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Author(s)	R.M. Williams, J.M. Zwier, J.W. Verhoeven, G.H. Nachttegaal, A.P.M. Kentgens
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Interactions of Fullerenes and Calixarenes in the Solid State Studied with ^{13}C CP-MAS NMR

René M. Williams, Jurriaan M. Zwier, and Jan W. Verhoeven*

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

Gerda H. Nachtegaal and Arno P. M. Kentgens

SON National HF-NMR Facility, University of Nijmegen
Toernooiveld, 6525 ED Nijmegen, The Netherlands

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Linking fullerene chemistry¹ with the wide field of chemistry of the calixarenes² is one of the aims of our current research.³ Understanding the interactions between fullerenes and calixarenes may lead not only to water-soluble fullerene complexes⁴ with a potential biomedical application⁵ 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.⁶

Previously we reported the solubilization of C_{60} , under conditions which leave C_{70} uncomplexed, by a water-soluble calix[8]arene.⁴ 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^{2a} 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.⁷ The material can be dissolved in carbon disulfide or chloroform, in which dissociation occurs and the magenta color of "free" C_{60} reappears. Unexpectedly, the material does not dissolve in benzene but forms a greenish suspension.

(1) For reviews, see: (a) *Acc. Chem. Res.* 1992, 25(3). (b) Schwarz, H. *Angew. Chem., Int. Ed. Engl.* 1992, 31(3), 293-298.

(2) (a) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, U.K., 1989. (b) Vicens, J.; Böhrer, V., Ed. *Calixarenes*; Kluwer: Dordrecht, The Netherlands, 1990.

(3) In earlier publications we reported, e.g., about the photophysical properties of fullerenes C_{70} and C_{60} : (a) Verhoeven, J. W.; Scherer, T.; Heymann, D.; *Recl. Trav. Chim. Pays-Bas* 1991, 110, 349-350. (b) Williams, R. M.; Verhoeven, J. W. *Chem. Phys. Lett.* 1992, 194, 446-451. (c) Williams, R. M.; Verhoeven, J. W. *Spectrochimica Acta* 1994, 50A(2), 251-254.

(4) (a) Williams, R. M.; Verhoeven, J. W. *Recl. Trav. Chim. Pays-Bas* 1992, 111, 531-532. (b) Our recent findings are that the obtained yellow aqueous phase consists of aggregates, as indicated by gel permeation chromatography (dead time elution) and light scattering experiments, and that the strong absorption around 450 nm in water is probably due to a resonant intermolecular transition, also found in the thin films^{4c} of C_{60} . The yellow aqueous solution, however, is stable for periods longer than 1 year! Micropore filtration (PVDF Gelman Acrodisc L.C.3 (0.45 μm) and Anotop membrane (0.02 μm) filters) indicates a cluster size between 4500 and 200 Å. The aggregation of a 1:1 complex of C_{60} and a water-soluble calixarene is expected on behalf of the proposed amphiphilic structure^{4a} of the complex, but also water-soluble covalent monoadducts of C_{60} form aggregates^{3b} and are expected to show a strong absorption around 450 nm in water. (c) Skumanich, A. *Chem. Phys. Lett.* 1991, 182(5), 486-490. Ross, R.; Kazaoui, S.; Minami, N. *Proc. 3rd Int. Conf. Adv. Matter. Tokyo*, (IUMRS-ICAM-93) 1993.

(5) (a) Friedman, S. H.; DeCamp, D. L.; Sijbesma, R. P.; Srdanov, G.; Wudl, F.; Kenyon, G. L. *J. Am. Chem. Soc.* 1993, 115, 6506-6509. (b) Tokuyama, H.; Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* 1993, 115, 7918-7919.

(6) Sariciftci, N. S.; Braun, D.; Zhang, C.; Srdanov, V. I.; Heeger, A. J.; Stucky, G.; Wudl, F. *Appl. Phys. Lett.* 1993, 62(6), 585-587.

