Anisotropic covalent bonding and photopolymerization of C\textsubscript{70}

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We report theoretical and experimental results demonstrating covalent bonding between C\textsubscript{70} molecules. Experimental results indicating the transformation of C\textsubscript{70} films upon exposure to visible or ultraviolet radiation into a strongly bonded solid phase, similar to the transformation observed in solid C\textsubscript{60} films, are presented. Unlike C\textsubscript{60} molecules, however, the covalent bonding between C\textsubscript{70} molecules is found to be highly directional, strongly favoring certain relative intermolecular orientations. This theoretical finding is consistent with recent laser desorption mass spectroscopy results for visible or UV light irradiated C\textsubscript{70} films which find the cross section for the phototransformation to a new toluene-insoluble solid phase to be considerably smaller than observed for solid C\textsubscript{60}. The combined results suggest that the photochemical 2+2 cycloaddition reaction is responsible for the transformation.

I. INTRODUCTION

The recent discovery of phototransformation of solid C\textsubscript{60} (Ref. 1) into a covalently bonded solid has generated considerable interest. When exposed to visible or ultraviolet light, C\textsubscript{60} molecules arranged in a fcc lattice by a weak van der Waals-type intermolecular bonding appear to undergo a phase transformation resulting in a photopolymerized state.\textsuperscript{1,2} The well-known photochemical 2+2 cycloaddition reaction has been proposed as the mechanism for this transformation.\textsuperscript{1,2} In this reaction, which appears to involve the first excited triplet state in C\textsubscript{60},\textsuperscript{1,2} parallel double bonds on adjacent molecules (or monomers) separated by less than 4.2 Å (Ref. 2) are proposed to break and reform into a four-membered ring cross-linking the molecules. The proposal of a four-membered ring between C\textsubscript{60} molecules is supported indirectly by recent reports that benzene is joined to C\textsubscript{60} in this way, as documented by NMR.\textsuperscript{3,4} The pristine van der Waals bonded solid can be recovered by heating the photopolymerized C\textsubscript{60} film under vacuum to \(\approx 150^\circ\text{C}\),\textsuperscript{5} suggesting that the polymerization does not involve the removal of carbon atoms from the icosahedral cage.

The next natural question is whether larger carbon molecules with less than perfect icosahedral symmetry of C\textsubscript{60} (\(I_h\)) can also cross-link via covalent bond formation. Among the large carbon molecules, C\textsubscript{60} is unique with regard to the high degree of symmetry it possesses: All 60 atoms are in chemically equivalent positions, and there are only two types of bonds (short and long, or double and single). This, combined with the weak van der Waals–type intermolecular interactions between molecules, allows the C\textsubscript{60} molecules to spin freely about randomly oriented axes centered on fcc lattice positions.\textsuperscript{6} Since phototransformation must involve the reactive C=C double bonds, their relative abundance in C\textsubscript{60} (30/90) makes the cross section for this process larger under favorable conditions. C\textsubscript{70}, on the other hand, provides far fewer of these reactive double bonds (10/105) confined to the polar caps of the molecule. Thus, comparison of the phototransformation of C\textsubscript{60} and C\textsubscript{70} films provides important clues to the reaction mechanism.

In this paper we report results of a theoretical investigation of various possible covalent C\textsubscript{70} dimer configurations. The generalized tight-binding molecular dynamics technique (GTBMD) of Menon and Subbaswamy\textsuperscript{7,8} is used to determine the most stable bonding geometry. This method has been previously used successfully to predict the lowest energy configuration for the C\textsubscript{60} dimer,\textsuperscript{11} C\textsubscript{60}O,\textsuperscript{7,9} as well as the structure of small carbon and silicon clusters.\textsuperscript{10,8}

The method is based on van Schilfgaarde and Harrison's\textsuperscript{12,13} generalization of total energy calculations in tight-binding theory by explicitly incorporating the nonorthogonality of the atomic orbitals. The corresponding generalization of the force calculations using the Hellmann–Feynman theorem allows us to perform molec-
ular dynamics for covalent systems with nontetrahedral and multicoordinated structures without invoking any cutoff in the interactions. The electronic tight-binding parameters used here for carbon are given in Ref. 10. The force evaluation involves only two disposable parameters that are fixed by the bond length and vibrational frequency of the carbon dimer.10

It is reasonable to assume that covalent intermolecular bonding between large carbon clusters can proceed most easily via the rearrangement of adjacent reactive, intramolecular double bonds. The perfect icosahedral symmetry \( (I_h) \) in C\(_{60} \) allows for the presence of 30 reactive double bonds in the molecule, distributed isotropically. The lower symmetry of C\(_{70} \) \( (D_{3h}) \), on the other hand, leads to four discrete shorter bond lengths in C\(_{70} \) (Ref. 14) and is expected to exhibit interesting consequences in the bonding mechanism, making it curvature dependent.15

