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# The Regioselectivity of Fullerenols $C_{60}(OH)_x$ Determined by High-Resolution Solid-State $^{13}C$ and $^1H$ NMR Analysis

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**Abstract:** Fullerenols  $C_{60}(OH)_x$  with different number of OH-groups (3–12 per molecule) were obtained by using a specially developed two-step grafting procedure. The regioselectivity of bound to fullerene molecule hydroxyls was proved by solid-state  $^1H$  and  $^{13}C$  NMR. It has been found that the fullerenols with 2–3 OH groups per  $C_{60}$  contain some amount of non-converted residual t-Bu groups and the solo grafting of one hydroxyl to one bond occurs due to the structure of the intermediate product. Therefore, the fullerenols with a medium number of hydroxyls seem to be the most proper derivatives for further covalent conversions.

**Keywords:** Fullerene; Hydroxylation; NMR spectroscopy; Regioselectivity

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## INTRODUCTION

Fullerene, being a polycarbon molecule, has a potentially wide field of applications in combination with ordinary or specific polymers. The conventional way to make fullerene bind to organic materials is activation, e.g., the introduction of reactive groups into fullerene's structure. In particular, polyhydroxylated fullerene can be applied as a spherical core in the synthesis of star-like polymers<sup>[1]</sup> or can be used as a molecular sorbent in medicine.<sup>[2]</sup> Recently, several attempts have been made to develop the proper methods of efficient synthesis of fullerenols. The hydroxyls were introduced by hydrolysis of fullerene's intermediate obtained by the reaction of fullerenes with sulfuric and nitric acids, oleum, nitrogen dioxide radicals, or hydroboration. The yield of hydroxylation was reported between 12 and 40. However, the high degree of the fullerene modification leads to structural perturbations such as the cage-opening process. Moreover, the principal question is whether the modified molecule has any of the initial fullerene properties. On the other hand, the most perspective fullerene/polymer complexes are supposed to keep the electronic configuration of Buckyball unchanged. Obviously, this condition can be fulfilled only with modest substitution numbers. An additional gain is the knowledge of their distribution or *regioselectivity*. Thus, the fullerenols with less than 12 OH-groups are still desirable.<sup>[3,4]</sup> Another problem concerning fullerene hydroxylation is the formation of side-products. Several Fourier transform-infrared spectroscopy (FT-IR) studies<sup>[5]</sup> on modified fullerenes showed bands at  $1590\text{ cm}^{-1}$  and  $1710\text{ cm}^{-1}$ , which can be attributed to hemiacetal and carbonyl groups, respectively. Xing et al.<sup>[6]</sup> studied the stability of fullerenol molecules by laser-induced dissociation, X-ray photoelectron spectroscopy (XPS), and FT-IR spectroscopy and concluded that these impurities strongly decreased the stability of the modified species. The question is whether an alternative modification method could prevent fullerene's oxygenation or if by using more favorable conditions we could just reduce the concentration of such impurities.

A novel method of fullerene hydroxylation that obtains fullerenols with a minimum concentration of introduced hydroxyls groups was used in this work. The synthesis included two steps. Fullerene with attached tert-butoxy groups<sup>[7]</sup> was synthesized first via free radical reaction of  $\text{C}_{60}$  with the excess of tert-butyl-peroxide under heating or ultraviolet irradiation. This process was carried out in degassed o-dichlorobenzene or toluene. In the second step, the resulting  $\text{C}_{60}(\text{OH})_x$  was obtained after the elimination of tert-butyl groups from  $\text{C}_{60}(\text{O-tert-Bu})_x$  by acid treatment (strong trifluoroacetic acid was used for this purpose). To prove the efficiency of this method, the modification was also carried out according to the known conventional method.<sup>[10]</sup>

The combination of high-resolution nuclear magnetic resonance (NMR) techniques and computer modeling methods was found to be very informative in the investigation of aromaticity changes caused by fullerene modifications.<sup>[8-11]</sup> In the present study, we applied  $^{13}\text{C}$  and  $^1\text{H}$  NMR in solid state to characterize the structure of both intermediates and the resulting products.