(7) Anal. Calcd for $\text{C}_{148}\text{H}_{112}\text{O}_8 \cdot 1.5 \text{CS}_2$: C, 84.20; H, 5.29. Found: C, 84.54; H, 5.82.

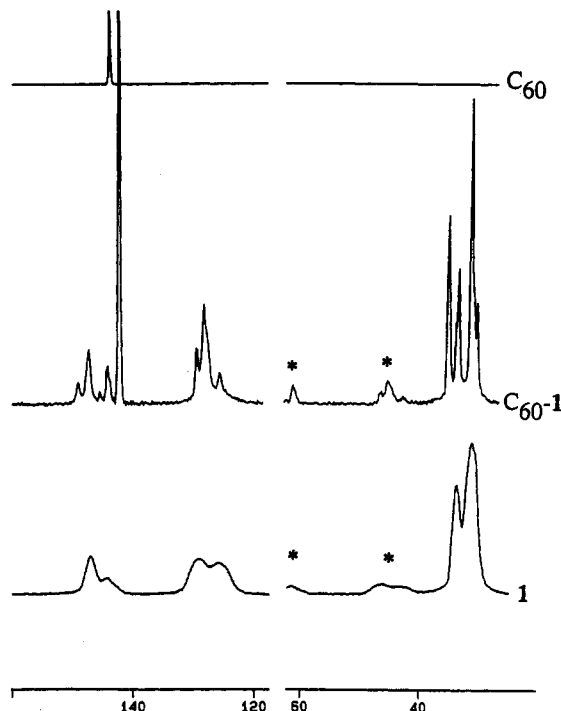


Figure 1. ^{13}C MAS NMR of C_{60} and ^{13}C CP-MAS NMR of 1 and the C_{60} -1 complex (see ref 11 for details). Spinning sidebands are denoted with an asterisk.

The size-specific complexation found in the aqueous-phase experiments⁴ using a water-soluble analog of 1 reappears in complexation studies using fullerenes dissolved in benzene. Whereas addition of a benzene solution of 1 to a 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 spectra⁸ 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.⁹ 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^{2a}) are in agreement with literature¹⁰ 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^{2a} ($Z = 4$). 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 complexation¹¹ are a slight but significant upfield shift of the resonance of C_{60} of 1.4 ppm¹² (the significance of this shift was checked by ^{13}C NMR of a mixture of C_{60} and the C_{60} -1 complex), sharpening of 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} molecules⁹ is still present in the complex, as a static spectrum shows an only slightly broader

(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.

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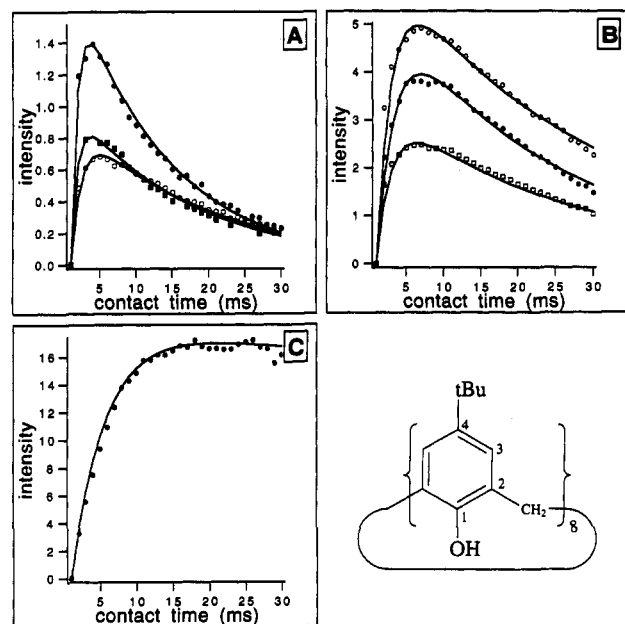


Figure 2. Cross polarization curves (data and fits)¹¹ of the signals (in ppm) at the following positions: (A) 125.50 (■), 128.16 (●), 147.30 (○); (B) 31.53 (○), 33.59 (□), 35.36 (●); (C) 142.30 (C₆₀). A representation of calixarene 1 used in this study¹⁵ is given at the bottom right.

signal for C₆₀ in the complex. The T_1 relaxation time of complexed C₆₀ was determined to be ca. 2 s (using inversion recovery technique), drastically shortened compared to 28 s reported⁹ for uncomplexed C₆₀.

