



## Evidence of a Host:Guest Complex between *p*-t-Butylcalix[4]arene and Carbon Dioxide\*

B.F. GRAHAM, J.M. HARROWFIELD and R.D. TENGROVE\*\*

Special Research Center for Advanced Mineral and Materials Processing, Department of Chemistry, The University of Western Australia, Stirling Hwy, Nedlands, W.A. 6907 Australia

A.F. LAGALANTE\*\*\* and T.J. BRUNO

Physical and Chemical Properties Division, National Institute of Standards and Technology, 325 Broadway MS 838.00, Boulder, CO 80305 U.S.A.

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### Abstract

In this paper we report evidence for an inclusion complex between carbon dioxide and *p*-t-butylcalix[4]arene. The complex was studied with infrared spectroscopy, single-crystal X-ray diffraction, solid-state NMR, and thermogravimetric analysis. Results indicate that 70% of the *p*-t-butylcalix[4]arene cavities could be occupied by a CO<sub>2</sub> molecule following exposure at 30 MPa and 40 °C.

An extensively researched area of calixarene chemistry is the ability of calixarenes to trap molecules and form inclusion complexes [1, 2]. In the solid state, the smaller members of the calixarene family have a cone shape that is stabilized by hydrogen bonding through the phenolic hydroxyl groups on the lower rim. This cone shape gives the smaller calixarenes, especially *p*-t-butylcalix[4]arene, a cavity that is capable of forming inclusion complexes with small molecules, both charged and neutral [3, 4]. The lifetimes of these inclusion complexes vary greatly. Some complexes last for days at high vacuum and high temperature (*p*-t-butylcalix[4]arene:toluene), while others last only a few minutes at ambient conditions (*p*-t-butylcalix[8]arene:chloroform) [5]. The lifetime of these complexes is dependent on both the interaction between the guest and host molecules, and on the surrounding molecules in the crystal lattice. Brouwer *et al.* [5] have synthesized a *p*-t-butylcalix[4]arene:nitrobenzene:xenon complex with xenon occupying approximately 17% of the cavities. This complex was short lived, and it was concluded that the nitrobenzene molecule was necessary to hold the xenon in the cavity. Brouwer *et al.* [6] have also synthesized a *p*-t-butylcalix[4]arene:nitrobenzene:propane complex and find that at elevated pressures (1.21 MPa), the propane is surprisingly absent from the <sup>13</sup>C NMR spectrum.

Herein, we report evidence of a relatively long-lived inclusion complex between *p*-t-butylcalix[4]arene and carbon dioxide (CO<sub>2</sub>). During our solubility measurements of several calixarenes in supercritical CO<sub>2</sub> [7], residual undissolved solid calixarene from the experiment was examined to determine whether the lower phenolic hydroxyls were reacting with the CO<sub>2</sub>. Following a solubility isotherm (that was terminated at 40 °C, 30 MPa), CO<sub>2</sub> exposed *p*-t-butylcalix[4]arene was dissolved in deuterated chloroform, and <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were taken. These spectra were identical to the NMR spectra of unexposed *p*-t-butylcalix[4]arene, indicating that a chemical reaction did not occur. Following a second identical solubility isotherm, KBr disks were prepared containing the residual CO<sub>2</sub> exposed *p*-t-butylcalix[4]arene. Infrared (IR) spectra of the KBr disks containing both the before and after CO<sub>2</sub> exposed *p*-t-butylcalix[4]arene were measured and are shown in Figure 1. The CO<sub>2</sub> exposed *p*-t-butylcalix[4]arene spectrum contained a strong vibrational band at 2333 cm<sup>-1</sup> and a small band at 2320 cm<sup>-1</sup> that were not present in the spectrum of the unexposed *p*-t-butylcalix[4]arene. The band at 2333 cm<sup>-1</sup> gradually diminished over the next two hours, leaving the spectrum identical to that of the unexposed *p*-t-butylcalix[4]arene. The center of these bands (2326 cm<sup>-1</sup>) is red-shifted by 23 cm<sup>-1</sup> from the center of the P and R bands of pure gaseous CO<sub>2</sub>. The two bands in Figure 2 showed no fine rotational structure, as would be expected for a free gas. This behavior is similar to the vibrational spectrum of surface-adsorbed CO<sub>2</sub>, which also is red-shifted by 10–20 cm<sup>-1</sup> and exhibits no fine rotational structure [8]. Keresztury *et al.* [9] have reported that the vibrational spec-

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\*\* Present address: Murdoch University, South Street, Murdoch, Western Australia, 6150.

