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Williams, R.M.; Zwier, J.M.; Verhoeven, J.W.; Nachtegaal, G.H.; Kentgens, A.P.M.

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Interactions of Fullerenes and Calixarenes in the Solid State Studied with $^{13}$C CP-MAS NMR

René M. Williams, Jurriana M. Zwier, and Jan W. Verhoeven

Laboratory of Organic Chemistry
University of Amsterdam
Nieuwe Achtergracht 129
1018 WS Amsterdam, The Netherlands

Gerda H. Nachttegaal and Arno P. M. Kentsgens
SON National HF-NMR Facility, University of Nijmegen
Toernooiveld, 6525 ED Nijmegen, The Netherlands

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Linking fullerene chemistry with the wide field of chemistry of the calixarenes is one of the aims of our current research. Understanding the interactions between fullerenes and calixarenes may lead not only to water-soluble fullerene complexes with a potential biomedical application but also to phase-transfer purification of fullerenes, self-assembly of macroscopic fullerene structures using supramolecular architecture, solar energy conversion materials, and new electronic devices.

Previously we reported the solubilization of C$_{60}$ under conditions which leave C$_{60}$ uncomplexed, by a water-soluble calixarene. Here we report our findings on the interactions of fullerenes with calixarenes, forming a solid-state complex between C$_{60}$ and 4-tert-butylcalix[8]arene, and solid-state NMR of this complex.

Calixarene 1 (Figure 2) and C$_{60}$ (MER Corp.) dissolved in a 1:1 stoichiometry in carbon disulfide yield after an extended period at low temperature a greenish microcrystalline material. IR spectroscopy (KBr) indicates that the intramolecular hydrogen bonding normally present in the calixarene is partly disrupted (indicated by a shift from 3200 to 3400 cm$^{-1}$). Elemental analysis of the metallic green material is consistent with a 1:1 stoichiometry. The material can be dissolved in carbon disulfide or chloroform, in which dissociation occurs and the magenta color of "free" calixarene reappears. Unexpectedly, the material does not dissolve in benzene but forms a greenish suspension.

The size-specific complexation found in the aqueous-phase experiments using a water-soluble analog of 1 reappears in complexation studies using fullerenes dissolved in benzene. Whereas addition of a benzene solution of C$_{60}$ in benzene leads to discoloration of the magenta solution and formation of a green precipitate, addition to a benzene solution of a mixture of C$_{60}$ and C$_{70}$ leads to selective complexation of C$_{60}$ leaving C$_{70}$ in solution.

$^{13}$C solid-state NMR spectra of C$_{60}$, the 4-tert-butylcalix[8]arene (1), and the C$_{60}$-1 complex are shown in Figure 1. The narrow line of C$_{60}$ at 143.7 ppm is in excellent agreement with literature reports. The rather broad aromatic resonances and the signals in the aliphatic region of the free calixarene (its solid-state structure is described as a pleated loop) are in agreement with literature and can be understood on the basis of the distorted solid-state structure of 1 and the large unit cell found in the X-ray data (Z = 4). The spectrum of the green powder consisting of C$_{60}$ and 1 obtained from CS$_{2}$ washed with benzene, however, shows rather narrow lines for the calixarene carbons.

Changes occurring upon C$_{60}$-1 complexation are a slight but significant upfield shift of the resonance of C$_{60}$ of 1.4 ppm (the significance of this shift was checked by $^{13}$C NMR of a mixture of C$_{60}$ and the C$_{60}$-1 complex). Upon complexation, the calixarene signals, the appearance of a total of five signals (and an additional shoulder) in the 30-35 ppm region, and splitting of the signals of the aromatic calixarene carbons into four and three lines (146- and 128-ppm region, respectively), clearly indicating complex formation accompanied by a conformational change of the calixarene. Isotropic rotation of the C$_{60}$ molecules is still present in the complex, as a static spectrum shows an only slightly broader

Figure 1. $^{13}$C MAS NMR of C$_{60}$ and $^{13}$C CP-MAS NMR of 1 and the C$_{60}$-1 complex (see ref 11 for details). Spinning sidebands are denoted with an asterisk.

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(8) Room temperature solid-state MAS NMR data were obtained on a Bruker AM 500 spectrometer equipped with a magic angle spinning probe; number of scans, 450; rotorspeed, 4000-5000 Hz. The magic angle was checked by addition of a small amount of KBr to each sample (sample size ca. 250 mg) in the zirconium oxide sample holder.


signal for C_{60} in the complex. The $T_1$ relaxation time of complexed C_{60} was determined to be ca. 2 s (using inversion recovery technique), drastically shortened compared to 28 s reported for uncomplexed C_{60}.

