Molecular Dynamics of C$_{60}$ in Cocrystals of C$_{60}$ and *p*-Bromocalix[4]arene Propyl Ether

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Solid-state NMR experiments have been performed to determine the nature of the molecular motion of C$_{60}$ in cocrystals of C$_{60}$/*p*-bromocalix[4]arene propyl ether. Throughout the temperature range of this work (room temperature to 130 K), C$_{60}$ undergoes fast isotropic reorientation. The C$_{60}$ molecular dynamics in the cocrystal are similar to that found in the fcc crystal structure of pure C$_{60}$. The activation energy of C$_{60}$ reorientation in the cocrystal is 5.6 ± 0.2 kJ/mol, and the rotational diffusion constant of C$_{60}$ is 11×10^9 s^{-1} at room temperature.

Introduction

An unusual packing arrangement of C$_{60}$ molecules in cocrystals of C$_{60}$ and *p*-bromocalix[4]arene propyl ether was recently reported by Barbour et al.[1] The chemical structure of *p*-bromocalix[4]arene propyl ether is shown below. X-ray diffraction analysis of a single crystal of the material performed by Barbour et al. provided a space group of *P4bm* and showed that the calixarene molecules are configured in a head-to-tail arrangement, forming columns running parallel to [001]. The C$_{60}$ molecules also form columns running parallel to [001] at 0, 0, *z* and ¹/₂, ¹/₂, *z*, and the C$_{60}$ columns are isolated from each other by the stacks of calixarene molecules. Although the centers of the C$_{60}$ molecules occupy well-defined lattice sites, the X-ray data suggest that the C$_{60}$ molecules are orientationally disordered. The center-to-center distance between adjacent C$_{60}$ molecules in the cocrystal was found to be 9.92 Å at room temperature, and the shortest center-to-center distance between adjacent columns of C$_{60}$ molecules was determined to be 12.81 Å. The crystal structure found at room temperature was similar to that observed at 163 K.[1]

R = CH$_2$CH$_2$CH$_3$
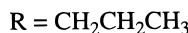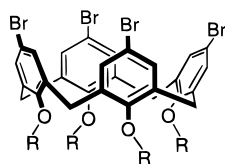
Pure C$_{60}$ has a structural phase transition at 249 K.[2] The crystal structure above 249 K is face-centered-cubic (fcc), and below 249 K the crystal structure is simple-cubic (sc). The packing arrangement of the C$_{60}$ molecules in the fcc and sc crystal structures are very similar, and the shortest center-to-center distance between molecules is approximately 10.0 Å. In the fcc crystal structure, the C$_{60}$ molecules are orientationally disordered and have been characterized by solid-state NMR experiments as having fast isotropic rotational motion about their respective lattice sites.[3,4] The molecules show orientational ordering in the sc crystal structure. However, solid-state NMR

experiments show that there is fast reorientational motion of the molecules in the sc phase as well. The molecular dynamics of the C$_{60}$ molecules in the sc crystal structure consists of fast jumps between symmetry-equivalent orientations instead of the rapid isotropic reorientation found in the fcc crystal structure.[3,4]

The nature of the orientational dynamics of the C$_{60}$ molecules in the C$_{60}$/*p*-bromocalix[4]arene propyl ether cocrystal are reported in this work. In particular, spin−lattice relaxation times, T_1, have been measured as a function of temperature for the cocrystal. From the T_1 measurements, the rotational correlation times and activation energy of molecular reorientation can be obtained. A comparison is made between the C$_{60}$ molecular motions found in pure C$_{60}$ and in the C$_{60}$/*p*-bromocalix[4]arene propyl ether cocrystal.

Experimental Section

Synthesis. The *p*-bromocalix[4]arene propyl ether was prepared using standard synthetic procedures.[5] Due to the amount of material required for solid-state NMR experiments, the *p-tert*-butylcalix[4]arene precursor was prepared using the base-catalyzed condensation of *p*-tert butyl phenol with formaldehyde. A four-step synthesis was performed to obtain the final product.

p-*tert*-Butylcalix[4]arene. Procedures described by Gutsche and Iqbal were followed.[5] However, the amounts used were reduced by a factor of 10. First, 10.0 g (67 mmol) of *p-tert*-butylphenol was dissolved in 6.2 mL of 37% formaldehyde solution (83 mmol). Next, 0.12 g (3 mmol) of sodium hydroxide was added and the solution was heated to 383 K for 2 h in an open flask. The solid that formed was allowed to cool. After it reached room temperature, 80 mL of warm diphenyl ether was added while nitrogen gas was passed over the solution. After the solution was refluxed for 2 h, 150 mL of ethyl acetate was added to the solution, which was stirred for 30 min at room temperature. Upon standing for 30 min, a precipitate formed, which was filtered off, washed with two 10 mL volumes of ethyl acetate, then washed with 20 mL of acetic acid, and finally washed twice with 10 mL of water. The crude product was dried on a vacuum line.