\*\*\* Present address: Penn State University Worthington Scranton, 120 Ridgeview Drive, Dunmore, PA 18512 U.S.A.

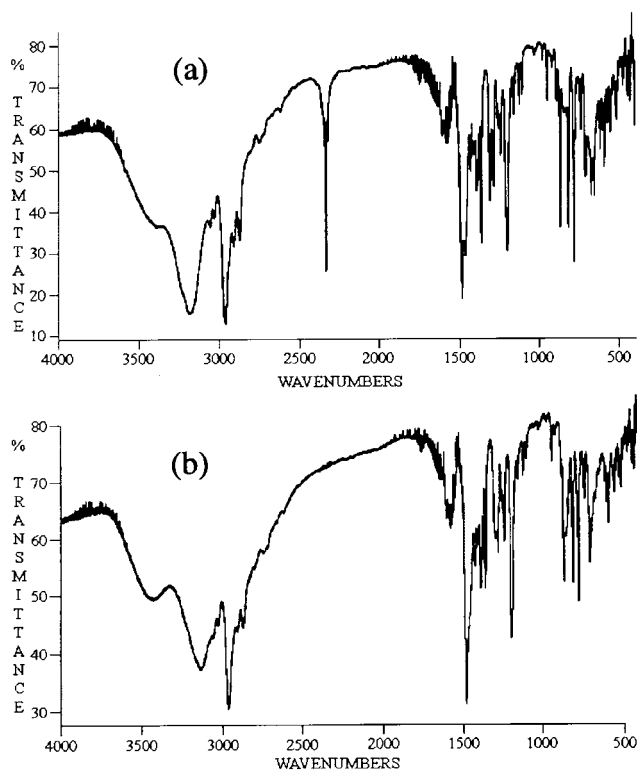


Figure 1. IR spectrum of KBr disk containing *p*-*t*-butylcalix[4]arene (a) after and (b) before exposure to supercritical CO<sub>2</sub>.

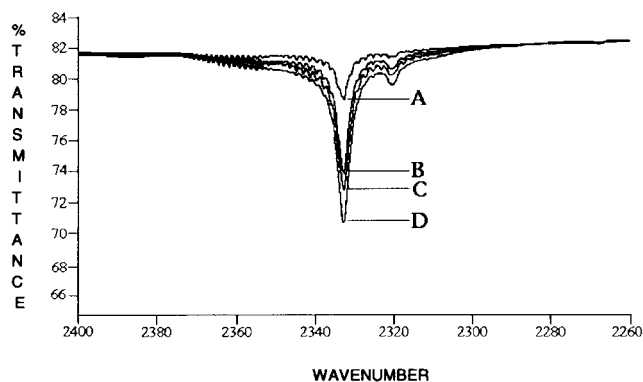


Figure 2. Pressure dependence of the CO<sub>2</sub> vibrational band A) 8.1 MPa; B) 9.1 MPa; C) 11.5 MPa, and D) 28.1 MPa.

trum of gaseous CO<sub>2</sub> trapped in a KBr disk is also red shifted and rotational structure is lost.