Although relatively few reports of the chemical activity of C\(_{70} \) are available, one can compare C\(_{70} \) to C\(_{60} \) in terms of iridium (Ir) complex chemistry. Balch et al.16 found that the \( [\text{Ir}^{(CO)}]Cl[PPh_3]_2 \) complex prefers to bond at one of the five C=C double bonds in a polar cap of the C\(_{70} \) molecule, rather than to add across the bonds in the hexagons of the equatorial belt, suggesting that the polar caps are “C\(_{60}\)-like” and the belt bonds are sufficiently different, and relatively unreactive.15

For the 2+2 photochemical cycloaddition to occur two topochemical conditions must be met:17 (1) The distance between C=C double bonds on adjacent monomers should be less than 4.2 Å, and (2) these bonds should be aligned nearly parallel to each other. The structural phase diagram for C\(_{70} \) has been recently discussed by Verheijen et al.18 and Vaughan et al.19 Sublimed C\(_{70} \) can grow as either fcc (ABC sequence) or hcp (AB sequence) phases on room temperature substrates,18,19 with the ABC stacked phase as the majority phase. At \( T =300 \) K, in both the ABC and AB stacked phases, the C\(_{70} \) molecules are randomly spinning about their major (long) axis and the major axes of the C\(_{70} \) molecules are aligned parallel to one another.18,19 For \( T =573 \) K, the C\(_{70} \) molecules possess totally random or free rotation.18,19

The interplanar separation in solid C\(_{70} \) is 9.2 Å. The nearest neighbor, intraplanar distance between C\(_{70} \) molecules on a triangular lattice (hcp) is \( \approx10.12 \) Å, almost identical to the nearest neighbor distance in solid C\(_{60} \). In the case of the fcc phase of solid C\(_{70} \), the stacking sequence is ABC\( ABC \) and the nearest neighbor intermolecular alignment is identical to that for the hcp.19

Thus, it can be seen that the hcp and fcc phases both satisfy the topochemical requirements for 2+2 cycloaddition.

II. THEORETICAL RESULTS

It is clear from the above discussion that a detailed understanding of the intermolecular bonding mechanism between fullerene molecules requires that all inequivalent configurations must be considered. With this in mind, we have carried out a detailed theoretical analysis of covalent bonding between C\(_{70} \) monomers considering several important initial relative orientations between monomers. In all our simulations the four initial configurations were chosen in such a way that the C=C bonds on adjacent C\(_{70} \) monomers were well within covalent bonding range of each other (\( \approx2 \) Å). Damped molecular dynamics relaxation was then performed by removing 1% of each velocity during each time step. No symmetry restrictions were imposed while the optimization is being carried out. The process is stopped when the atoms no longer move.

The four different starting configurations considered in our molecular dynamics simulations are (I) equatorial bonds parallel, (II) polar pentagons parallel, (III) one equatorial and one polar pentagonal bond parallel, and finally, (IV) polar double bonds parallel. Configurations (I), (III), and (IV) all satisfy the topochemical requirements17 discussed above for 2+2 cycloaddition. Configuration (I) is found to be the least bound on relaxation, with an intermolecular bond length of 1.90 Å. This can be viewed as due to the absence of electron rich C=C double bonds around the equatorial belt. All the deviations in the bond lengths from a pristine C\(_{70} \) molecule were found to be confined to nearest and next-nearest neighbor carbon atoms surrounding the four atoms participating in the intermolecular bonding. The final geometry for configuration (I) exhibits \( D_{2h} \) symmetry. The symmetries, relative energies, and bond lengths of the cross-linking bonds for this and other stable dimers found in this work are presented in Table I. The final, relaxed configurations of the dimer calculated for these four starting configurations are shown in Fig. 1, and the covalent bonds between C atoms on adjacent molecules are indicated by the dashed lines. The relaxed configuration (II) is found to be more stable (Table I) with an intermolecular bond length of 1.57 Å. Once again, all the deviations from pristine C\(_{70} \) are found to be confined to

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Symmetry</th>
<th>Relative energy (eV)</th>
<th>Length of cross-linking bond (Å)</th>
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<td>( C_1 )</td>
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<td>( C_{2h} )</td>
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Two isolated C\(_{70} \) molecules

-5.3
FIG. 1. Results of the GTBMD calculations for C_{70} monomers arranged in four different starting configurations discussed in the text. In the lowest energy relaxed configuration (IV), the four-membered ring (indicated by the dashed lines) and the intermolecular C-C bond length are both found to be identical to that obtained earlier (Ref. 11) configuration for the C_{60} dimer.