## EXPERIMENTAL SECTION

### Synthesis of Fullerenols

The two-step method of synthesis of hydroxylated fullerenes (fullerenols) was proposed. The first step represents the reaction of fullerene with *tert*-butyl peroxide. The reaction takes place in aromatic solvent at UV-irradiation or at elevated temperature. The method is based on the ability of fullerene to add free radicals. It was established that the time of radiation and the temperature determined the degree of fullerene conversion and the number of radicals attached to the fullerene molecule. The second step includes an elimination of *tert*-butyl groups after the treatment of the product with trifluoroacetic acid (TFA). In this reaction, the OH-groups covalently bound to fullerene molecule are formed. In general, the reaction proceeds in a heterogeneous medium because the fullerene with attached *tert*-butyl groups has very poor solubility in organic solvents and is not dissolved in water.

The reaction between fullerene and *tert*-butyl peroxide was performed in a quartz flask under vacuum ( $10^{-3}$  Torr) and UV-irradiation. Degassed *o*-dichlorobenzene was used as a solvent; the fullerene concentration was about 20 mg/mL and 10- to 50-fold excess of *tert*-butyl peroxide was used. The time of radiation treatment varied from 30 to 90 min. The formation of dark brown precipitate was observed. This precipitate was isolated by filtration, washed with methanol, treated with TFA for 10–30 min, and, finally, washed with water.

### NMR Experiments

All  $^{13}\text{C}$  NMR measurements were performed using a Varian Infinity Plus 300 instrument, operating at 7 tesla and equipped with a Chemagnetics-Varian variable temperature 6 mm pencil cross polarization magic-angle spinning (CPMAS) probe. The spectra were recorded employing the  $\{^1\text{H}\}$ - $^{13}\text{C}$  CPMAS NMR experiment. A cross polarization (CP) contact time of 2 ms was employed. The  $^{13}\text{C}$  chemical shifts were referenced to liquid tetramethylsilane (TMS).

$^1\text{H}$  MAS NMR experiments were carried out at 300 MHz with a Chemagnetics-Varian 2.5 mm pencil MAS probe. Single-pulse excitation

was applied; the repetition time of measurements was 1 s and the MAS rate was about 20 kHz. The  $^1\text{H}$  chemical shifts were referenced to external solid TSP (3-(trimethylsilyl) sodium propionate). In some cases, the Hahn-echo NMR technique was used to suppress broad background signals characterized by short  $T_2$  relaxation times. All NMR experiments were performed at the Free University Berlin.

## Calculations

Ab initio calculations were performed with the Gaussian 98 software program using an Indy Silicon Graphics computer at the Freie Universität, Berlin. The chemical shifts were calculated using the B3LYP 6–31  $g^*$ .