There are three possibilities for where the CO<sub>2</sub> is residing in the *p*-*t*-butylcalix[4]arene: (1) the CO<sub>2</sub> may be adsorbed on the surface of the *p*-*t*-butylcalix[4]arene, (2) the CO<sub>2</sub> may be dissolved in the solid *p*-*t*-butylcalix[4]arene, or (3) the CO<sub>2</sub> may reside in the *p*-*t*-butylcalix[4]arene cavity forming a host:guest inclusion complex. First, we will address the possibility of surface-adsorbed CO<sub>2</sub> on the *p*-*t*-butylcalix[4]arene. An experiment was performed where *p*-*t*-butylcalix[4]arene was exposed to gaseous CO<sub>2</sub> at ambient pressure for 3 hours. Subsequent IR analysis on the exposed *p*-*t*-butylcalix[4]arene solid did not contain any CO<sub>2</sub> vibrational bands. This suggests that elevated pressure is necessary for the appearance of the CO<sub>2</sub> vibrational band in the *p*-*t*-butylcalix[4]arene IR spectrum and that either the

CO<sub>2</sub> is dissolved in the solid *p*-*t*-butylcalix[4]arene or a guest:host complex has been formed.

The pressure dependence of the vibrational band was investigated by varying the pressure of CO<sub>2</sub> on identical amounts of solid *p*-*t*-butylcalix[4]arene at 40 °C using a commercial supercritical fluid extractor (SFE) operated in the static extraction mode. The *p*-*t*-butylcalix[4]arene was placed in the extraction cell and heated to 40 °C and pressurized for 60 min. Immediately after the depressurization was complete, a high-resolution IR spectrum was measured on the exposed *p*-*t*-butylcalix[4]arene in a KBr disk. The pressure dependence on the intensity of the vibrational band is shown in Figure 2. As the pressure of the CO<sub>2</sub> was increased, the intensity of the IR vibrational band also increased.

To investigate the possibility of CO<sub>2</sub> solubility in the solid *p*-*t*-butylcalix[4]arene, we exposed the larger oligomers, *p*-*t*-butylcalix[6]arene and *p*-*t*-butylcalix[8]arene, to CO<sub>2</sub>. The larger calixarenes possess more planar conformations, with *p*-*t*-butylcalix[8]arene forming a nearly planar, pleated loop. These flatter conformations do not have the cone-shaped cavity of the smaller *p*-*t*-butylcalix[4]arene. If CO<sub>2</sub> was indeed soluble only in the solid calixarenes, and not residing in the cavity of *p*-*t*-butylcalix[4]arene, then one might infer that all three *p*-*t*-butylcalix[*n*]arenes might exhibit the CO<sub>2</sub> vibrational band in their respective IR spectra. The *p*-*t*-butylcalix[6]arene and *p*-*t*-butylcalix[8]arene were exposed to CO<sub>2</sub> (60 min static soak, 40 °C, 30 MPa) in the commercial SFE apparatus. Infrared spectra were taken on KBr disks containing the exposed *p*-*t*-butylcalix[6]arene and *p*-*t*-butylcalix[8]arene solids, and showed no CO<sub>2</sub> vibrational band near 2333 cm<sup>-1</sup>. The absence of the CO<sub>2</sub> vibrational band in the exposed *p*-*t*-butylcalix[6]arene and *p*-*t*-butylcalix[8]arene suggests that what we have observed is not CO<sub>2</sub> solubility in solid *p*-*t*-butylcalix[4]arene, but rather a host:guest complex formed between CO<sub>2</sub> and solid *p*-*t*-butylcalix[4]arene in the conical cavity of the *p*-*t*-butylcalix[4]arene.

In an attempt to further verify a host:guest complex, a single-crystal X-ray diffraction (XRD) structure was attempted. Crystals of *p*-*t*-butylcalix[4]arene were exposed to supercritical CO<sub>2</sub> (60 min static soak, 40 °C, 30 MPa) in the SFE before attempting to mount a crystal for XRD. After exposure, the crystals had changed from translucent in color to opaque, and when mechanically contacted, collapsed into a powder. Although the crystals still exhibited the infrared vibrational band, indicating the CO<sub>2</sub> molecule was present, they had lost all mechanical strength, prohibiting a crystal structure analysis. Closer examination under magnification showed some crystals were crumbling and “exploding” as the CO<sub>2</sub> outgassed. We exposed a stable crystal of an already formed host:guest complex of *p*-*t*-butylcalix[4]arene:toluene to CO<sub>2</sub>, envisioning that the CO<sub>2</sub> would simply exchange with the toluene molecule that was already present in the pre-formed cavity. However, these crystals also were destroyed following CO<sub>2</sub> depressurization, prohibiting XRD analysis.

