16] The C_{36} solid films were found to be insoluble in toluene and benzene indicating that the bonding is covalent and not van der Waals–type. Furthermore, electron diffraction patterns suggested an intermolecular separation of 6.68 Å. Also, a large increase in the electrical conductivity was observed on doping the solid with alkali metals. Soon after the synthesis of the C_{36} solid was reported, a number of theoretical calculations on various plausible structures were carried out by some groups.[17–19] All these works predict the C_{36} solid to be covalent. We note, however, that none of these works incorporate symmetry unconstrained optimization for any of the structures proposed for the C_{36} solid. Even when optimizations were carried out, the symmetries were fixed at their respective starting configurations. In view of the relatively small energy differences found between various isomers by these theoretical calculations, we believe an accurate estimation of relative stabilities requires the use of molecular dynamics.

In this paper we report results of theoretical investigations of the structure of the C_{36} solid using a physically motivated approach that takes into consideration available experimental results. A major consideration was the detailed analysis of the energetic ordering of a number of competing structures obtained using molecular-dynamics relaxations with no symmetry constraints to determine the most stable geometry. The geometries studied here include C_{36} molecular dimers, C_{36} polymeric solids, and clathrate structures with fourfold coordination for all carbon atoms.

The theoretical method used in the present work is the generalized tight-binding molecular-dynamics (GTBMD) scheme of Menon and Subbaswamy[20] that allows for full relaxation of covalent systems with no symmetry constraints. The GTBMD has been found reliable in obtaining good agreement with experimental and local density approximation (LDA) results for the structural and vibrational properties of fullerenes and nanotubes.[20] The GTBMD gives a graphite-C_{60} energy difference of -0.41 eV/atom, in very good agreement with the experimental estimate of -0.44 eV/atom.[12] The efficacy of the scheme has been further enhanced by the incorporation of a constant pressure ensemble method into the GTBMD scheme to allow for simultaneous relaxation of lattice and basis degrees of freedom when applied to bulk solids. The constant pressure MD method was first introduced by Andersen[21] and subsequently extended by Parrinello and Rahman.[22] Its usefulness in applications to structural changes in the solid state phases has been amply demonstrated in recent work.[22–24] In all our cal-

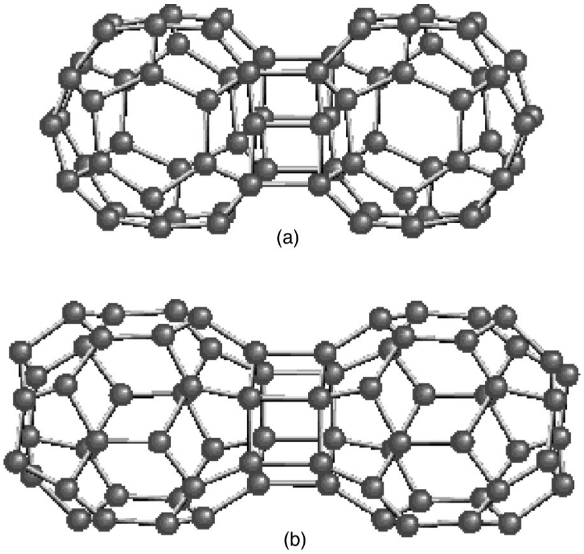

FIG. 1. Two of the most stable dimer configurations for the C_{36} molecule obtained using GTBMD relaxation. The structure (a) is the most stable.

culations for the solid forms using the supercell, an adequate number of k points were used and checked for convergence. As a further check for stability, vibrational frequencies were computed for each of these relaxed structures within the GTBMD scheme.[20] None of the structures proposed here had any imaginary frequencies, indicating them to be true local minima of the total energy.

Although there are many possible isomers of C_{36}, including some with high symmetry (D_{6h}, for example), molecular-dynamics relaxation with no symmetry constraints results in structures with lower symmetries. Since the experimental results for the C_{36} solid point to D_{6h} symmetry, we restrict our theoretical investigations to this isomeric unit. We begin our investigations by a detailed computational analysis of covalent bonding between two C_{36} dimers by considering all possible relative orientations as the initial configuration in our molecular dynamics relaxations. Two of the most stable configurations obtained on MD relaxation (see Fig. 1) consisted of hexagonal faces of the dimers facing each other in ''eclipsed'' geometries. This intermolecular connectivity is in striking contrast to the case of C_{60} dimer where the most stable cross-linking involved a four-membered carbon ring. The intermolecular bond length was determined to be 1.58 Å indicating strong covalent bonding between the molecules. We find the dimer formation to be slightly endothermic (≈ 0.1 eV). Detailed vibrational analysis using the GTBMD scheme[20] for the C_{36} dimer yields intermolecular librational modes of frequencies 113, 126, and 127 cm^{-1}. Although C_{36} dimers were studied previously using LDA total energy methods,[25] a direct comparison with the present work is not possible since the authors of Ref. 25 did not use molecular-dynamics methods to obtain the geometries as done here. It should be noted that molecular-dynamics relaxation results in considerable lowering of symmetry, especially for the C_{36} dimers with mixed sp^2 and sp^3 bonding as seen in Fig. 1.

