plastic deformation of a Au surface passivated by a self-assembling monolayer film. The shear-stress value of ~1 GPa agrees remarkably well with the 0.74-GPa figure calculated for the intrinsic Au lattice (12). It has long been recognized that an adhesive interaction between probe and substrate in indenter experiments can have a dramatic effect on the measured contact-deformation results (13). The interaction gives rise to an enhanced production of defects in the high-stress region near the edges of the contact area, which results in plastic deformation under reduced loading. The effect has been dramatically illustrated by recent model calculations (10). Furthermore, it is known that oxide and carbon contamination films of greater than ~5-nm thickness on metal surfaces can cause large changes in indenter behavior (14). However, these films can produce such effects as a result of their own mechanical properties. In contrast, one monolayer of molecules, interacting with one another through van der Waals forces, is not expected to support significant levels of shear stress. Thus, it is the monolayer film's ability to passivate the interfacial adhesion interaction that is primarily responsible for our being able to measure plastic shear-stress thresholds near the theoretical limit.

Passivating films, such as the alkanethiols used here, that are stable under high loads can be important in surface mechanical property studies of materials and show great potential for aiding in understanding the role of the interface in defect production and migration. These attributes are, of course, in addition to the function of passivating films as highly breakdown-resistant, surface-specific lubricants.

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15. The authors wish to thank S. A. Joyce for his many helpful discussions. R.C.T. acknowledges the support of Associated Western Universities through a Department of Energy laboratory graduate fellowship. J.E.H. and T.A.M. acknowledge support by the Office of Basic Energy Sciences Division of Material Sciences, Department of Energy, under contract DE-AC04-76DP00789. R.M.C. acknowledges the support of the Office of Naval Research (Young Investigator Program).

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$C_{60}H_2$: Synthesis of the Simplest C_{60} Hydrocarbon Derivative

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The reaction of C_{60} with BH_3:tetrahydrofuran in toluene followed by hydrolysis yielded $C_{60}H_2$. This product was separated by high-performance liquid chromatography and characterized as the addition product of H_2 to a 6,6-ring fusion (1a1b isomer). The ^1H nuclear magnetic resonance (NMR) spectrum of the product remained a sharp singlet between −80° and +100°C, which suggests a static structure on the NMR time scale. Hydrolysis of the proposed borane addition product with acetic acid–d_1 or D_2O yielded $C_{60}HD$, and its $^3J_{HD}$ coupling constant is consistent with vicinal addition. The observation of a single $C_{60}H_2$ isomer is in complete agreement with earlier calculations that indicated that at most 2 of the 23 possible isomers of C_{60} would be observable at equilibrium at room temperature. These results suggest that organoborane chemistry may be applied to further functionalization of fullerenes.

The synthesis of macroscopic amounts of C_{60} has generated much interest in the physical and chemical properties of this spherical molecule (1). Fully characterized synthetic derivatives of C_{60} have largely been limited to the epoxide, $C_{60}O$ (2), $C_{60}CR_2$ fulleroids (3) and related compounds, osmate esters (4), polybrominated derivatives (5), and organometallic compounds, including several iridium (6) and platinum (7) complexes. The dihydride derivative is somewhat different from many known derivatives because the hydrogen atoms would, in principle, be free to add to any two carbon atoms.

We had previously studied $C_{60}H_2$ computationally to gain insight into which, if any, of the 23 isomers of $C_{60}H_2$ would be preferentially populated at equilibrium at room temperature (8). A nomenclature system (8) was devised for enumerating these isomers (it appears in slightly revised form in Fig. 1), in which C_{60} is composed of eight layers, labeled a, b, c, d, d′, c′, b′, and a′, in a manner that emphasizes the symmetry of this molecule. Each carbon atom in a given layer is then labeled numerically to identify it uniquely. Addition of functional groups, such as H_2 addition to a 6,6 or 6,5 ring fusion is then identified by the carbon label, for example, 1a,1b-$C_{60}H_2$ or 1a,2a-$C_{60}H_2$, respectively. Semiempirical calculations suggested that the 1a1b and 1a2c isomers of $C_{60}H_2$ have the lowest heats of formation, with the 1a2c isomer (1,4 addition across a 6-ring) having a heat of formation 3.8 kcal/mol higher in energy. Similar calculations on the 143 isomers of $C_{70}H_2$ indicate that four isomers, 1c2c, 1a1b, 1a2c, and 1d10d′, have the lowest heats of formation (9).