Calix[4]arene. The starting point for the synthesis of calix[4]arene was dissolving 1.0 g (1.54 mmol) of *p-tert*-butylcalix[4]arene in 10.0 g of dry toluene. The solution was then added to a mixture of AlCl$_3$ in toluene: 1.25 mol of AlCl$_3$ per 1.00 mol of −OH groups and, for each gram of AlCl$_3$, 5.0 mL of

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toluene were used.[6] The mixture was heated to 313 K with a condenser in place and under a nitrogen gas atmosphere for 3 h. The reaction was cooled to room temperature and stopped by the addition of 10% HCl (20 mL/g of AlCl₃). The organic layer was separated, washed with water, dried over magnesium sulfate, and then recrystallized from methanol.

Calix[4]arene Propyl Ether. Calix[4]arene (0.65 g, 1.54 mmol) was treated with 1.0 g of 60% oil dispersed sodium hydride in distilled THF (25 mL) and DMF (2.5 mL). Next, 7.34 mL (80.8 mmol) of *n*-bromopropane was added to the solution. The mixture was refluxed under nitrogen gas for 2 h. After cooling to room termperature, excess NaH was reacted with methanol. The product was diluted with 300 mL of water, and then the organic component was extracted into chloroform (100 mL × 2). The chloroform layer was separated and then dried over magnesium sulfate.[7] After filtration, the filtrate was concentrated to dryness. The residue was separated into cone and partial cone components using flash chromatography with a silica gel column and an 8:10 ratio of chloroform to hexane solvent.

***p*-Bromocalix[4]arene Propyl Ether.** Calix[4]arene propyl ether (0.3 g, 0.506 mmol) was dissolved in 11 mL of methyl ethyl ketone. *N*-Bromosuccinimide (0.61 g, 3.42 mmol) was added to the solution, which was then covered and stirred for 24 h at room temperature. The reaction mixture was washed with 10 mL of NaHSO₄ and water. The organic layer was separated and dried over magnesium sulfate and then filtered and evaporated. The product was subjected to flash chromatography in the same manner described above.

C₆₀/*p*-Bromocalix[4]arene Propyl Ether Complex. *p*-Bromocalix[4]arene propyl ether (0.5 g) and 0.079 g of C₆₀ were dissolved in *o*-dichlorobenzene in a test tube with a large diameter. 2-Propanol was then slowly poured onto the top of the *o*-dichlorobenzene solution such that two layers formed. After slow diffusion over a period of one month, crystals formed at the interface of the two solvents.

X-ray Diffraction. The unit cell parameters and the lattice type of a crystal of the C₆₀/*p*-bromocalix[4]arene propyl ether compound were determined with an automated Siemens P4 automated X-ray diffractometer equipped with a graphite monochromator using Mo Kα radiation ($\lambda = 0.710\,73$ Å). The reflections used to determine the unit cell parameters were located and indexed by the automatic peak search routine provided with the XSCANS (Version 2.0; developed by Siemens Analytical X-ray Instruments, Madison, WI) diffractometer control system.

The final lattice parameters were calculated from a nonlinear least-squares fit of the orientation angles of 42 reflections ($10° < 2\theta < 25°$) obtained at 295 K. The unit cell parameters of $a = b = 18.211(1)$ Å, $c = 9.915(1)$ Å, $\alpha = \beta = \gamma = 90°$, and $V = 3288.3(7)$ Å³ are consistent with a tetragonal crystal lattice. Further examination of the Miller indices for the reflections used in the unit cell determination indicate that the tetragonal unit cell is primitive. Of the eight possible primitive tetragonal space groups of Laue symmetry 4*mm*, six can be eliminated on the basis of the incompatibility of their systematic absences with the Miller indices of the 42 observed reflections used for the cell determination. Of the two remaining space groups, P4*mm* (C_{4v}^1, No. 99) has no systematic absences whereas P4*bm* (C_{4v}^2, No. 100) has the systematic condition that for {0*kl*} data reflections with $k = 2n + 1$ are absent. Although there were insufficient data available to differentiate between these two space groups, the magnitudes of the lattice parameters for this primitive tetragonal crystal system are entirely compatible with the lattice parameters reported by Barbour et al.[1] of $a = b = 18.1160(6)$ Å, $c = 9.8782(5)$ Å, and $\alpha = \beta = \gamma = 90°$, which were determined at 173 K for this same compound. At room temperature they found that $c = 9.9231(6)$ Å, which is comparable in magnitude to the value of *c* obtained from our unit cell determination. Their structural analysis of C₆₀/*p*-bromocalix[4]arene propyl ether cocrystal was further based on the primitive tetragonal space group P4*bm* (C_{4v}^2, No. 100) as being the correct one. Therefore, the results of our determination of the lattice parameters and crystal lattice type completely agree with their X-ray structural analysis and confirm that the crystals of C₆₀/*p*-bromocalix[4]arene propyl ether that we prepared are of the same material.

