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Langmuir Films of C_{60} at the Air–Water Interface

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We report the formation of highly incompressible, stable Langmuir films of C_{60} at the air–water interface. The limiting area per molecule calculated from the pressure–area (Π–A) isotherms yields a radius of 5.6 ± 0.7 Å for the fullerene molecule in the film.

The recently developed methodology for the macroscale syntheses of C_{60} and C_{70} has led to a number of studies of their physical and chemical properties, as well as interest in possible applications of these molecules.[1,2] C_{60} molecules have been shown by STM to be spherical and to stack in a close-packed array with a lattice spacing of about 11 Å.[3] This structure is also supported by X-ray powder diffraction data,[1a] although the X-ray crystal structure of osmylated C_{60} shows an average radius of 3.51 Å.[1e] The intercluster spacing has been explained as the sum of the diameter of the fullerene molecule and the outer-fringe distance of the π-electron cloud extending outward from the molecule.[3]

Thin films of C_{60} are also of interest. For example, conductive films of C_{60} and C_{70} can be produced by alkali-metal doping of vapor-deposited fullerene films.[4] Electrochemical studies of thin C_{60} films on Pt microelectrodes have also been reported.[5]

Although C_{60} is insoluble in water, it is not a self-assembling amphiphilic molecule of the type usually used to form layers on a film balance. However, recent studies have shown that rigid films of roughly spherical hydrophobic molecules, e.g., tris(diphenylphenanthroline)ruthenium(II) perchlorate, can be formed at the air–water interface.[6]

To form films of the reported limiting molecular radius, 100 μL of a 0.05–0.1 mM solution of C_{60} in benzene was introduced to about 400 cm² of the air–water interface on a Lauda Model P film balance and the benzene was allowed to evaporate for 10–15 min. A typical Π–A isotherm is shown in Figure 1. The fully compressed C_{60} monolayer films were remarkably rigid and sustained high surface pressures ($\Pi > 65$ mN/m); films could be maintained at 35 mN/m for >2 h without any noticeable area loss. The molecular radius calculated from pressure–area isotherms, 5.6 ± 0.7 Å, is near that found by STM and X-ray powder diffraction. Films produced from larger sample sizes routinely yielded limiting radii of 3.5 Å and produced yellow crystallites on the trough. These observations suggest the formation of bi- or multilayers of C_{60} instead of a single monolayer at the interface. Such multilayers sustained $\Pi > 100$ mN/m for ~8 h without collapsing. The behavior of monolayer and multilayer C_{60} films was reproducible for a number of different samples, over the investigated temperature range, 5–35 °C.

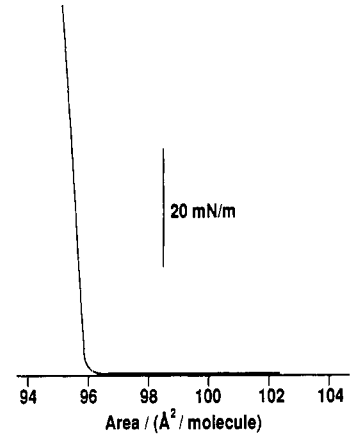

Figure 1. Pressure–area (Π–A) isotherm of C_{60} on water (Milli-Q) at 25 °C.

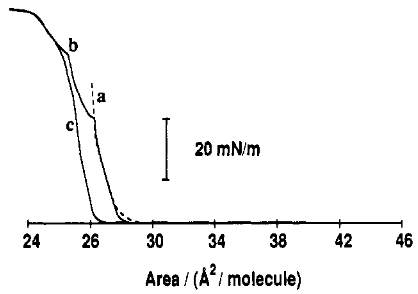

Figure 2. Pressure–area (Π–A) isotherm for (a) pure eicosanoic (arachidic) acid; (b) mixed film of (1:1) C_{60} and eicosanoic acid during the initial compression; and (c) the same film as in part b after ½-h relaxation at <1 mN/m. Subsequent relaxation and recompression cycles followed part c.

Cox et al. have suggested some similarities between the electronic structures and projected molecular areas of C_{60} and triphenylene, based on their chromatographic retention on dinitroanilinopropyl-silica (5-μm diameter, 300-Å pore diameter) columns.[7] We thus examined the polynuclear aromatic molecules anthracene and 2-aminoanthracene at the air–water interface for similar film formation. However, these did not form Langmuir films comparable to those formed by C_{60}; e.g., 2-aminoanthracene films collapsed at 1 mN/m.[6]

The C_{60} molecules also form stable mixed films with eicosanoic (arachidic) acid (AA) at the air–water interface. For films where the ratio $[AA]/[C_{60}]$ was 1 in the spreading solution, the average limiting molecular area was ~28 Å²/(molecule of AA), about the same as that found in a pure AA film (Figure 2). This suggests that there are no C_{60} moieties at the air–water interface at high pressures and that the C_{60} molecules were squeezed into the AA film. Similar observations have previously been made on mixed films containing molecules of very different sizes, e.g., mixed films of stearic acid and tri-*p*-cresyl phosphate, where the smaller molecules determined the limiting area at high pressures.[8] That the C_{60} films are pushed off the air–water interface into the more hydrophobic environment created by the packed hydrocarbon tails of the AA molecules is consistent with the hydrophobicity of the fullerenes. The presence of C_{60} in the hydrophobic regions of the compact AA films affected the strength of the resultant composite films. While pure AA films broke at ~45 mN/m, the mixed films routinely survived $\Pi > 70$ mN/m (Figure 2). The mixed films appear to be solid at $\Pi > 40$ mN/m. In contrast to the pure C_{60} films, which showed no change in their Π–A

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isotherms on relaxing and recompression, the mixed films showed significant changes at $\Pi < 40$ mN/m (Figure 2, b and c).

