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CHEMISTRY AND PHYSICS OF FULLEROIDS AND METHANOFULLERENES

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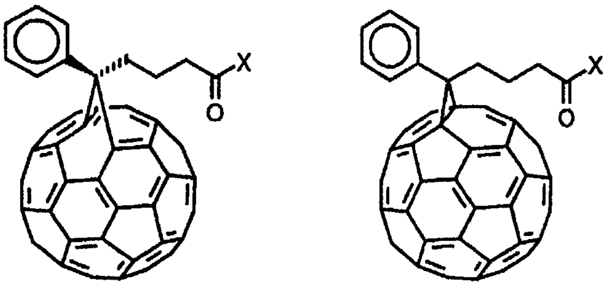
1. Introduction

There exist a large number of reactions for the functionalization of C_{60} [1-13]. Of these, the addition of diazoalkanes is the one we have exploited in our group. The discovery of biological properties [14-18] as well as materials properties [19] of some of these adducts prompted us to devise a general strategy for the preparation of C_{61} derivatives which would have the versatility of being useful for a large variety of studies in both fields. A methanofullerene for a specific function, namely electrospray mass spectroscopy has been described [20].

The approach consists of the preparation of a stable diazo compound which could be generated in situ and which would have a functional group, compatible with C_{60} chemistry, for attachment of a large variety of moieties (“handle”) [21]. After some thought, we settled on both isomers ([5,6] fulleroid **F** and [6,6] methanofullerene **M**) of structure **1**, below. To the best of our knowledge[1], the addition of unsymmetrically substituted diazoalkanes is the only approach which will produce fulleroid. Carbene additions produce only methanofullerenes[1].

Scheme I



F1 [5.6] **M1 [6.6]**

W. Andreoni (ed.), The Chemical Physics of Fullerenes 10 (and 5) Years Later, 257-265.

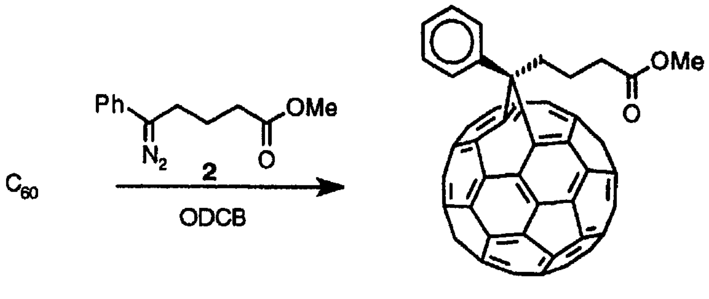
The phenyl ring is just for synthetic convenience; a phenyl ketone is easier to obtain, is more robust, and its hydrazone is more stable than the corresponding alkane aldehyde hydrazone. We settled on the trimethylene tether because we assumed it was long enough to provide solubility and act as a flexible and inert spacer between the ball and the handle (COX in **1**); it was also part of a commercially available compound. The carboxy functional group is among the most versatile and one of the few which is compatible with the electrophilic nature of C_{60}.

Here we describe initial results of *in situ* doping of a methanofullerene derivative and the preparation and some properties of some very electronegative C_{60} derivatives.

2. Results

The Scheme below describes the preparation of **F1-OMe** by a typical diazo addition route [7, 22, 23]:

Scheme II



F1-OMe

Remarkably, addition of **2** to C_{60} gives, of the two possible [5,6] isomers, essentially only the isomer with the phenyl ring over the former pentagon. This is likely due to stereoelectronic effects which remain to be studied in detail [24]. No difference in product isomer distribution was observed when **2** was generated in situ. Conversion of the [5,6] to the [6,6] isomer was accomplished by heating. Unlike previous cases [7, 25], higher temperature and prolonged heating was required in the case of **F1-OMe** (180°, 2 - 7 h). From our experience with diaryl, aryl-alkyl, and dialkyl C_{61} fulleroids, it became clear that the ease of thermal isomerization to the corresponding methanofullerene decreases in that order. A simple kinetic study indicated that the rate of conversion of **F1-OMe** to **M1-OMe** is independent of the substrate concentration; a zero order reaction. A classic interpretation of such a result is that the reaction is dependent on the adsorption onto a surface, as in the case of the decomposition of HI on a gold surface [26]. It is possible that in this case the vessel wall is participating in the reaction. The isomerization reaction is also mediated by acid [27] as well as by photoexcitation [28].