Since XRD analysis of the *p*-*t*-butylcalix[4]arene:CO<sub>2</sub> complex was not feasible, a solid-state NMR spectrum of the exposed *p*-*t*-butylcalix[4]arene was measured in an

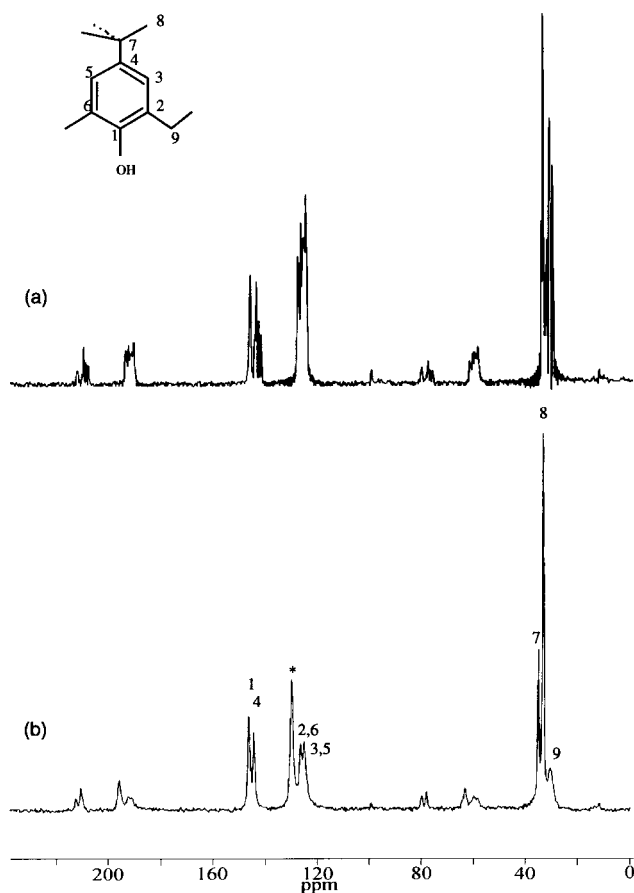


Figure 3. Solid-state CP-MAS  $^{13}\text{C}$  NMR spectra of *p*-*t*-butylcalix[4]arene (a) before and (b) after exposure to supercritical  $\text{CO}_2$  ( $\text{CO}_2$  indicated by \*).

attempt to compare the spectrum with the reported *p*-*t*-butylcalix[4]arene:propane complex [6]. Solid state CP-MAS  $^{13}\text{C}$  NMR spectra of *p*-*t*-butylcalix[4]arene before and after exposure to supercritical  $\text{CO}_2$  (60 min static soak,  $40^\circ\text{C}$ , 30 MPa) were collected and are shown in Figure 3. The spectrum of *p*-*t*-butylcalix[4]arene before exposure contained the expected series of alkyl carbon signals between 30 and 40 ppm and the two sets of aromatic carbon signals below 130 ppm and at 145 ppm. The signals between 50 and 80 ppm and above 150 ppm are spinning sidebands. The  $^{13}\text{C}$  signal from solid  $\text{CO}_2$  is expected to occur at 133 ppm [10] while the gas phase value for  $\text{CO}_2$  is 124.2 ppm [11], in both cases referenced to TMS. In the  $\text{CO}_2$  exposed *p*-*t*-butylcalix[4]arene, a carbon signal attributable to the  $\text{CO}_2$  molecule is observed at 129.9 ppm. This observed value for the chemical shift of  $\text{CO}_2$  indicates that the carbon dioxide resides in an environment that is somewhere in-between the solid and gas states. The closer proximity to the  $^{13}\text{C}$  signal from solid  $\text{CO}_2$  implies that the  $\text{CO}_2$  is more solid-like than gas-like. We might infer that the  $\text{CO}_2$  is locked into a certain lattice devoid of free molecular motion such as inside the basket of a *p*-*t*-butylcalix[4]arene host molecule. Comparing the two spectra, it is evident that the unexposed *p*-*t*-butylcalix[4]arene has a higher degree of crystallinity than the exposed *p*-*t*-butylcalix[4]arene. Although exposure to supercritical carbon dioxide usually results in an increase