We were unable to transfer monolayer Langmuir–Blodgett (L–B) films of C_{60} by vertical dipping onto a variety of substrates, e.g., freshly cleaved, highly oriented pyrolytic graphite, polycrystalline Pt or Au, indium tin oxide on glass, or glassy carbon. Attempts to transfer films with larger samples apparently led to aggregation of the C_{60} at the air–water interface, as discussed above. Thus, independent of the substrate, films transferred at ~30 mN/m were not uniform but appeared visibly patchy with yellow clumps interspersed with large domains of clean substrate surface. Contact angle (θ) measurements with water on C_{60} patches showed them to be very hydrophobic (θ ~100°). Exposure of the immobilized C_{60} on any of the substrates to 3:1 H_2SO_4/H_2O_2, followed by copious water and EtOH washes and drying in Ar, did not remove the C_{60}. Contact angles on the C_{60} patches after such treatment were much lower (θ ~25°), suggesting that the C_{60} surface had oxidized and become more hydrophilic. This preliminary experiment suggests that films containing small amounts of C_{60}, characterized by contact angle, spectroscopic, or electrochemical measurements, might be useful in studies of the chemical modification of C_{60}.

The high surface pressures sustained by C_{60} monolayers at the air–water interface suggest large attractive interactions between the C_{60} molecules with the formation of rigid films. Similarly, the electrochemical studies of C_{60} films suggest a high degree of structural organization.[5] Although C_{60} has been proposed as a potential lubricant, the strong intermolecular interactions and film stiffness suggest that this application of unmodified C_{60} is unlikely.

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Photochemistry of Codeinone Derivatives. Development of Potential Photoaffinity Labeling Techniques for Opiate Receptors

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Although the chemistry and pharmacology of morphine and related opium alkaloids has been studied in great detail,[1] very little is known about the photochemistry of this important class of naturally occurring materials.[2,3] Herein, we report photochemistry of codeinone derivatives that involves unique photoreactivity of the benzodihydrofuran ring system.[4] The photorearrangements to be described are carried out by utilization of 366-nm ultraviolet irradiation and appear to offer a conceptually new approach to opiate receptor photoaffinity labeling.[5]

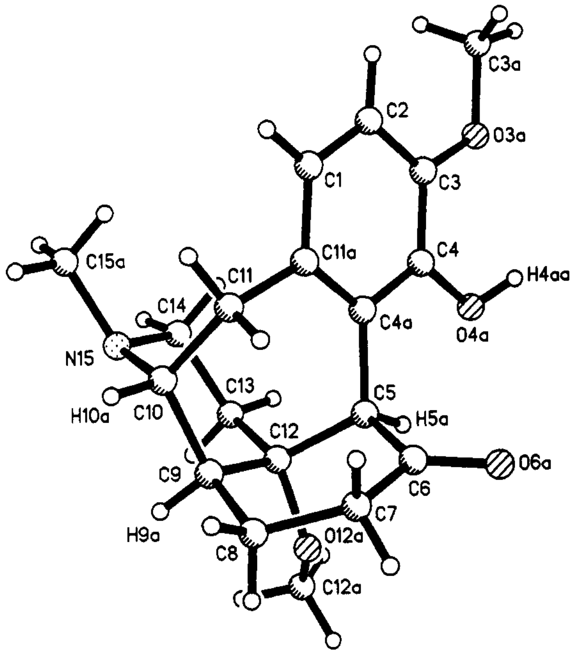
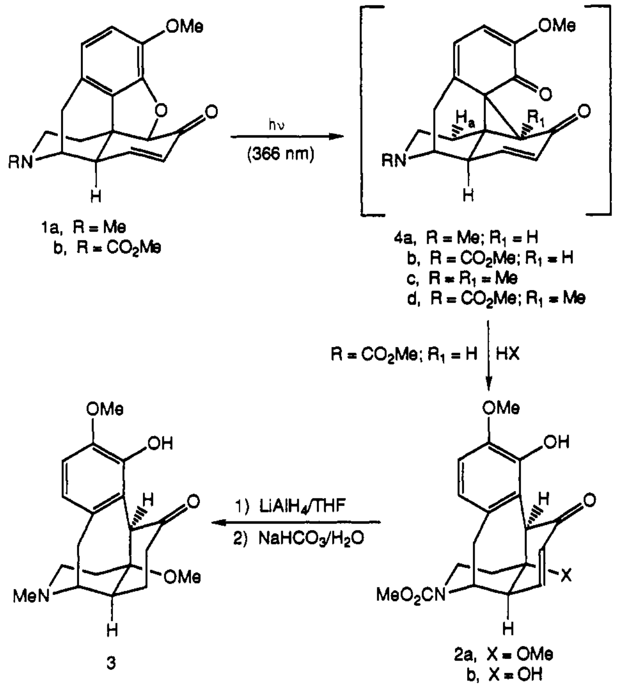


Figure 1. Molecular structure of 3.

Scheme I



Codeinone (**1a**) has been reported to be photostable,[2b,6] and we have found that irradiations at 366 nm in benzene or methanol solutions result in recovery of **1a**. By contrast, irradiation of *N*-carbomethoxynorcodeinone (**1b**) in methanol (0.02 M, 20 h) gave the rearranged methyl ether **2a** in 90% isolated yield (Scheme I).[7] In THF–H_2O solution, **1b** gave the analogous alcohol **2b**

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