NMR Spectroscopy. ¹H solution-state NMR spectra were taken at each step of the synthesis of *p*-bromocalix[4]arene propyl ether with a JEOL 270 spectrometer. High-resolution, solid-state ¹³C-observe NMR experiments were performed with powdered samples on a Chemagnetics CMX II spectrometer with ¹H and ¹³C Larmor frequencies of 359.830 and 90.488 MHz, respectively. Cross-polarization magic-angle sample spinning (CPMAS) experiments[8] were performed with a double-tuned Chemagnetics Pencil probe (7.5 mm rotor) at a spinning rate of approximately 5.7 kHz. A 16 mg sample of the C₆₀/*p*-bromocalix[4]arene propyl ether cocrystal was centered within the NMR coil using Teflon spacers for the solid-state NMR experiments. Proton $\pi/2$ pulse lengths were 4 μs and ¹H decoupling field strengths were 80 kHz. For the cross-polarization experiments, ¹H–¹³C contact times were 1 ms and between 7 and 10 ms for pure *p*-bromocalix[4]arene propyl ether and for the C₆₀/*p*-bromocalix[4]arene propyl ether cocrystal, respectively. TPPM proton decoupling was used during data acquisition for the CPMAS experiments.[9]

Spin–lattice relaxation times, T_1, of the ¹³C nuclei were measured as a function of temperature using a saturation recovery pulse sequence[10] with the probe mentioned above and a Chemagnetics temperature controller. The temperature was measured with a thermocouple placed close to the sample. The sample was spun at 1.1 kHz and proton decoupling was not performed during these experiments. Slow MAS was used for the T_1 experiments to eliminate isotropic susceptibility broadening. Measurements of T_1 were made from 273 to 130 K.

Results and Discussion

CPMAS Spectra. Figure 1a shows a CPMAS ¹³C spectrum of *p*-bromocalix[4]arene propyl ether taken at room temperature. The numbered resonances correspond to the numbering of the unique chemical sites in the molecule shown in the inset above the spectrum. The ¹³C resonance assignments were made by referring to solution-state ¹³C spectra obtained on solutions of *p*-bromocalix[4]arene propyl ether and by using interrupted proton decoupling on the solid sample. The latter technique was particularly useful in distinguishing between the resonances labeled 6 and 7. The spectral features that are not numbered are spinning sidebands. Each of the ¹³C resonances in this spectrum show splittings that arise from the C_{2v} symmetry of the molecule and from the crystal packing.

Figure 1b shows a room-temperature CPMAS ¹³C spectrum of the C₆₀/*p*-bromocalix[4]arene propyl ether cocrystalline material. The ¹³C resonance from C₆₀ is the intense peak at 142 ppm. Since the spectrum was acquired with ¹H–¹³C cross-polarization, the appearance of the C₆₀ ¹³C resonance is further evidence that the cocrystal formed. There are no spinning
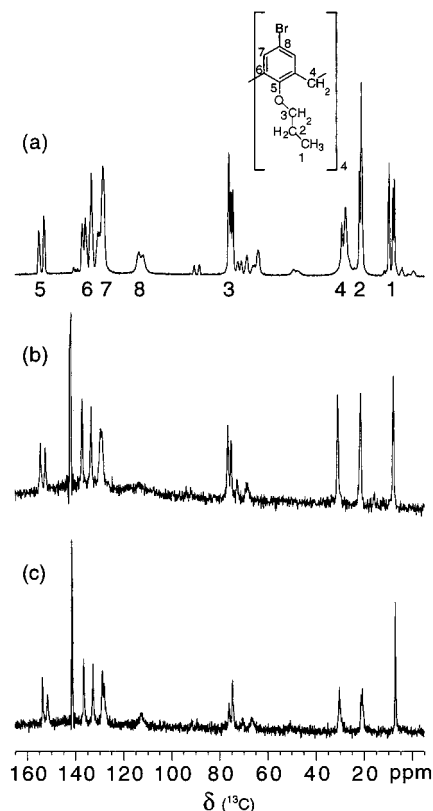
Figure 1. (a) CPMAS ^{13}C spectrum of of *p*-bromocalix[4]arene propyl ether taken with a 1 ms CP contact time, a 2 s recycle time, an 81 ms data acquisition time, and 8000 scans. (b) CPMAS ^{13}C spectrum of and C$_{60}$/*p*-bromocalix[4]arene propyl ether cocrystal obtained at room temperature with a 7 ms CP contact time, 20 s recycle time, a 40 ms data acquisition time, and 6800 scans. (c) CPMAS ^{13}C spectrum of the cocrystal obtained at 180 K with a 10 ms CP contact time, 5 s recycle time, an 81 ms data acquisition time, and 3000 scans. The ^{13}C resonance of C$_{60}$ occurs at 142 ppm and has been cropped at approximately one-fifth of its intensity in the spectra shown in (b) and (c).