We next study the polymer formation with C_{36} molecular units. Since the electron diffraction pattern of the C_{36} solid is reported to be hexagonal,[16] we restrict our initial starting configurations to have hexagonal symmetry. Geometry of the most stable C_{36} dimer was used as a guide in the construction of the initial hexagonal polymer configuration with hexagonal faces at the closest approach for each molecular pair. Molecular-dynamics relaxation using the GTBMD method incorporating constant pressure ensemble is then performed to determine the relaxed geometry. Due to the relatively small size of the unit cell a large sampling of k points (a uniform grid consisting of 343 points in the full zone) was considered in the calculation of the forces and further checked for convergence. The relaxed structure is shown in Fig. 2. We label this structure Poly1 for future reference. As can be seen in the figure, the hexagonal symmetry has now been reduced somewhat on relaxation. The structure contains mixed sp^2 and sp^3 bonding for the atoms. The polymeric solid is found to be stable with an energy difference of 0.58 eV/atom with graphite. The intermolecular spacing along the symmetry axis is determined to be 6.85 Å and in the plane of the hexagons to be 6.58 Å. This is in very good agreement with electron diffraction patterns that suggest an intermolecular spacing of 6.68 Å.[16] Another stable hexagonal polymeric form can be obtained by rotating the unit cell by 30 degrees about the symmetry axis relative to Poly1. The relaxation resulted in a stable polymer, but 0.6 eV/atom higher in energy when compared with the former. We label this structure Poly2.

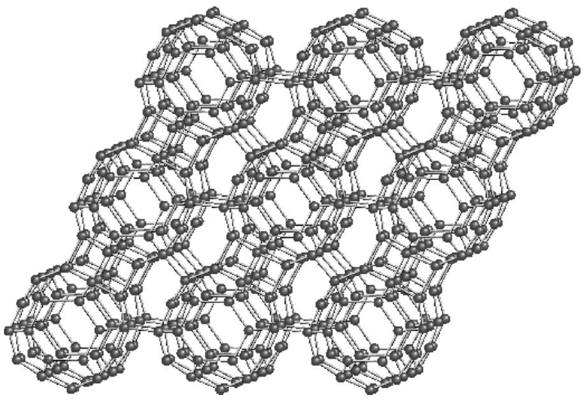

FIG. 2. The most stable polymeric C_{36} solid (Poly1) obtained using the GTBMD relaxation.

By introducing C_2 dimers in the interstitial regions of the C_{36} hexagonal polymer, aligned along the symmetry axis, another new solid form can be obtained. This is called the clathrate form[26] in which all the atoms have fourfold coordination (sp^3 bonding). Clathrates differ from diamond in that their bond angles deviate from the ideal tetrahedral value found in the diamond structure. GTBMD relaxation with the constant pressure ensemble results in the structure shown in Fig. 3. We denote this structure by Clath36A. As can be seen in the figure, the full D_{6h} symmetry has now been restored on relaxation as a result of the sp^3 bonding for all atoms. This solid is, however, 0.33 eV/atom less stable than the solid Poly1. Another isomer of the C_{36} clathrate can be obtained by displacing the interstitial C_2 dimers along the symmetry axis. The relaxed structure (called Clath36B), also of D_{6h} symmetry, is found to be higher in energy when compared with the solid Clath36A. In Table I we list energy values relative to graphite for all these relaxed structures.

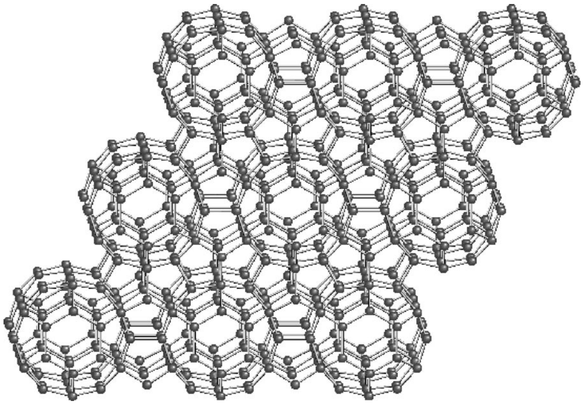

FIG. 3. Relaxed C_{36} clathrate structure (Clath36A) obtained using the GTBMD scheme. All atoms have sp^3 bonding.

TABLE I. Structures, symmetries, and relative energies as calculated from GTBMD. The energies quoted are for fully optimized structures and relative to graphite.

