

RAMAN- AND ^{13}C -NMR-INVESTIGATIONS IN C_{60} - INTERHALOGEN COMPOUNDS

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Introduction

Halogenated fullerenes are known to be important synthetic intermediates, for example in order to prepare water-soluble fullerols of definite stoichiometry. Therefore the preparation and characterization of halogenofullerenes were of particular interest^[Lit.]. The conversion with iodine proved to result in intercalation compounds without any evidence for significant charge transfer^[1]. Bromine, chlorine and iodine have been confirmed to make covalent bonds to C_{60} ^[2]. In C_{60} derivatives with interhalogen compounds like IBr and ICl the possibility of superconductivity was discussed^[3]. Here we report on the results of ^{13}C NMR- and Raman-investigations on C_{60} converted with IBr, ICl and ICl_3 . The object was to collect informations about the structure of the obtained products and about the charge transfer to or from the carbon atoms in C_{60} .

Experimental

All chemicals were of reagent grade and were used without further purification. C_{60} , IBr, ICl and ICl_3 were prepared as reported elsewhere^[4]. For chemical analysis the C_{60} derivatives were disintegrated in boiling 20% NaOH solution containing 2% Na_2SO_3 . The residue, consisting of C_{60} , was rinsed with water and subsequently dried and weighed. In the solution I^- , Br^- and/or Cl^- were determined by potentiometric titration with 0.1M AgNO_3 .

Raman spectra were recorded at room temperature with a Bruker IFS 66 spectrometer attached to a Bruker FRA 106 Raman unit (Nd: YAG-laser, 1064 nm, 0-300 mW, resolution 1cm^{-1}).

^{13}C solid state NMR spectra were recorded using a Bruker Avance DSX 360 spectrometer at 84.6 kG.

Results and Discussion

C_{60} was converted with interhalogen compounds IBr, ICl and ICl_3 . The fullerene material was exposed to the vapour phase of the respective interhalogen compound in

a sealed glass ampoule at 60-70°C for two weeks. After removing excess IBr, ICl or ICl_3 , respectively, by passing over N_2 at room temperature, the reaction products were analyzed. The compositions were found to be $\text{C}_{60}(\text{IBr})_{4.3}$, $\text{C}_{60}(\text{ICl})_{15.9}$ and $\text{C}_{60}\text{I}_{3.2}\text{Cl}_{27.4}$.

All products proved to contain various amounts of unreacted C_{60} and were unstable on air.

In the Raman spectra (Fig. 1) some fundamental vibrations of pure C_{60} , as well as C-Br or C-Cl vibrational bands can be detected.

Furthermore the $\text{C}_{60}(\text{IBr})_{4.3}$ sample reveals some Raman modes (Fig. 2) which are typically attributed to C_{60} dimers^[5].

The ^{13}C solid state NMR spectra were analysed in terms of the chemical shift anisotropy (CSA).

The ^{13}C NMR spectrum of $\text{C}_{60}\text{I}_{3.2}\text{Cl}_{27.4}$ (Fig. 3) shows a main peak at 64.30 ppm, which corresponds to C-Cl bonds. The sample contained only very small amounts of pure C_{60} causing the signal at 140.46 ppm.

In the case of the $\text{C}_{60}(\text{ICl})_{15.9}$ two different sites can be resolved. The signal at 142.22 ppm can be attributed to freely rotating C_{60} molecules. The CSA effect is discussed in terms of the variation of the electron density at two various carbon sites caused by a charge transfer effect.

Also in the NMR spectra of $\text{C}_{60}(\text{IBr})_x$ an anisotropy effect appears. The main peak at 141.62 ppm is almost unshifted relative to the peak of the pure C_{60} . The chemical shift anisotropy in this sample is slightly different in comparison with $\text{C}_{60}(\text{ICl})_{15.9}$, which can be explained by a reduced charge transfer effect.

Conclusions

It was found that by conversion of C_{60} with ICl_3 a complete chlorination of the C_{60} cluster is achieved. I_2 , which is formed by the decomposition of ICl_3 during the reaction, is located in the interlayer gaps.

Upon the reaction with ICl only part of the C_{60} molecules were chlorinated. A strong charge transfer effect could be observed by ^{13}C NMR investigations.