Cross polarization (cp) curves of the C₆₀–1 complex are shown in Figure 2. The cp curve obtained for C₆₀ indicates rather efficient polarization transfer from 1 to C₆₀ (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.¹³ The difference in depolarization rates of C₆₀ compared to the calixarene carbons indicates that in the latter the carbon spin–lattice relaxation time in the rotating frame ($T_{1\rho}(C)$) dominates (i.e., is shorter than $T_{1\rho}(H)$). Methyl rotation in the *tert*-butyl groups and spin diffusion possibly slow down proton relaxation rates.¹⁴

(11) ¹³C NMR data (in ppm). C₆₀ solid state: δ 143.73. C₆₀–1 complex solid state: δ 30.48 (w) (CH₃); 31.09 (w, sh) (CH₂); 31.53 (vs) (CH₃); 33.59 (m) (CH₂); 33.96 (w) (Cq); 35.36 (s) (Cq); 125.53, 128.16, 129.37 (C₂, C₃); 142.30 (C₆₀); 144.21 (C₄); 145.45 (C₄); 147.3 (C₁); 149.13 (C₁). 1 solid state: δ 31.20, 33.54 (CH₃, CH₂, Cq); 125.57 (br) (C₃); 128.97 (br) (C₂); 144.30 (br) (C₄); 146.86 (br) (C₁). 1 in CDCl₃: δ 31.45 (CH₃); 32.31 (CH₂); 33.99 (Cq); 125.50 (C₃); 128.68 (C₂); 144.69 (C₄); 146.39 (C₁). Cross polarization times (T_{ch}) based on peak intensities were calculated by using a fit procedure described in ref 13a. C₆₀–1 complex solid state: δ 31.53 (T_{ch} = 0.45 ms), 33.59 (0.45), 35.36 (0.55), 125.53 (0.21), 128.16 (0.21), 142.30 (1.1), 147.3 (0.33).

(12) (a) One of the referees pointed out that application of the Spiess–Schneider correlation^{12b} to this shift would suggest a ground-state charge-transfer character of 53%. This appears unrealistically high, and therefore it is likely that other factors besides charge density determine the shift in the complex. (b) Olah, G. A.; Mateescu, G. D. *J. Am. Chem. Soc.* 1970, 92, 1430–1432.

(13) (a) Lawrence, B. A.; Grant, D. M.; Pugmire, R. J.; Alger, T. D.; Zilm, K. W. *J. Am. Chem. Soc.* 1983, 105, 2133–2141. (b) Lawrence, B. A.; Grant, D. M.; Pugmire, R. J.; Alger, T. D.; Zilm, K. W. *J. Am. Chem. Soc.* 1983, 105, 2142–2147.

Conclusions. Complexation of C₆₀ with calix[8]arene 1¹⁵ can occur in CS₂ and in benzene solution, leading to the formation of a solid-state complex. The experiments indicate a 1:1 stoichiometry for the complex. C₇₀ does not form similar complexes with calix[8]arenes, leading to the possibility of transferring C₆₀ to the solid phase, separating it from C₇₀ remaining in solution.

The solid-state complexation in benzene, leading to precipitation, provides strong evidence for establishment of an interaction between C₆₀ 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 C₁ and C₄ 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 given¹⁰ 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 difference¹⁰).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 C₆₀ resonance of 1.4 ppm and the large effect of complexation on calixarene resonances provide further proof that an interaction between C₆₀ 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 complex¹⁶ and to the recently reported¹⁷ unexpectedly good “induced fit” (π -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 fullerenes, 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 C₆₀ 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 ¹³C 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.

(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).

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