Cross polarization (CP) curves of the C_{60} complex are shown in Figure 2. The CP curve obtained for C_{60} indicates rather efficient polarization transfer from 1 to C_{60} (CP time 1.1 ms) and very slow depolarization. The short CP times of the aromatic and aliphatic carbons of 1 are in agreement with literature reports.\(^\text{13}\) The difference in depolarization rates of C_{60} compared to the calixarene carbons indicates that in the latter the carbon spin–lattice relaxation time in the rotating frame ($T_1^{\text{R}}(C)$) dominates (i.e., is shorter than $T_1^{\text{R}}(H)$). Methyl rotation in the tert-butyl groups and spin diffusion possibly slow down proton relaxation rates.\(^\text{14}\)

Conclusions. Complexation of C_{60} with calix[8]arene\(^\text{1}\) can occur in CS\(_2\) and in benzene solution, leading to the formation of a solid-state complex. The experiments indicate a 1:1 stoichiometry for the complex. C_{60} does not form similar complexes with calix[8]arenes, leading to the possibility of transferring C_{60} to the solid phase, separating it from C_{70} remaining in solution.

The solid-state complexation in benzene, leading to precipitation, provides strong evidence for establishment of an interaction between C_{60} and 1. A change of the conformation of the calixarene upon complexation is indicated by the OH shift in the IR and the solid-state CP-MAS NMR data. From the NMR data the following can be concluded. (i) The complexed calixarene does not have a pleated loop conformation. (ii) The signals of C and C_{60} at 147.3 and 144.2 ppm show two small side peaks at 149.1 and 145.4 ppm, indicating the presence of two conformational types of phenolic units in a ratio of 2:6 (based on integrals of the 149.1- and 147.3-ppm signals), in agreement with a two-winged conformation. (iii) Interpretation of the three main aliphatic signals analogously to that given\(^\text{10}\) in the case of the octaacetate of 1 suggests the presence of two types of tert-butyl groups (ratio 2:6) and two types of bridging methylene groups (ratio 1:1, with a 2.6-ppm difference).\(^\text{11}\) These conclusions are in agreement with a two-winged or alternate cone conformation of the calixarene (with the 1 and 5 phenolic units "out" or "down" being most likely).

The shift of the C_{60} resonance of 1.4 ppm and the large effect of complexation on calixarene resonances provide further proof that an interaction between C_{60} and the (aromatic) units of the calixarene is established.

We would like to draw attention to the agreement of our NMR data with the reported data for the 4-tert-butylcalix[4]arene–toluene complex\(^\text{16}\) and to the recently reported\(^\text{17}\) unexpectedly good "induced fit" ($\pi$-accepting) solvent complexation of 1 used as a sensor.

We are currently further investigating this interesting complex with other NMR techniques, studying the interactions of other calixarenes with fullerences, and extending these systems in a supramolecular way.

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Note Added in Proof: After submission of our original manuscript, selective complexation of C_{60} by calixarenes was also reported by J. L. Atwood, G. A. Koutsantonis, and C. L. Raston (Nature 1994, 368, 229–231) and by T. Suzuki, K. Nakasima, and S. Shinkai (Chem. Lett. 1994, 699–702). In the latter paper, a limited amount of $^{13}$C NMR data are presented that agree well with the more extensive data discussed here. We are grateful to Prof. Shinkai for making available his data to us prior to publication.

\(^{11}\) NMR data (in ppm). C_{60} solid state: $\delta$ 143.73. C_{60}–1 complex solid state: $\delta$ 30.48 (w) (CH_{3}); 31.09 (w, sh) (CH_{2}); 31.53 (v) (CH_{2}); 33.59 (m) (CH_{3}); 33.96 (w) (C_{q}); 35.36 (s) (C_{q}); 125.53, 128.16, 129.37 (C_{q}, C_{i}); 142.30 (C_{e}); 144.21 (C_{e}); 145.45 (G); 147.30 (O); 149.13 (Cl). C_{60} solid state: $\delta$ 31.20, 33.54 (CH_{1}, CH_{2}, C_{q}); 125.53, 128.16, 129.37 (22); 144.30 (m). Ca solid state: $\delta$ 31.20, 33.54 (CH_{2}, CH_{3}, C_{q}); 125.50 (m), 128.68 (C_{q}; 144.69 (C_{q}); 144.30 (br (C_{q}); 146.86 (br (C_{q})). 


\(^{14}\) We are grateful to one of the referees for pointing out this effect.

\(^{15}\) Calixarene 1 (purified by crystallization from chloroform before use) is commercially available (Janssen Chimica).