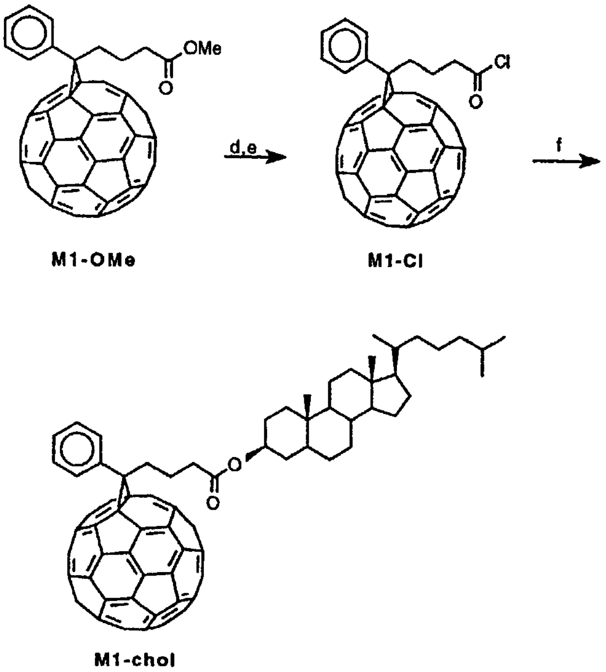
2.1. ELECTROCHEMICAL PROPERTIES OF **F1-OME** AND **M1-OME**

The cyclic voltammograms of both the [5,6] and [6,6] isomers of the methyl ester **1-OMe** are shown in Figure 2. In *o*-dichlorobenzene [29], each isomer exhibits 3 well-defined, single-electron, quasi-reversible waves [30]. The half cell potentials (defined as $E_1 = 0.5[E_{p,c}+E_{p,a}]$) for the reduction of the [5,6] and [6,6] isomers of **1-OMe** relative to Fc/Fc^+, were -1135, -1525, -2000 mV and -1169, -1549, -2050 mV, respectively. Under the same conditions, the E_1 values for C_{60} were -1056, -1451, and -1906 mV.

The first two reduction waves of the [5,6] isomer occur at almost the same potential as in the parent C_{60}. This is not unexpected, since fulleroids and C_{60} are isoelectronic [25]. It is interesting to note that the reduction potentials of the [6,6] isomer are all shifted significantly towards more negative values than in C_{60} itself. This suggests that the removal of only one double bond from C_{60} significantly alters its electron-accepting ability.

In order to test the scope of our strategy, we prepared a few derivatives of **M1**. In order to convert the methyl ester **M1-OMe** to any other derivative, it had to be converted, in a relatively straightforward fashion, to the key intermediate, the acid chloride (**M1-Cl**). This is shown in the scheme below:

Scheme III



d, aq HCl/AcOH/1,2-dichlorobenzene; *e*, $SOCl_2/CS_2$; *f*, cholestanol/pyr/toluene.

The acid **M1-OH** was found to be insoluble in most organic solvents, most likely due to the combination of intermolecular hydrogen bonding and C_{60}-C_{60} interactions. It is only slightly soluble in carbon disulfide, pyridine, and CS_2/formic acid. In contrast to the acid, the acid chloride appeared to be a relatively soluble derivative, especially in aromatic solvents and CS_2. Most important for further transformations is its solubility in pyridine. It can be kept as a powder under an atmosphere of nitrogen for a few days without significant decomposition. The recalcitrant insolubility and attendant low volatility of **M1-OH** and **F1-OH** [27] prevented mass spectral analysis by the usual FAB-MS techniques, frequently used in fullerene research. As in a previous case [16], we had to resort to MALDI-FTMS (matrix-assisted laser desorption/ionization Fourier transform mass spectra) as a method for the molecular mass determination.

