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Synthesis of N-Acylated Fulleropyrrolidines: New Materials for the Preparation of Langmuir-Blodgett Films Containing Fullerenes

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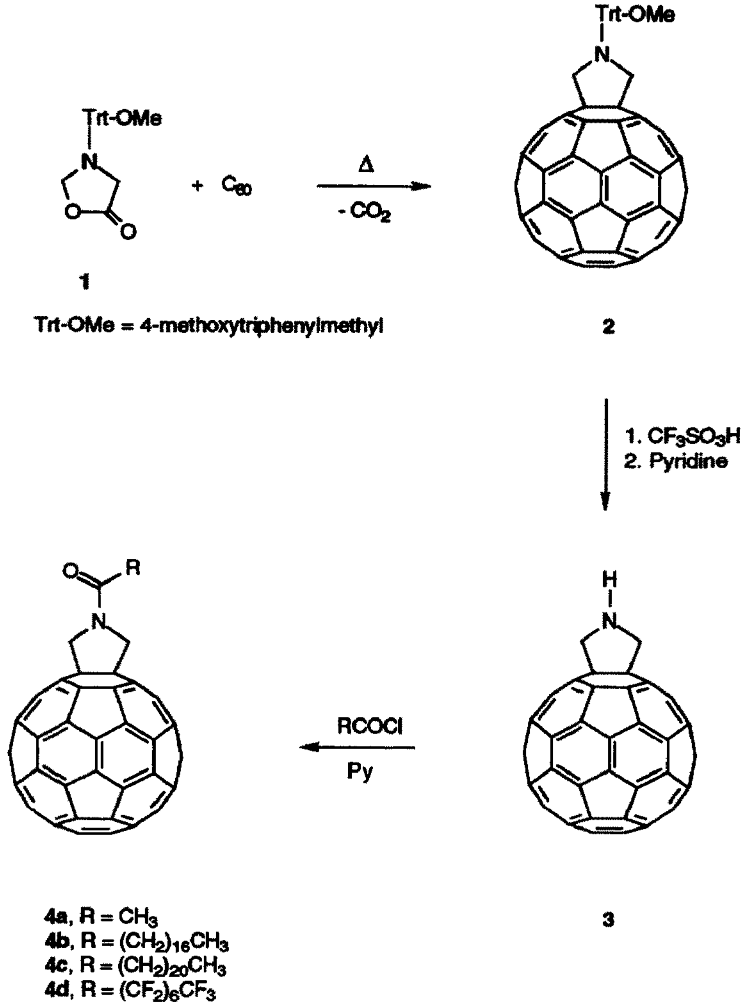
Abstract: The synthesis of a series of new C_{60} derivatives of interest for their potential in the study of LB properties of fullerenes is reported. Besides that of compounds **4b** and **4c**, featuring fatty acid chains, the preparation of the well-characterized, perfluorinated fulleropyrrolidine **4d** is described. A preliminary investigation of LB behavior of the N-acetyl compound **4a** gives very promising results.

The increasingly large availability of C_{60}[1] has offered the possibility of exploring in great detail the outstanding physical and chemical properties of this fullerene.[2] One of the most impressive results of these studies is that thin films of C_{60}, doped with alkali-metals, become superconducting.[3] In this context, the use of Langmuir-Blodgett (LB) technique for the preparation of monomolecular layers is a very attractive way to control the deposition of films containing C_{60}.[4,5] However, C_{60} is not an amphiphilic compound, and in fact the deposition of LB films of C_{60} has proven particularly difficult and not very reproducible.[6] Apparently, better results can be obtained with C_{60} derivatives.[7] Indeed, the organic functionalization of C_{60} has become a very active research field[8] and the *ad hoc* preparation of compounds suitable for LB studies is a very interesting challenge.[9]

We report herein the synthesis of novel fullerene derivatives and one preliminary example of their potential to form LB films. The whole strategy was aimed at obtaining compounds with a polar head and also containing long alkyl chains (hydrogenated and perfluorinated) known to form monomolecular layers.[4]

N-acylated fulleropyrrolidines **4** were prepared according to Scheme 1.[10] The addition of azomethine ylides to C_{60} leading to substituted fulleropyrrolidines has been reported.[11] The original approach to the parent N-H fulleropyrrolidine **3** has been improved here with the employment of the methoxytrityl oxazolidinone **1**. The introduction of an oxygenated species greatly facilitates the separation of **2** from C_{60}, allowing the isolation in 48% yield of pure **2** (89% corrected for C_{60} recovery) in one single chromatographic operation and with a noteworthy reduction of solvent volumes.

