Solid $C_{36}$: Crystal structures, formation, and effects of doping

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We employ plane-wave pseudopotential density functional calculations to show that the lowest energy $D_{6h}$ $C_{36}$ crystal is a highly bonded network of hexagonal planes of $C_{36}$ units with $AB$ stacking. This crystal is significantly more dense and lower in energy than previously proposed structures. We demonstrate that Na is the largest alkali atom that can be intercalated into the crystal structure without causing severe structural distortion. Further, we predict the reaction pathway to form a neutral $C_{36}$ dimer to be barrierless, while negatively charged $C_{36}$ molecules are less likely to bond due to a substantial barrier of formation.

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Recent theoretical calculations have shown that $D_{6h}$ $C_{36}$ solids may have enhanced superconducting transition temperatures compared with $C_{60}$ solids due to stronger electron-phonon coupling. The synthesis and purification of abundant quantities of $C_{36}$ by Piskoti, et al. successfully demonstrates that new materials based on smaller fullerenes can form. A number of properties of these solids have been measured and theoretically calculated; however, characterization of solid $C_{36}$ is not yet well understood. Two previously proposed $C_{36}$ crystal structures served as basic examples in the context of work which concentrated on electron-phonon coupling. In order to aid in the experimental characterization and to help guide further investigations—the ultimate goal of obtaining superconductivity—it is crucial to provide a better understanding of the possible structures and formation process of $C_{36}$ crystals.

In this paper, we focus on the nature of $C_{36}$ solid formation through extensive calculations involving six different crystal structures. Our results show that the lowest energy crystal structure has a density of 0.76 $C_{36}$/a.u., contains 24 intermolecular bonds per $C_{36}$ unit, and possesses a gap of 0.5 eV and a binding energy of 7.7 eV/$C_{36}$. Other proposed crystals display a surprising sensitivity in electronic properties, such as density of states, to the specific crystal symmetry imposed. In addition, we study the effects of doping on the lowest energy crystal with several different alkali metals and we show that a structural transition can occur for metal atoms larger than Na. Further, we calculate the reaction pathway to $C_{36}$ dimer formation and predict a barrierless transition which should make the formation of such crystals highly plausible. Our calculations for the same reaction involving $C_{36}^-$ molecules illustrate that the effect of negative charge is to raise the barrier to formation, contrary to the effect of charging $C_{60}$.

Calculations on solids reported in the present study have been carried out using a plane-wave pseudopotential total-energy scheme within the local density approximation (LDA). Details of the methods employed in this work are described in Ref. 1. Structural and electronic properties are carefully and fully converged with respect to $k$-point sampling and energy cutoff. For the reaction calculations, all properties are calculated with DMol version 960 (Ref. 5) using the frozen-core approximation, a fine integration grid mesh, and double numerical plus polarization basis sets.

The originally proposed $C_{36}$ solid was formed by stacking planes of unbonded $C_{36}$ molecules in an $ABC$ stacking sequence. We refer to this fundamental stacking plane as sheet 1 ($S_1$) and to the corresponding solid as $S_1-ABC$. Subsequently, we found that a structure based on the same sheet but with $AB$ stacking was substantially lower in energy and had completely different electronic properties. In particular, our calculations of the density of states (DOS) revealed that...
TABLE I. LDA binding energy (eV/C wrath), density (C wrath/a.u. wrath), gap (eV), and k-point grid for each crystal considered here. S1/S2 correspond to sheets without/with intralayer bonding. For reference, our calculated binding energy of isolated C 36 is 8.14 eV/atom.

<table>
<thead>
<tr>
<th></th>
<th>Binding</th>
<th>Density</th>
<th>Gap</th>
<th>k-point grid</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.00</td>
<td>–</td>
<td>0.50</td>
<td>1X1X1</td>
</tr>
<tr>
<td>S1-AB</td>
<td>6.92</td>
<td>0.49</td>
<td>1.95</td>
<td>5X5X5</td>
</tr>
<tr>
<td>S1-ABC</td>
<td>3.53</td>
<td>0.51</td>
<td>metal</td>
<td>5X5X5</td>
</tr>
<tr>
<td>S2</td>
<td>1.67</td>
<td>–</td>
<td>1.09</td>
<td>6X6X1</td>
</tr>
<tr>
<td>S2-AA</td>
<td>3.98</td>
<td>0.72</td>
<td>0.86</td>
<td>5X5X5</td>
</tr>
<tr>
<td>S2-AB</td>
<td>7.71</td>
<td>0.76</td>
<td>0.61</td>
<td>4X4X4</td>
</tr>
<tr>
<td>S2-ABC</td>
<td>1.84</td>
<td>0.63</td>
<td>0.15</td>
<td>4X4X4</td>
</tr>
</tbody>
</table>

S1-ABC is metallic with a large peak at the Fermi energy (E_F), whereas S1-AB is insulating with a large gap of ~2 eV. Furthermore, S1-AB was found to have a significantly larger binding energy per molecule than S1-ABC.