It was shown in the past that the methanofullerenes exhibit diagnostic, sharp bands at 430 and 700 nm [25, 31]. We found that all derivatives of **M1** also show a diagnostic set of FTIR bands at 585 (m), 572 (m), 564 (w), 559 (w), 550 (m), and 527 (s) cm^{-1}, which are perhaps more useful for structure assignment. Derivatives of **F1** show a different diagnostic pattern, consisting of 16 peaks between 500 and 600 cm^{-1}. The assignment of the protons of the trimethylene group in all derivatives **1** in the 500 MHz ^1H NMR was facilitated by the observation that, consistently, the α-methylene protons appear as a triplet, while the β-methylene protons appear as a multiplet and the γ-methylene protons appear as a multiplet. The chemical shift values of the γ-methylene protons in the isomeric derivatives of **F1** and in derivatives of **M1** are in agreement with those previously observed for [5,6] and [6,6] 1-methyl-1-p-methoxyphenyl-C_{61} [25]. Although for **F1** and **M1** compounds, respectively 36 and 35 different sp^2-carbon resonances (including those for the phenyl ring) could be expected in ^{13}C NMR, not all are resolved at 125 MHz. Instead, 28 (**F1**) and 24-26 (**M1**) line patterns are observed between 127 and 150 ppm. The assignment of the resonances observed for **M1-chol** was based in part on the values reported for cholestanyl acetate [32, 33]. Typical [5,6]- and [6,6] adduct absorption maxima in UV-vis spectroscopy were found for all compounds **F1** and **M1**, respectively.

The acid chloride **M1-Cl** was converted to a number of carboxy derivatives. Here we describe only one; cholestanyl ester **M1-chol**.

The cholestanyl ester **M1-chol** was prepared from **M1-Cl** and cholestanol in toluene/pyridine. It is one of the most soluble methanofullerenes prepared to date. It forms composites with conjugated polymers such as MEH-PPV and BeCHA-PPV (bis-epicholestanoxy-PPV) [34]. Compound **M1-chol** was found to form very high quality films by spin-casting from ODCB. X-ray powder diffractometry showed that the films were completely amorphous.

With these amorphous films on band, we decided to explore their spectroscopic properties as a function of doping. In figure 1 we show the absorption spectra of C_{60} and **M1-chol**. It is clear that three out of the four features of C_{60} are present in **M1-chol**, except that they are slightly blue-shifted. This is not surprising since **M1-chol** is a methanofullerene and has 58, instead of 60 π electrons. In Fig. 2 we show the changes in spectra as a function of doping and in the inset we show the changes in conductivity. It can be seen clearly that in the case of the methanofullerene there are two maxima, rather than one. The second inset in the Fig. shows the calculated electronic energy levels of the parent methanofullerene [35]; shown in detail in Figure 3. The observation exhibited in the right inset can be interpreted in terms of the left inset as well as figure 3 as follows: the unprecedented double maximum in the conductivity as a function of potassium dopant concentration correspond to 2 and 5 potassiums and the minimum with four potassiums. The fist maximum would give a half-filled band formed from the lowest LUMO (t_{1u}) and the second maximum would be due to half-filled band formed from the next-lowest LUMO (t_{1g}). The minimum of conductivity, then, would be at the filled t_{1u} band state. It should be pointed out that the conductivity of this particular methanofullerene is only about 1/10,000 that of C_{60}, or ca. 10^{-2} Scm^{-1} at the maximum.