Structure	Energy (eV/atom)
C_{36} molecule	0.662
C_{36} dimer *A*	0.769
C_{36} dimer *B*	0.794
Poly1	0.576
Poly2	1.18
Clath36A	0.81
Clath36B	1.28

In order to make a further comparison with experiment we calculate the theoretical electron diffraction patterns. The space group for Poly1 is (C: $2/m,2/m,2/m$) and for Clath36A is (P: $6/m,2/m,2/m$). If the discrepancy in the experimental resolution is ignored, the experimental result is more compatible with the D_{6h} symmetry. This would suggest that our Clath36A structure is more compatible with experiment than Poly1. Our electron diffraction pattern for Clath36A is, in fact, in excellent agreement with those reported in Ref. 18.

The implications of these findings are intriguing. Because of the smaller radius of curvature, the C_{36} molecule is known to be very reactive; more so than either C_{60} or C_{70}. As a result, when optimum conditions exist for their production, they can be expected to readily coalesce to form solids with strong covalent intermolecular bonding. Our calculations indicate that this intermolecular connectivity is through the alignment of the hexagonal faces in an ''eclipsed'' position. The most stable solid form is found to be polymeric with a combination of sp^2 and sp^3 bonding for the atoms. Comparison of relative energies listed in Table I shows the polymer phase to be more stable than the isolated C_{36} molecule. This explains the relative ease of production of C_{36} solid in arc-discharge methods. This is in striking contrast to the case of C_{60} polymers where this energetic ordering is reversed.[5] It should be recalled that van der Waals bonded solid C_{60} films had to be irradiated with visible or ultraviolet light in order to form the polymerized solid which was found to disintegrate into C_{60} molecules on heating.

In summary, we have proposed a stable polymeric structure for synthesized C_{36} solid. Furthermore, formation of this polymer is found to be an exothermic process. In view of the experimental synthesis of the C_{36} solid, and the theoretical support for the structure in the present work, existence of fullerene solids formed from other caged molecular units seems very plausible.

We are grateful for useful discussions with Professor A. Zettl. This research was supported by NSF Grant No. OSR 94-52895, a Semiconductor Research Corporation (SRC) grant, and by the University of Kentucky Center for Computational Sciences.

---

*Electronic address: super250@pop.uky.edu

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

[2] M.S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1995), and references therein.

[3] P. A. Heiney *et al.*, Phys. Rev. Lett. **66**, 2911 (1991).

[4] A. M. Rao *et al.*, Science **259**, 955 (1993).

[5] M. Menon, K. R. Subbaswamy, and M. Sawtarie, Phys. Rev. B **49**, 13 966 (1994).

[6] M. Menon and K.R. Subbaswamy (to be published).

[7] D. L. Strout *et al.*, Chem. Phys. Lett. **214**, 576 (1993).

[8] Gary Adams *et al.*, Phys. Rev. B **50**, 17 471 (1994).

[9] S. Stafström, M. Boman, and J. Fagerstöm, Europhys. Lett. **30**, 295 (1995).

[10] S. Pekker, A. Janossy, L. Mihaly, O. Chauvet, M. Carrard, and L. Forro, Science **265**, 1077 (1994).

[11] S. R. Flom, R. G. S. Pong, F. J. Bartoli, and Z. H. Kafafi, Mol. Cryst. Liq. Cryst. **256**, 289 (1994).

[12] R. D. Beck, P. Weis, J. Rockenberger, and M. M. Kappes, J. Phys. Chem. **99**, 3990 (1995).

[13] R. Winkler, T. Pichler, and H. Kuzmany, Z. Phys. B **96**, 39 (1994).

[14] K. L. Akers, C. Douketis, T. L. Haslett, and M. Moskovits, J. Phys. Chem. **98**, 10824 (1994).

[15] P. W. Stephens, G. Bortel, G. Faigel, M. Tegze, A. Janossy, S. Pekker, G. Oszlanyi, and L. Forro, Nature (London) **370**, 636 (1994).

[16] C. Piskoti, J. Yarger, and A. Zettl, Nature (London) **393**, 771 (1998).

[17] M. Cote, J. C. Grossman, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. **81**, 697 (1998).

[18] P. G. Colins, J. C. Grossman, M. Cote, M. Ishigami, C. Piskoti, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. **82**, 165 (1999).

[19] P. W. Fowler *et al.*, Chem. Phys. Lett. **300**, 369 (1999).

[20] M. Menon, E. Richter, and K. R. Subbaswamy, J. Chem. Phys. **104**, 5875 (1996).

[21] H. C. Andersen, J. Chem. Phys. **72**, 2384 (1980).

[22] M. Parinello and A. Rahman, Phys. Rev. Lett. **45**, 1196 (1980).

[23] S. Nose, J. Chem. Phys. **81**, 511 (1984).

[24] W. G. Hoover, Phys. Rev. B **31**, 1695 (1985).

[25] J. C. Grossman, M. Cote, S. G. Louie, and M. L. Cohen, Chem. Phys. Lett. **284**, 344 (1998).

[26] M. Menon, E. Richter, and K. R. Subbaswamy, Phys. Rev. B **56**, 12 290 (1997).