The synthesis, separation, and characterization of $C_{60}H_2$ appeared reasonable, given these computational results. Methods of reducing C_{60} to yield polyhydride mixtures have been published (10), and several other standard reduction approaches are

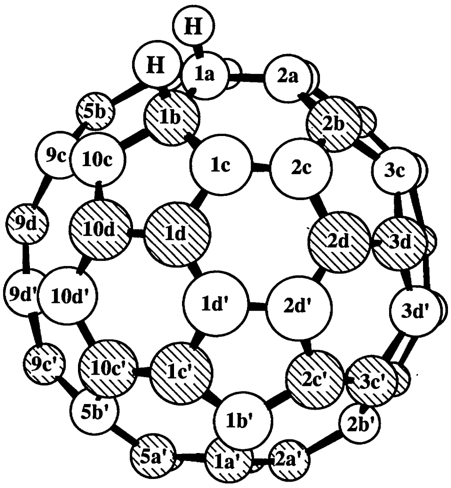

Fig. 1. Structure of the observed 1a1b isomer of $C_{60}H_2$ showing the proposed nomenclature system for addition products of C_{60}. A similar system for C_{70} includes an "e" equatorial layer.

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well established in organic chemistry (*11*). Of these, the reaction with borane followed by hydrolysis might provide access to further functionalization through the intermediate $C_{60}(H)(BH_2)$. Addition of one to two equivalents of BH_3:tetrahydrofuran (1 M) to C_{60} in dry toluene (10- to 100-mg scale, 1 mg/ml concentration) at 5°C for 45 min, followed by slow warming to room temperature and hydrolysis with acetic acid or water, yielded a single isolable and soluble product in 10 to 30% yields that was subsequently shown to be $C_{60}H_2$.

Typical high-performance liquid chromatography (HPLC) traces of C_{60} and $C_{60}H_2$ separated on a "buckyclutcher" column (*12*) are shown in Fig. 2. Unreacted C_{60} and traces of C_{70} were cleanly separated from the $C_{60}H_2$ product. Collection of the tail of the C_{60} peak and reseparation at lower concentration yielded both C_{60} and $C_{60}O$, which was identified by its electronic spectrum (*2*). Similar reseparation of the $C_{60}H_2$ tail yielded $C_{60}H_2$ and a compound tentatively identified as 2a,2b-dihydro-C_{60}-1a,1b-epoxide (*13*).

Negative-ion fast atom bombardment mass spectrometry (FAB MS) confirmed the molecular composition of the isolated product as $C_{60}H_2$. Only $C_{60}H_2^-$, $C_{60}H^-$, and C_{60}^- were observed under these very mild ionization conditions as shown in Fig. 3. Positive-ion FAB MS yielded a similar peak pattern and was used for high-resolution measurements that verified the composition (calculated mass for $C_{60}H_2$: 722.01565; observed, 722.01500). Elemental analyses of $C_{60}H_2$ indicated that the hydrogen content was high, indicating that this product, like C_{60}, retains toluene or hexane or both even after extended vacuum drying.

The presumed intermediate compound is $C_{60}(H)(BH_2)$, which is formulated as the product of vicinal addition of H-BH_2 to a C_{60} double bond (6,6 ring fusion). Resonances for ^1H or ^{11}B nuclei could not be obtained on unhydrolyzed reaction mixtures by NMR spectroscopy, possibly because of the asymmetric environment of the quadrupolar ^{11}B nucleus, which would lead to rapid relaxation of both nuclei.

A sharp singlet resonance (0.5-Hz full width at half maximum) at δ 5.93 ppm in the ^1H NMR spectrum was observed immediately upon hydrolysis of the reaction mixture. This chemical shift is downfield of chemical shifts for both difluorenyl (δ 4.81 ppm) and triphenylmethane (δ 5.57 ppm). The low-field chemical shift is thus consistent with known compounds if the electron-withdrawing effect of the fullerene is taken into account. This resonance remained a sharp singlet in toluene-d_8 between −80° and +100°C, which suggests a static structure on the NMR time scale. Because isomerization was not detected by NMR spectroscopy at high temperatures, the possibility remains that the observed isomer is a kinetic product with a high energy barrier to rearrangement and not a thermodynamic product. When the presumed intermediate borane was hydrolyzed with D_2O, a mixture of $C_{60}H_2$ and $C_{60}HD$ was observed by ^1H NMR spectroscopy (Fig. 4). The magnitudes of the D–H coupling ($^nJ_{DH}$) of 2.4 Hz and the ^{n}DH(D) upfield shift of 1.75 Hz (8.7 ppb) are consistent with vicinal, *cis*, hydrogen substitution (*14*), that is, $n = 3$. These observations are inconsistent with intermolecular exchange of H(D) on the NMR time scale, but intramolecular rearrangements cannot be ruled out (*15*). Only the 1a1b and 1a2a isomers of $C_{60}H_2$ have vicinal hydrogens, and the 1a2a isomer is virtually eliminated on the basis of the computational results. The isolated material was therefore identified as a single product, the 1a1b isomer (*16*).