3. Conclusions

We have shown, in this presentation, that C_{60} can now be modified at will to produce molecules for investigation of materials and condensed matter properties. We have revealed, for the first time that a room temperature processable, film-forming methanofullerene can be doped with potassium metal vapor. Furthermore, the doping exhibits an unprecedented double maximum in the conductivity as a function of potassium concentration. The maxima are proposed to coincide with 2 and 5 potassiums and the minimum with four potassiums.

4. Experimental Section

4.1. ELECTROCHEMISTRY

All electrochemical measurements were performed using a Bioanalytical Systems 100A electrochemical workstation inside an inert atmosphere dry box. Solutions consisted of approximately 1 mM analyte in *o*-dichlorobenzene with 0.1 M tetrabutylammonium tetrafluoroborate. All experiments were done in the presence of 0.5 mM ferrocene added as an internal reference. The experimental setup consisted of a single-compartment cell with a Pt disc working electrode and a Pt wire counter electrode. A silver wire immersed in a solution of 0.01 M $AgNO_3$ and 0.09 M tetrabutylammonium hexafluorophosphate, which was separated form the remainder of the cell by a ceramic tip, served as the reference electrode. The working electrode was polished using a 0.1 μm

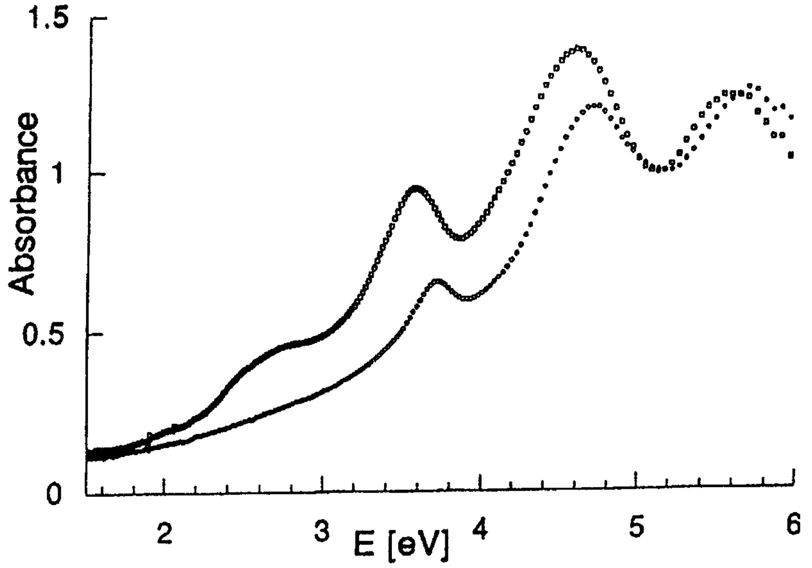


Figure 1. Electronic absorption spectra of thin films of C_{60} (top) and **M1-chol** (bottom).