In Table I we list the binding energy, density, gap, and k-point sampling for each of these crystals. The same information for a single S1 sheet is also given, although these data simply correspond to an isolated C 36 molecule since the C 36 units are essentially noninteracting within an S1 sheet. Note the dramatic differences in electronic and structural properties, despite the fact that the densities are roughly the same. The S1-ABC crystal binding energy of 3.53/C wrath is larger than our previous result of 2.2 eV/C wrath (Ref. 1) due to k-point convergence: in the present study we use 23 k-points in the irreducible part of the Brillouin zone whereas in the previous calculation we used six k points for structural relaxation.

The significant differences in electronic properties between S1-ABC and S1-AB can be reproduced in isolated C 36 hexa molecules, where the H atoms are attached to the same six sites of adjacent intermolecular bonds in the crystals. Upon structural relaxation, we find that D 3d C 36H 6 has a large gap of 2.2 eV and is energetically favored by 3.1 eV over D 3h C 36H 6, which has a much smaller gap of 0.4 eV.

The D 3d symmetry form disrupts all six aromatic rings in the belt of six fused benzenes and the D 3h form disrupts only alternate benzene rings. However, our calculations for various dihydrogenated forms of C 36 show that simple resonance concepts that accurately predict the hydrogenation pattern in small polycyrenes do not explain the results seen for C 36. This could be the case either because the action of resonance stabilization is not valid in such fused ring systems, or because other effects such as ring strain are counteracting the expected resonance pattern. A thorough study of hydrogenation patterns in C 36 and its component fragments, including the determination of overall strain and resonance energies, is relegated to a separate work.7

Recent calculations6 demonstrated that units of D 6h C 36 form stable dimers and trimers with two intermolecular bonds for the dimer and 6 intermolecular bonds for the trimer (i.e., dimer C and the trimer in Fig. 3 of Ref. 3). Further, C 36 molecules may be added in the same manner to form an infinite sheet of bonded units. We refer to this layer as sheet 2 (S2) and note that our calculations give a binding energy for such a sheet of 1.67 eV/C wrath (see Table I). In Fig. 1 a top view of S2 is shown as well as side views of three different relaxed crystal structures formed by stacking S2 layers according to AA, AB, or ABC sequences. All three stacking types lead to energetically bound layers.

For S2-AA, there is bonding between all 6 C atoms of the hexagon rings on top and bottom, as in the case of S1-AB. Such a stacking scheme therefore leads to intermolecular bonds for 24 of the 36 C atoms in each molecule. As shown in Table I, S2-AA has a much higher density than the structures based on S1. Nonetheless, its binding energy is only slightly larger than that of S1-ABC and still 3 eV/C wrath less than the binding of S1-AB.

Stacking S2 sheets in the AB sequence results in a slightly larger density and a substantially larger binding energy than S2-AA. In fact, S2-AB is the lowest energy crystal structure we have studied to date. It has the same number of intermolecular bonds as S2-AA and a d spacing of 6.55 Å. This calculated distance is in much better agreement with the experimentally measured d spacing of 6.68 Å (Ref. 2) than the next lowest energy structure, S1-AB.

The S2-ABC crystal structure contains no interlayer bonding and has a much smaller total binding energy (1.8 eV/C wrath) than the other solids. Since the interlayer bonding is <0.2 eV/molecule, it should be rather easy for sheets stacked in this manner to “slip” over one another into the much more energetically favorable AB stacking scheme. Thus, we believe that the S2-ABC solid is unlikely to remain stable.

In Fig. 2 we show the electronic density of states for the lowest energy (S2-AB) structure. The large, isolated peaks just above and below E_F account for roughly two electrons,
which implies that half filling of a band can be achieved through electron/hole doping with one electron donor/acceptor per C_{36}. Upon closer inspection we observe that in S2-AB there are two cavities per C_{36}/H_2O849 centered above and below each molecule/H_2O850 which have a radius of roughly 1.4 Å. These are the largest empty spaces and would therefore be appropriate for intercalation with alkali-metal atoms. The ionic radii of Na and K are 0.95 and 1.33, respectively, indicating that Na should fit well but that perhaps K is too large. Li is a more complicated electron donor due to its stronger potential, and it is therefore not included in the present work.

In order to test the effects of these dopants, we have carried out calculations of the S2-AB crystal with both Na and K intercalated at the above-mentioned sites (2 metal atoms per C_{36}). Relaxed structures of both Na and K doped crystals are shown in Fig. 3. Note that Na_2C_{36} maintains the original crystal structure and little relaxation occurs upon introducing the intercalant. In contrast, K_2C_{36} is highly strained in the original crystal and therefore undergoes a structural transition. In this case, the top and bottom hexagons of each C_{36} molecule are “opened up” to relieve the strain of accommodating the large K atom, and intermolecular bonds within the planes are broken as the C_{36} molecules push away from one another.