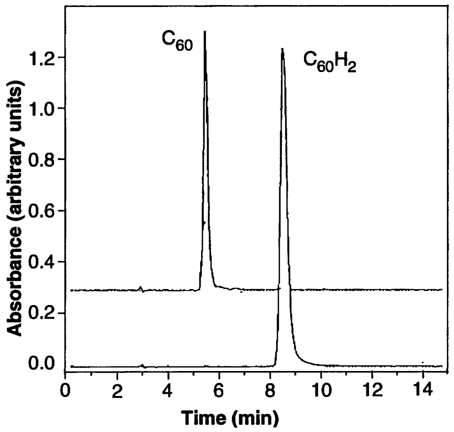

Fig. 2. Results of HPLC of $C_{60}H_2$, 50:50 hexane:toluene eluent, "buckyclutcher" stationary phase.

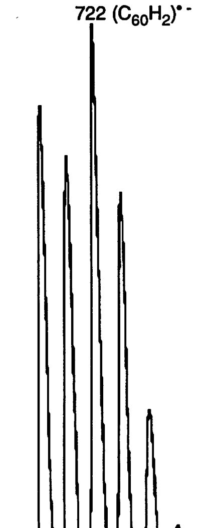

Fig. 3. Negative-ion FAB mass spectrum of $C_{60}H_2$; *m/e*, mass-to-charge ratio; amu, atomic mass unit. The peaks at higher mass are due to the natural abundance of ^{13}C.

The electronic absorption spectra of C_{60} and $C_{60}H_2$ in hexane are shown in Fig. 5. Relative to C_{60}, slight blue shifts in the absorption maxima are observed. These ultraviolet absorptions tail through the visible region and give rise to the yellow to brown color of this material in solution. The infrared absorption spectrum of $C_{60}H_2$ is complex because of the lower symmetry of this derivative but shows sharp structure in the region from 500 to 600 cm^{-1}. A weak C–H stretch is observed at ≈2900 cm^{-1}, and the main $C_{60}H_2$ C–C vibrations are shifted slightly from those in C_{60} (corresponding C_{60} absorbance): 1426 (1429), 1178 (1181), 860.0, 575.5/574.0/566.0 (576), 552.0/550.0/545.5, 531.5, and 526.5/522.5/517.0 (527) cm^{-1}.

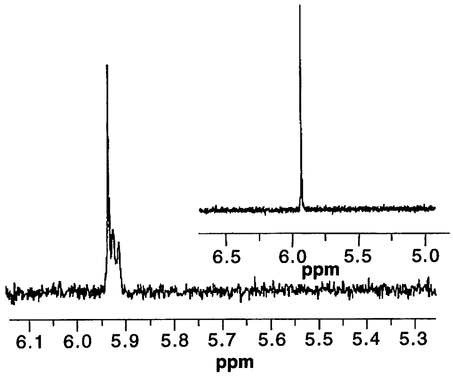

Fig. 4. The ^1H NMR spectrum of a mixture of $C_{60}H_2$ and $C_{60}HD$ showing the ^{3}DH(D) shift (8.7 ppb) and $^3J_{HD}$ coupling (2.4 Hz). (Inset) The $C_{60}H_2$ ^1H NMR spectrum.

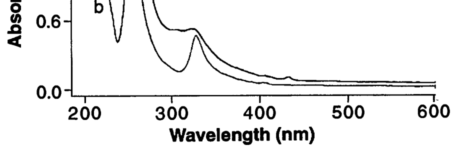

Fig. 5. Electronic absorption spectra of $C_{60}H_2$ (curve a) and C_{60} (curve b) in hexane. The absorption maxima for $C_{60}H_2$ are at 207.5, 254.0, and 324.0 nm; corresponding values for C_{60} are at 208.5, 257.0, and 328.0 nm.

Buckminsterfullerene dihydride, $C_{60}H_2$, has been synthesized, isolated in pure form, and characterized as the 1a1b isomer. As the simplest hydrocarbon derivative of C_{60}, this molecule provides fundamental information regarding the structure of C_{60} derivatives. The results are entirely consistent with the thermodynamic isomer predicted from semiempirical calculations on the 23 possible $C_{60}H_2$ isomers. The presumed borane intermediate, $C_{60}(H)BH_2$, may provide a route to further functionalization of C_{60} and, in a similar fashion, higher fullerenes.