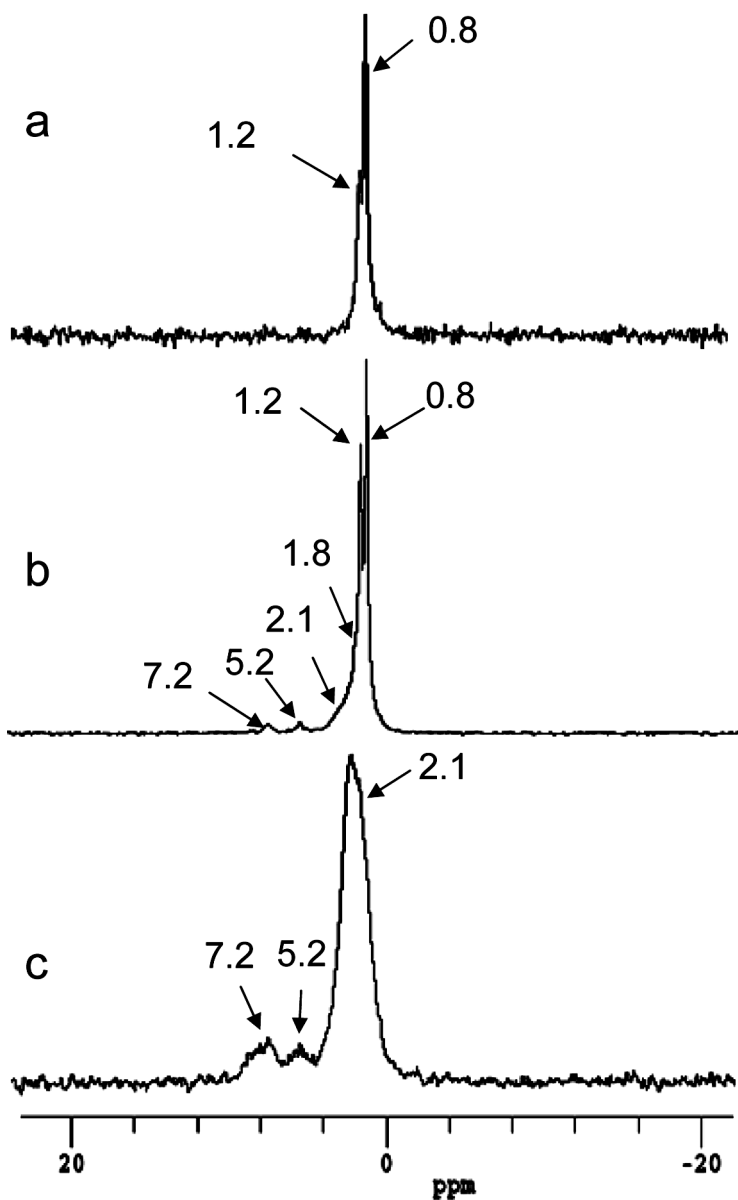
## RESULTS AND DISCUSSION

### Calculated Results

It is known that double bonds of six-membered rings, combined with two five-membered rings, are the most preferable for grafting (activation) in  $\text{C}_{60}$  molecule.<sup>[4]</sup> Therefore, we assume two ways of possible OH-location, namely, one or two hydroxylic groups can be conjugated to the single bond. In the first case, the paired position is occupied by a proton or t-But-group. The calculations of NMR proton chemical shifts showed that it depends on the both the quantity and the location of the hydroxyls. The paired grafting of two hydroxyls is thought to cause a signal at 0.7 ppm. The increase of hydroxyl concentration shifts the signal to the high field at 1.2 ppm. Another case is when a hydroxylic group shares the bond with a proton, and, consequently, two kinds of protons appear in resulting  $^1\text{H}$  NMR spectra. The protons of OH-groups absorb within a 1.8–2.5 ppm range, and the protons next to adjusted carbon should be observed between 4 and 7 ppm, depending on degree of modification.

### $^1\text{H}$ MAS Solid-State NMR Study

The  $^1\text{H}$  MAS NMR spectra of poly hydroxylated fullerenes (Figure 1) contain a few sharp lines between 0.8 and 2.5 ppm and two broad lines at 5.2–7.2 ppm, corresponding to the OH-group protons and aromatic protons, respectively.  $^1\text{H}$  NMR spectra of fullerenes with two to three OH groups per molecule demonstrate two sharp signals at 0.8 and 1.2 ppm (Figure 1(a)). According to the calculations, the signal at 0.8 ppm might be attributed to the paired OH-grafting. The signal at 1.2 ppm cannot be identified so unambiguously. At this range, both



**Figure 1.**  $^1\text{H}$  NMR spectra of  $\text{C}_{60}(\text{OH})_x$ , where  $X =$  (a) 2–3, (b) 5–6, (c)  $>12$  groups per molecule.

paired grafted OH-groups (for the case if their number exceeds five to six) and the residual t-But-groups reveal the absorption. When the yield of modification reaches five to six OH-groups per molecule, the low-field