III. EXPERIMENTAL RESULTS

C_{70} films were prepared by vacuum sublimation of chromatographically purified C_{70} powder which had been first degassed at 300 °C for 6 h in 10^{-5} Torr. Details regarding the fullerene extraction from the carbon soot, the chromatographic purification of C_{70}, and the subsequent film deposition have been previously reported. After the film deposition, the film-substrate samples (e.g., C_{70}:KBr) were transferred from the deposition apparatus in a He atmosphere glovebox to a gas-tight cell with a quartz window for irradiation by an Ar ion laser (visible) or a 300 W Hg arc lamp (visible UV).

Laser desorption mass spectroscopy (LDMS) results on C_{70} films (d ≈ 2000 Å) are shown in Fig. 3. In this work, we used a pulsed N_{2} laser (337 nm, 8 ns, 10 mJ per pulse), with parameter values similar to those reported recently.

FIG. 2. Energy levels in the vicinity of the Fermi level for an isolated C_{70} and the lowest energy configuration (IV) for the C_{70} dimers.

FIG. 3. Laser desorption mass spectrum (LDMS) of a C_{70} film (d ≈ 2000 Å) phototransformed with UV-visible radiation from a 300 W Hg arc lamp for 10 days. Inset: LDMS spectrum of a pristine C_{70} film not exposed to light from a 300 W Hg arc lamp.
for the LDMS of photopolymerized C₆₀. The mass spectrum for a C₇₀ film (d ≈ 2000 Å) deposited on stainless steel substrates and irradiated in vacuum using a Hg arc lamp is presented in Fig. 3. The LDMS data exhibit a strong mass peak at m/z = (70 × 12) 840 amu, along with a series of weaker peaks at m/z = N × 840, where N = 2, 3, and 4. The N = 2–4 peaks are identified with the C₇₀ dimers, trimers, etc. The presence of the weak peak at m/z = 720 amu is, of course, associated with the presence of C₆₀ in the sample. It should be noted that in earlier LDMS studies on photopolymerized solid C₆₀ using nearly identical conditions, a series of mass peaks N × 720 amu, for N as high as 21, were observed. In Fig. 3, we show the mass spectrum for a pristine (non-irradiated) C₇₀ film deposited in the same batch as the sample featured in Fig. 3, and taken under identical conditions. This spectrum also shows a series of peaks spaced by 840 amu. However, the intensity of the N > 1 peaks is substantially reduced to those seen in the mass spectrum for irradiated C₇₀ films (Fig. 3). A comparison of mass spectra in Fig. 3 indicates (1) that irradiation of C₇₀ films with the Hg arc lamp has enhanced the number of C₇₀ dimers and trimers observed in the LDMS spectrum, and (2) that the N₂ laser itself can also produce photopolymerization in the mass spectrometer, similar to what was observed in solid C₆₀ films. However, when these results presented here are compared with similar studies on C₆₀, it is clear that the phototransformation of C₇₀ has a much lower cross section than observed for solid C₆₀.

In sharp contrast to our studies on phototransformed C₆₀, we were unable to find any clear signature for the phototransformation of solid C₇₀ in either the Raman spectrum or in the UV-visible electronic absorption spectrum. We did, however, see weak evidence for photoinduced changes in these irradiated films in the IR-active vibrational spectrum. A new, broadband (possibly a vibrational mode continuum), of width ≈ 200 cm⁻¹, is observed at ≈ 1100 cm⁻¹ by Fourier transform infrared (FTIR) spectroscopy. Studies on oxygen-doped C₇₀ (Ref. 23) showed that this broadband at 1100 cm⁻¹ is not due to oxygen chemisorbed in the sample. For pristine C₇₀, we observe 16 narrow IR lines, in good agreement with the 11 lines first reported by Bethune et al., and the additional 5 lines are in good agreement with the work of Chase et al. on very thick C₇₀ films (d ≈ 15 μm). Perhaps the simplest, and most direct, experimental result, indicating the existence of a photopolymerized form of C₇₀ is the observation that photon-irradiated films are no longer soluble in toluene at room temperature. Furthermore, similar to photopolymerized C₆₀, the toluene-insoluble photopolymerized C₇₀ films when heated under vacuum to 250°C for 3 h were then found to be highly soluble on toluene again.

In conclusion, we have performed a detailed molecular dynamics study of the covalent bonding between C₇₀ monomers using a generalized tight-binding molecular dynamics technique. The results show the configuration which involves the cross-linkage across the reactive double bonds near the poles to be the most stable. This suggests that the fourfold linkage in photopolymerized C₇₀ films involves molecules in adjacent crystal planes. A lower experimental yield than observed for C₆₀ film can be understood as due to the smaller number of reactive double bonds per C₇₀ molecule. The analysis of the phototransformation of both C₆₀ and C₇₀ films is consistent with 2+2 cycloaddition mechanism.

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