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13. Semiempirical calculations of a few isomers suggested that this isomer has the lowest heat of formation. The 200-MHz ^{1}H NMR spectrum of this compound shows an AB quartet centered at δ 5.35 ppm and $^3J_{HH}$ = 14.2 Hz, consistent with nonequivalent, vicinal hydrogenation. Such a product may result from subsequent air oxidation of $C_{60}H_2$ or from reduction of the small amount of $C_{60}O$ present in the reaction mixture. The nomenclature used here may also be used to denote fulleroid substitution patterns, such as C_{60}-1a,1b-diphenylfulleroid, which results from formal diphenylcarbene addition to a 6,6 ring fusion.
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15. A reviewer pointed out that observation of ^{13}C satellites in the ^{1}H NMR spectrum could be used to rule out a simultaneous intramolecular jump of both hydrogens to another C–C bond. The intensity of such satellites is at the limit of our signal-to-noise ratio because of the low solubility of $C_{60}H_2$. Work with 10% ^{13}C-labeled C_{60} is in progress and should allow us to address this point and to compute carbon hybridizations based on coupling constants.
16. The remote possibility exists that the observed product is the 1a2a (6,5 ring fusion) isomer. This alternate conclusion would represent addition of H_2 across a formal single bond in C_{60}. If it were the thermodynamic product, this would be a failure of both ab initio and semiempirical computational approaches. An x-ray crystal structure may provide conclusive evidence.
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Fabrication and Properties of Free-Standing C_{60} Membranes

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Van der Waals forces that bind C_{60} molecular solids are found to be sufficiently strong to allow the reproducible fabrication of free-standing C_{60} membranes on (100) silicon wafers. Membranes, 2000 to 6000 angstroms thick, were fabricated by a modified silicon micromachining process and were found to be smooth, flat, and mechanically robust. An important aspect of the silicon-compatible fabrication procedure is the demonstration that C_{60} films can be uniformly and nondestructively thinned in a CF_4 plasma. Young's modulus and fracture strength measurements were made on membranes with areas larger than 6 millimeters by 6 millimeters. It may be possible to use C_{60} membranes for physical property measurements and applications.

The description of a simple technique to produce macroscopic amounts of C_{60} molecules (*1*) has stimulated numerous investigations into how these molecules can be assembled into solid forms. Crystals (*1–3*) and films (*1, 4*), for example, have been obtained by the sublimation of pure C_{60} at controlled temperatures. These insulating molecular solids have a spherical, close-packed, face-centered-cubic (fcc) structure with a lattice constant of 14.1 Å (*2*) and van der Waals bonding between the molecules. There is ample space in the crystal structure (26% open volume for close-packed spheres) to accommodate guest atoms that, by donating electrons into the C_{60} molecular bands, can induce conducting (*5*) or superconducting (*6*) behavior. In addition, each molecule has degrees of freedom that allow the molecules to tumble independently at gigahertz rates at room temperature (*7, 8*). These remarkable properties alone provide ample motivation to consider novel ways to form and process C_{60} solids.

In this report, we describe the fabrication and characterization of free-standing C_{60} membranes supported at the edges by (100) oriented Si frames. Membranes have been made with thicknesses in the range 2000 to 6000 Å and areas larger than 6 mm by 6 mm. At first sight, it is remarkable that a van der Waals molecular solid, in which all the molecules are independently rotating at room temperature, should be robust enough to hold together as a free-standing membrane. An estimate of the magnitude of the cohesive forces can be obtained from the heat of sublimation found with the Knudsen technique, 1.65 eV per C_{60} (*9*). The density of molecular bonds for close-packed C_{60} molecules with a nearest-neighbor separation of 10 Å on the (111) plane of the fcc lattice is 1.16×10^{14} cm^{-2}, which, if we ignore near-neighbor correlation effects, at 1.65 eV for each C_{60}–C_{60} bond, gives an energy density of 310 ergs/cm^2. If we assume that this energy falls to zero when the surfaces are separated by, say, a molecular diameter (10 Å), then the specific cohesive force can be calculated as (310 ergs/cm)/1.0×10^{-7} cm = 3.1×10^9 dynes/cm^2. Typical van der Waals specific adhesion forces for chemically inert films are approximately 10^9 dynes/cm^2 (*10*). Thus, in a very approximate comparison, it is not unreasonable to expect that these forces, which are sufficiently strong to give rise to robust adhesion, should likewise be strong enough to give robust cohesion in a free-standing membrane. The observation that C_{60} films on substrates such as glass survive the Scotch Tape adhesion test (*4*) supports this line of reasoning.

In this report, we describe our fabrication procedure, which makes good use of conventional Si processing techniques. An important component of this procedure is the use of a CF_4 plasma to remove a Si_3N_4 etch-stop layer without damaging the C_{60} film. Then we demonstrate that such plasmas can also be used to uniformly thin a C_{60} film without damaging the remaining film. Characterization of the membranes by x-rays and bulge testing provides information about the structure and mechanical properties such as Young's modulus, internal stress, and fracture strength. We conclude with a discussion of how these membranes might be used in investigations of physical properties or in applications such as gas atom or ion filters and masks for x-ray lithography.

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