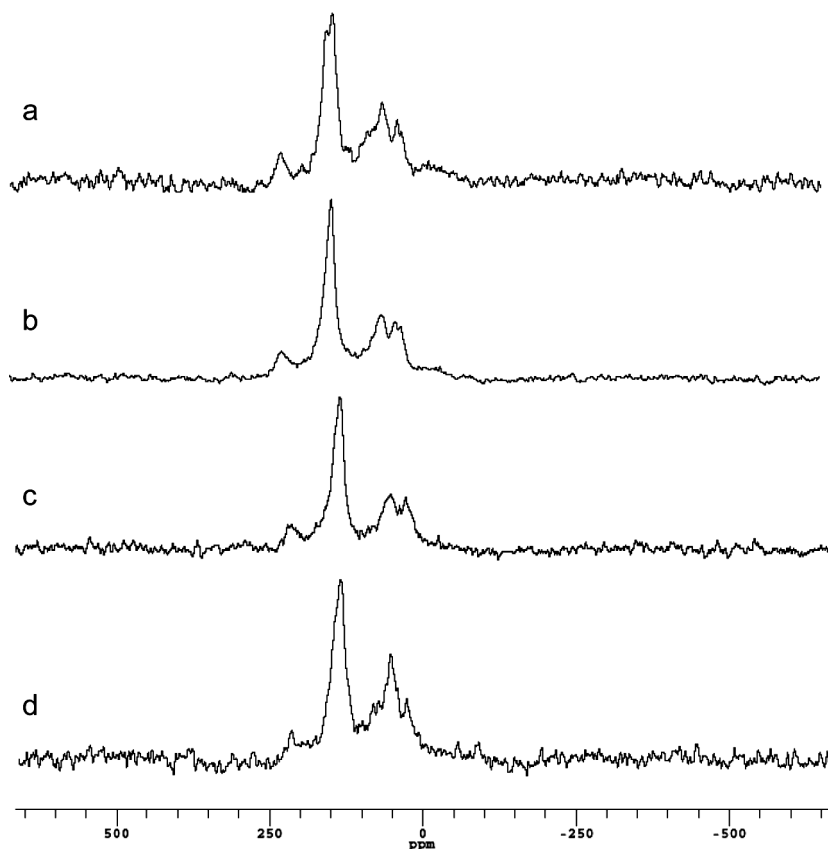
chemical shift is observed (Figure 1(b)). The signals at 0.8 and 1.2 ppm are still present, and 1.8, 2.1, 5.2, and 7.2 ppm signals appear. The signals at 1.8 and 2.1 ppm are seen as shoulders to the 1.2 ppm peak that was observed for the sample with two to three OH groups per molecule. We assigned these signals to single OH-groups attached to one bond due to the calculation results. The protons of single attached OH-groups are supposed to absorb within the 1.8 to 2.5 ppm range and the protons next to the adjoined carbon should be observed between 4 and 7 ppm, depending on the degree of modification. Obviously, the signals at 5.2 and 7.2 ppm relate to the aromatic protons. The  $^1\text{H}$  NMR spectrum of the sample with more than 12 hydroxyls per molecule (Figure 1(c)) is characterized by the same spectral pattern but the relative intensity is changed. The spectrum exhibits the overlapping of several signals between 1.8 and 2.3 ppm and two broad signals at 5.6 and 7.2 ppm. A deconvolution of these overlapped signals showed that the relative intensity of the 1.2 ppm signal decreased with increasing number of the attached hydroxyls. This might prove that this signal cannot be assigned to the paired grafting but should be attributed to methyl protons from residual t-But-groups. The spectrum of the samples with the highest degree of modification (the data are not shown here) exhibited the only broad signal at 1.2 ppm. The most probable explanation is that this signal is related to the pairs of hydroxyls conjugated to one bond.

### $^{13}\text{C}$ CP MAS NMR Predictions

The grafting of OH-groups or a carbon hydrogenation causes a high-field shift due to  $\text{sp}^3$  carbon hybridization. The chemical shifts were calculated in the region of 70 to 80 ppm for the hydroxylated carbons and at about 53 ppm for the adjusted hydrogenated carbons. When the yield of modification is increased the low-field chemical shift is observed. The chemical shift of the unmodified carbons should lie in the range of 135–150 ppm, similar to a not well-resolved broad signal.

### $^{13}\text{C}$ CP MAS NMR Results

$^{13}\text{C}$  CP MAS NMR results (Figure 2) show the high-field shifts of hydroxylated and hydrogenated carbon signals and, as predicted, the significantly broad signal within the 129 to 169 ppm range attributed to the adjoined carbons, which is caused by  $\text{sp}^2$ - $\text{sp}^3$  redistributions in modified fullerenes. Fullerenols with a low degree of modification are characterized by a signal at 30 ppm (Figure 2, spectrum a). This result confirms the presence of residual t-But-groups in the modified product. Due to this