Our results for the density of states of the Na_2C_{36} crystal (Fig. 2) show that the two electrons per C_{36} donated by the Na atoms fill the empty band above E_F of the undoped crystal in a rigid-band manner. There is some broadening of this band, although a small gap of ~0.2 eV remains in the crystal. Further doping of the S2-AB crystal by one or even more alkali atoms should result in a partially filled peak at E_F. While K_2C_{36} forms a very interesting crystal structure, our results suggest that fabrication of C_{36}-based superconductors with K would require the C_{36} molecules to be well separated at the time of intercalation.

Given the potential for C_{36} molecules to bond to one another and the fact that all solids considered here result in intermolecular bonds upon relaxation, we investigate the reaction pathway for the formation of a C_{36} dimer. We choose dimer C of Ref. 3 which can be viewed as a building block for the S2 sheet and is also the lowest energy dimer according to our calculations. The reaction coordinate is along the C_{36}-C_{36} bond axis.

Figure 4 shows the results of our LDA total-energy calculations for varying intermolecular separations. At each point, a full structural optimization is carried out with the constraint of fixed intermolecular bond distance. As the molecules are brought closer together, the onset of an attractive, van der Waals type of interaction appears at around 4.5 Å and possesses a minimum at about 3.0 Å. At roughly a 2.6 Å separation, a small barrier of ~0.1 eV is encountered before the dimer begins to covalently bond (reaching a stable minimum at 1.6 Å). Thus, the LDA calculations imply an effectively barrierless dimerization reaction since the peak of the barrier encountered remains below the initial reactant energies.

Previous ab initio calculations for C_{60} dimer formation did not include structural relaxation at each point on the reaction path and are therefore difficult to compare with the present calculations. In the work of Ref. 9, LDA total-energy calculations carried out on interpolated C_{60} dimer coordinates found a barrier of 2.2 eV. Experimentally, it is well known that undoped C_{60} has to be photoexcited or treated at high pressure to polymerize, whereas alkali doped C_{60} tends to polymerize spontaneously. Our calculations suggest that
spontaneous polymerization for C₆₀ is likely without doping. The strong dimer binding of 2.6 eV for C₆₀ (compared with 0.6 eV for our calculations of the C₆₀ dimer binding) lends further to the idea that C₆₀ naturally prefers to polymerize.

As an additional comparison with C₆₀, we have evaluated total energies in the same manner along the reaction path for C₆₀⁻ molecules (such that the dimer has a charge of −2). These results, shown as squares in Fig. 4, indicate that the presence of charge may substantially inhibit dimer formation. The two negatively charged molecules experience an electrostatic 1/r repulsion as they approach one another, which accounts for the fact that at 8 Å separation the dimer is more than 1 eV unbounded. At the equilibrium distance of 1.6 Å the charged system is energetically bound by roughly 0.4 eV within LDA; however, to reach this minimum the system must pass through an unfavorable barrier which is 0.35 eV above the energy at 8 Å separation and 1.5 eV above the energy of two isolated C₆₀⁻ molecules. Therefore, we propose that it may be necessary and desirable to provide a source of negative ions in order to prevent C₆₀⁻ molecules from bonding to one another. The opposite is true in C₆₀, for which it has been shown both theoretically and experimentally that presence of charge lowers the barrier to dimerization and significantly enhances polymerization,⁹–¹¹.

Note the tendency of LDA to underestimate transition state barriers. We performed generalized gradient approximation (GGA) calculations using the BPW91 functional for several points on the reaction path, and we find that the barrier is indeed higher by about 0.5 eV. However, the reaction barrier of the charged system also shifts higher in energy as do the C₆₀ results. Therefore, even if the reaction is not barrierless as LDA predicts, we believe that the important differences between C₆₀ and C₆₀⁻ and the effects of charge are qualitatively well described by LDA.

In summary, the calculations presented here provide a theoretical characterization of solid C₆₀. We have proposed a lowest energy crystal structure and demonstrated a large sensitivity of electronic properties to particular bonding character. We have also shown that Na is a good candidate for intercalation whereas K can lead to structural distortion. Finally, within LDA we have predicted the neutral dimer reaction to proceed without a barrier and the charged reaction to possess a significant barrier which may inhibit polymerization. We believe that these findings will contribute to the development of C₆₀-based materials.

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8. The appearance of a kink may imply that the reaction induces a change in the molecular state symmetry. LDA cannot represent such a symmetry crossing accurately; however, qualitatively the results would not change.