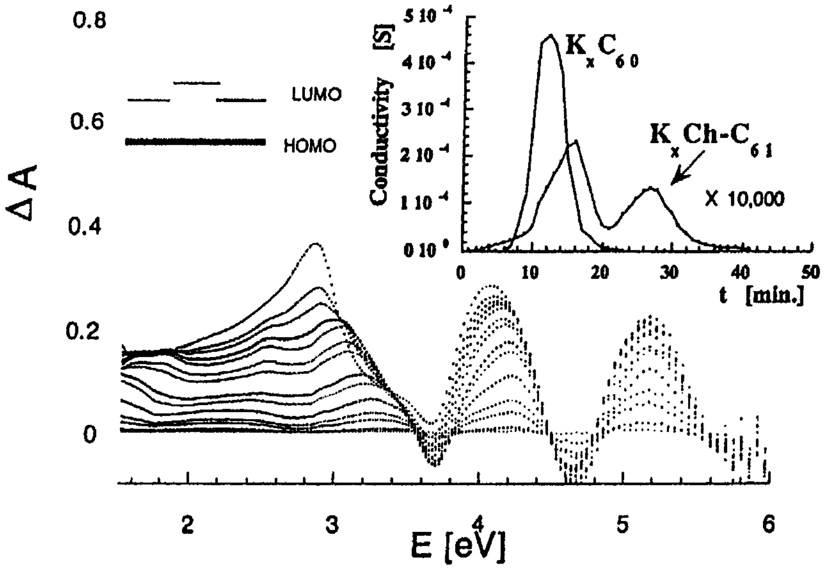


Figure 2. Differential absorption (A_t -A_{t0}; A_t = absorbance at time t, A_{t0} = absorbance at time = 0 = absorbance of pristine material) spectra of a potassium doped **M1-chol** film. Spectra were recorded every three minutes. Left insert, a qualitative description of the energy level diagram of a methanofullerene. Right insert, 2-probe conductivity measurement of simultaneous doping of a thin film of C_{60} and an **M1-chol** thin film.

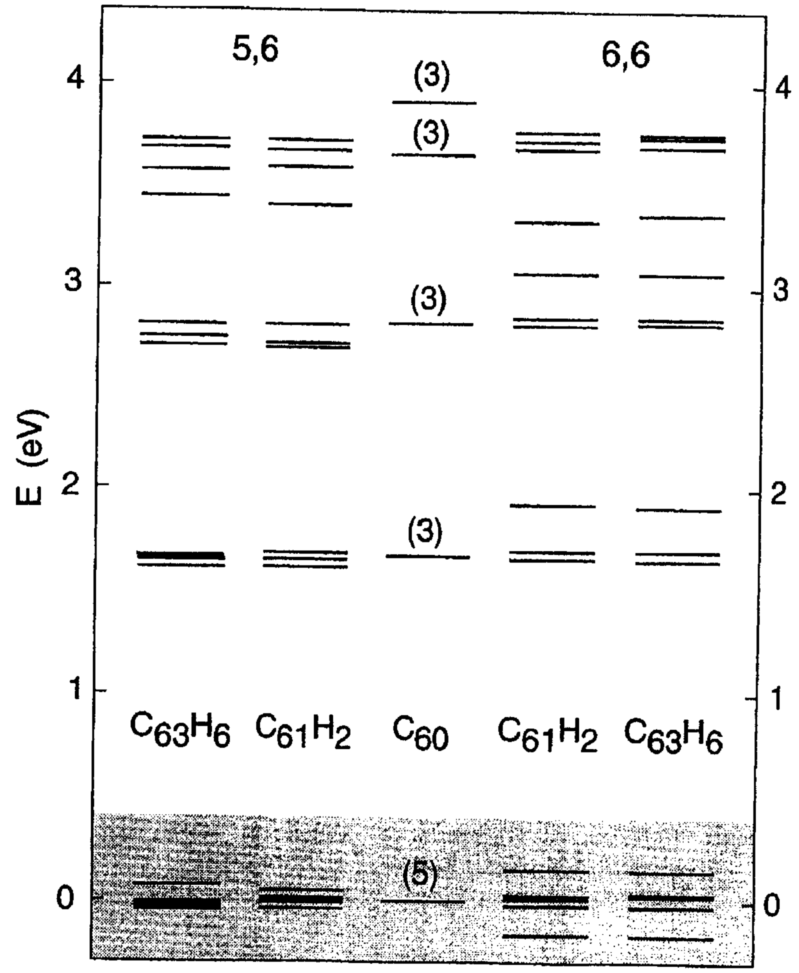


Figure 3. Kohn-Sham energy levels of $C_{61}H_2$ and $C_{63}H_6$ (both isomers). E=0 corresponds to the center of gravity of the C_{60} HOMO (h_u)-derived levels. From Ref. 35.

alumina slurry prior to each experiment. Anhydrous *o*-dichlorobenzene was obtained from Aldrich and used as received. Tetrabutylammonium tetrafluoroborate (Aldrich) was recrystallized three times from water/ethanol and dried *in vacuo* at 70° C. Ferrocene (Aldrich) was sublimed prior to use.

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