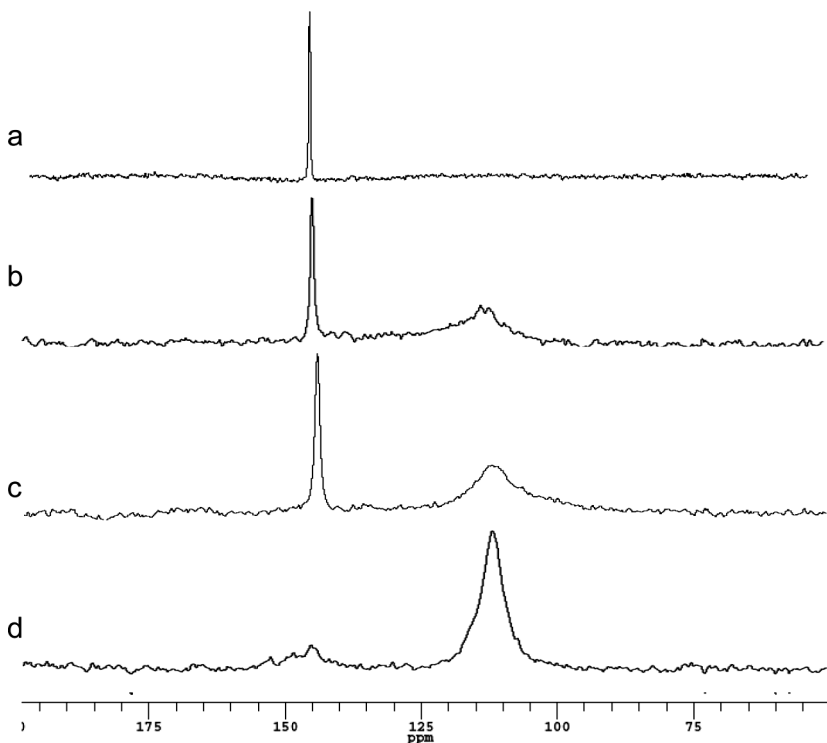


**Figure 2.**  $^{13}\text{C}$  CP MAS spectra of modified fullerenes: (a)  $\text{C}_{60}(\text{O}-t\text{-Bu})_x$ , (b)  $\text{C}_{60}(\text{OH})_{2-3}$ , (c)  $\text{C}_{60}(\text{OH})_{5-6}$ , (d)  $\text{C}_{60}(\text{OH})_{>12}$ .

intensive signal, the  $^{13}\text{C}$  spectra of the samples with a low degree of modification (2–3 hydroxyls per fullerene molecule) cannot be considered as informative with regard to the investigated grafting. When the number of hydroxyls reaches five to six groups per molecule, the signals at 53 and 26 ppm can be distinguished. The further increase of hydroxyls amount causes the low-field chemical shift up to 80 ppm. Similar results have been published elsewhere.<sup>[12]</sup> It was shown that the pair-grafted hydroxyls absorbed at around 80 to 84 ppm, whereas the absorption of single attached OH-group was observed at roughly 75 ppm. Accordingly, the fullerene epoxide form will have a signal in the range of  $\sim 90$  ppm.

We also used an internal reference to prove fullerene's modification. To identify the signal of unmodified fullerene, the  $\pi/2$  pulse sequence was applied. The  $^{13}\text{C}$  NMR spectra presented in Figure 3 demonstrate the





**Figure 3.**  $\pi/2$   $^{13}\text{C}$  MAS spectra of fullerene (a) and fullerenols with different degrees of modification: (b) 2–3, (c) 5–6 (c), and (d) >12 groups/molecule.

gradual increase of the signal broadness of pure fullerene. It was shown that at the degree of modification more than 12 OH-groups per fullerene molecule, the signal at 144 ppm became very broad due to a significant inhomogeneity within the fullerene electron structure.

## CONCLUSIONS

A new method of fullereneol synthesis with a low number of OH-groups has been proposed. The influence of regioselectivity of grafting hydroxyls on fullerene's electron state was proved by solid-state  $^1\text{H}$  and  $^{13}\text{C}$  NMR. It was found that the fullereneols with 2–3 OH-groups per molecule still had non-converted residual t-But groups. However, at hydroxyl concentrations of more than 12 per fullerene molecule, the electron structure was completely changed. Thus, the fullereneols with a medium modification number seem to be the most proper molecules for further organic conversions.

We also succeed in proving that the solo grafting of one hydroxyl to one bond occurs. The reason for this conclusion is the structure of intermediate product. Obviously, the O-t-But-groups are too voluminous for paired grafting, and only one O-tert-But radical can reach C-C bond due to the sterical effect.

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