After deprotection of **2** by means of trifluoromethanesulfonic acid, which results in the precipitation of the ammonium salt, the N-H pyrrolidine **3** was generated by treatment with excess pyridine and *in situ* functionalized by reaction with the corresponding acylating agents to give **4a-d** (90-95% yield from **2**).[12]



Scheme 1

As expected, compounds **4** exhibit a much higher solubility than C_{60} in all organic solvents. Their UV-vis spectra confirm that they retain the electronic properties of C_{60}. Their ^{13}C-NMR spectra show the decreased degree of symmetry due to the addition: the number of lines is highly dependent on the rate of rotation around the amide bond (17 fullerene peaks when rotation is fast as compared to the NMR time scale, 32 fullerene peaks when rotation is slower: usually the latter case is more common at room temperature). Accordingly, ^{1}H-NMR spectra show two singlets for the CH_2 protons of the pyrrolidine ring.

Compound **4d** represents a new fluorinated derivative of C_{60} with a well-defined structure.[13,14] In the present case, the rigid perfluorinated chain may confer peculiar properties to compound **4d** in LB film formation.

As a preliminary investigation of the behavior of these systems, N-acetyl pyrrolidine derivative **4a** was subjected to LB conditions. Thus, **4a** was dissolved in toluene and 100 μL of the resulting solution ($1.5 \cdot 10^{-4}$ M) was spread onto the subphase surface. The floating film was compressed at a rate of 5 mm/min and the surface pressure vs area per molecule was recorded on a KSV5000-System 3 LB apparatus (Fig. 1). Extrapolation of the isotherm to zero pressure gives a molecular area of 87 $Å^2$, a value close to the cross-sectional area of the C_{60} molecule.

The LB film was deposited from a $5.6 \cdot 10^{-4}$ M spreading solution. Z-type transfer of the floating film onto a hydrophilic quartz substrate occurred with a constant deposition ratio of 0.60 ± 0.05.[15] The UV-visible absorption spectrum of the slide after ten depositions is reported in Fig. 2.

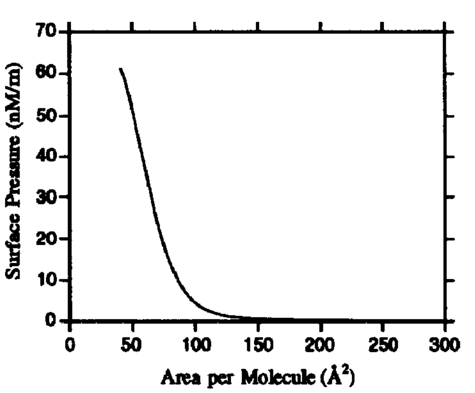


Fig. 1. Pressure vs. Area isotherm for compound **4a** at 20 °C.

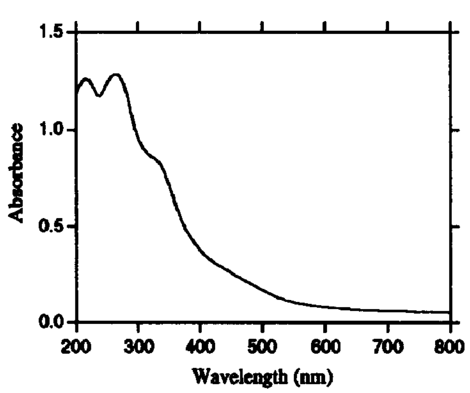


Fig. 2. UV-vis absorption spectrum of the quartz slide of **4a**.

In conclusion, we have synthesized novel derivatives of C_{60} containing an amide functionality. This new moiety should be polar enough to confer amphiphilic properties to these molecules.[4] As a consequence, the LB behavior of these new materials is expected to improve with respect to C_{60}. A partial confirmation of these speculations has been obtained in the LB study of **4a**. Further investigations on derivatives **4b-d**, which, owing to their much larger alkyl groups, may behave differently, will be reported in due course.

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