The reaction of C_{60} with IBr leads to the formation of covalent C_{60} -Br-bonds and again intercalation of I_2 ,

coming off the decomposition of IBr. We also found that the conversion of C₆₀ with IBr causes a dimerization of the C₆₀ molecules in part. Additionally a small charge transfer effect can be observed.

References

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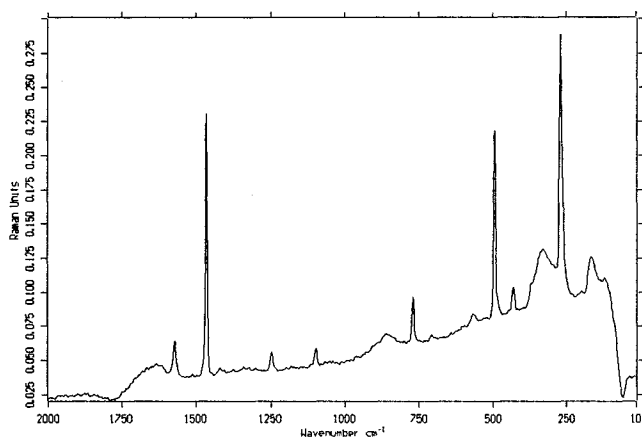


Figure 1. Raman spectrum of C₆₀(ICI)_{15.9}

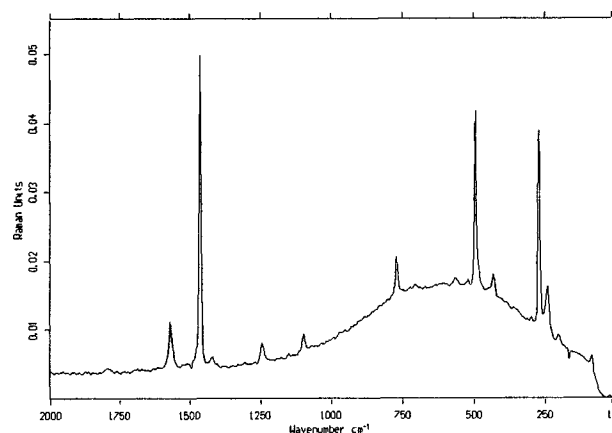


Figure 2. Raman spectrum of C₆₀(IBr)_{4.6}

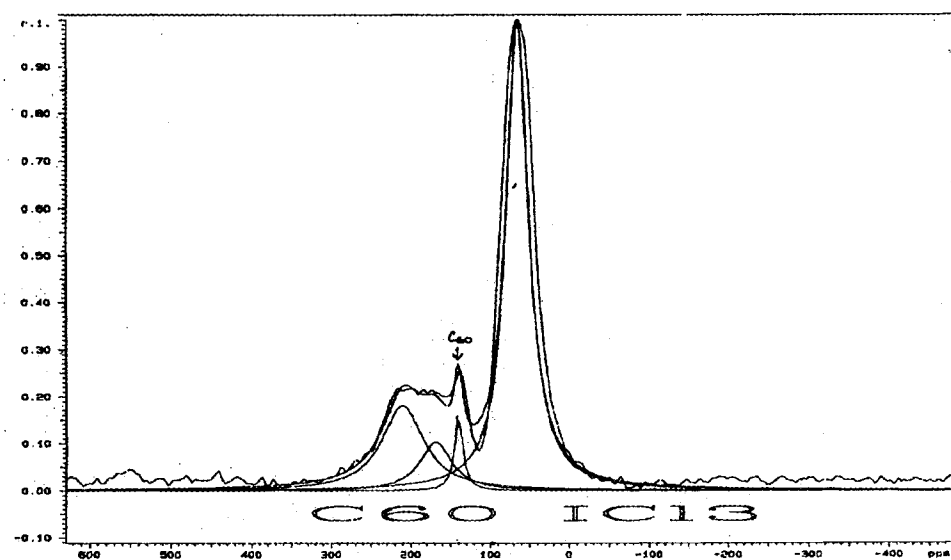


Figure 3. ¹³C NMR solid state spectrum of C₆₀I_{3.2}Cl_{27.4}