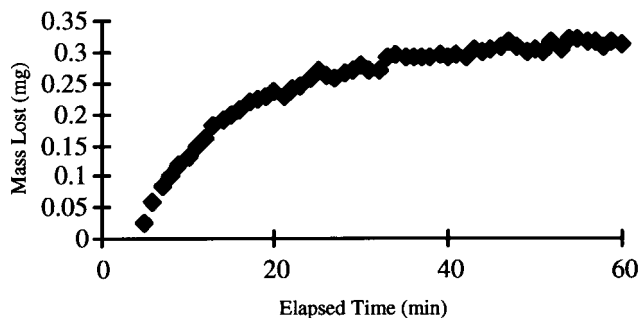


Figure 4. Mass loss from  $\text{CO}_2$  outgassing from *p*-*t*-butylcalix[4]arene.

in the crystallinity, the observed loss of mechanical integrity of the of the *p*-*t*-butylcalix[4]arene before the XRD analysis may account for the reduced crystallinity observed in the NMR spectrum. The sharpening of peaks following exposure is an indication that the *p*-*t*-butylcalix[4]arene cavity has a  $C_4$  symmetry and that if the  $\text{CO}_2$  molecule is truly inside the cavity, it is residing in an axial position. The high symmetry of this cavity and larger interstitial void spaces are thought to promote cavity-to-cavity and out-of-cavity migration of gaseous guests.

Lastly, we measured the rate of  $\text{CO}_2$  escaping from the *p*-*t*-butylcalix[4]arene and the molar ratio of  $\text{CO}_2$  to *p*-*t*-butylcalix[4]arene using thermogravimetric analysis (TGA). The *p*-*t*-butylcalix[4]arene exposed to  $\text{CO}_2$  (60 min static soak,  $40^\circ\text{C}$ , 30 MPa) was transferred to the TGA balance immediately following depressurization. A five-minute delay was necessary to set the sample on the TGA stage and allow the mass to stabilize. The mass loss as a function of time is shown in Figure 4. The plot exhibits a logarithmic decay of mass at ambient temperature ( $23^\circ\text{C}$ ). From this plot, we conclude that the  $\text{CO}_2$  had completely degassed in less than one hour, and subsequent IR analysis showed no  $\text{CO}_2$  vibrational bands. Extrapolation of the mass loss to zero time gave a calculated  $\text{CO}_2$ /*p*-*t*-butylcalix[4]arene molar ratio of 0.7, or 70% of the *p*-*t*-butylcalix[4]arene molecules could contain an incorporated  $\text{CO}_2$  molecule. Longer exposures to the supercritical  $\text{CO}_2$  did not result in higher  $\text{CO}_2$ /*p*-*t*-butylcalix[4]arene ratios.

We were not able to directly verify the formation of a *p*-*t*-butylcalix[4]arene: $\text{CO}_2$  complex through XRD. However, the results of the solid state  $^{13}\text{C}$  NMR, the inability of gaseous  $\text{CO}_2$  to adsorb to the surface of solid *p*-*t*-butylcalix[4]arene, and the absence of  $\text{CO}_2$  vibrational bands in the *p*-*t*-butylcalix[6]arene and *p*-*t*-butylcalix[8]arene IR spectra, strongly indicate the formation of a host:guest complex between *p*-*t*-butylcalix[4]arene and  $\text{CO}_2$ .

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