sidebands associated with the C$_{60}$ ^{13}C resonance. Since the chemical shift anisotropy (CSA) of the C$_{60}$ ^{13}C nuclei is large,[3] then the absence of spinning sidebands is suggestive that fast large-amplitude motions of the C$_{60}$ molecules are occurring. There are not as many splittings of the ^{13}C resonances in the C$_{60}$/*p*-bromocalix[4]arene propyl ether cocrystal as compared to pure *p*-bromocalix[4]arene propyl ether. The ^{13}C resonances arising from the calixarene rings (5, 6, and 7) are split into doublets that reflect the C_{2v} symmetry of the calixarene cage,[1] and the resonance from the bromine-substituted carbon position has been broadened considerably. The ^{13}C resonances labeled 2 and 4 are broader than their respective counterparts in Figure 1a, and it is difficult to conclude whether they are split into doublets.

The MAS ^{13}C spectrum of the C$_{60}$/*p*-bromocalix[4]arene propyl ether cocrystal shown in Figure 1c was acquired at 180 K. At this temperature, the bromine-substituted carbon ^{13}C resonance is clearly visible, and all other resonances are similar to those obtained at room temperature. The low-temperature spectrum was taken to see if spinning sidebands of the C$_{60}$ ^{13}C resonance would appear, which would indicate the freezing out of any motion. The absence of spinning sidebands for the C$_{60}$ ^{13}C resonance is indicative that fast molecular motion persists at this low temperature.

Spin−Lattice Relaxation Times. The molecular dynamics of C$_{60}$ can be analyzed by examining the temperature dependence of the spin−lattice relaxation. At our field strength, it is
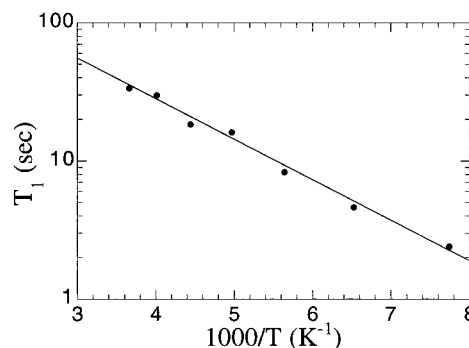

Figure 2. Temperature dependence of the spin−lattice relaxation time. The solid line is a fit of eq 3 to the data using an activation energy of 5.6 kJ/mol.

reasonable to assume that T_1 is dominated by the CSA relaxation mechanism.[3,4,11] The relaxation rate is given by

$$\frac{1}{T_1} = \gamma^2 B_o{}^2\left(\frac{2}{3}A^2\frac{3\tau}{1 + 9\omega^2\tau^2} + \frac{2}{15}S^2\frac{\tau}{1 + \omega^2\tau^2}\right) \quad (1)$$

where γ is the ^{13}C magnetogyric ratio, B_o is the applied magnetic field, $\omega = \gamma B_o$, and τ is the rotational correlation time.[12,13] The factors A^2 and S^2 originate from the antisymmetric and symmetric components of the shielding tensor, and their respective values for C$_{60}$ have been determined previously to be 1.4×10^{-10} and 3.17×10^{-8}.[13]

A simple model of the molecular dynamics applied successfully to pure C$_{60}$ assumed that the fast motion limit, $\omega\tau \ll 1$, and that the temperature dependence of the rotational correlation time is described by[3]

$$\frac{1}{\tau} = qe^{-E_a/kT} \quad (2)$$

where E_a is the activation energy of molecular reorientation. Using these assumptions, the spin−lattice relaxation time is

$$T_1 = \lambda e^{-E_a/kT} \quad (3)$$

with

$$\frac{1}{\lambda} = \frac{\omega^2}{q}\left(2A^2 + \frac{2}{15}S^2\right) \quad (4)$$

Figure 2 shows the temperature dependence of the ^{13}C spin−lattice relaxation time of C$_{60}$. No discontinuity is found in the T_1 data, which indicates that the nature of the molecular motion is the same over the entire temperature range. The data are described by eq 3 with an activation energy of 5.6 ± 0.2 kJ/mol, which supports the notion that the C$_{60}$ molecules execute fast isotropic reorientation in the cocrystal. Equation 1 and our T_1 data provide a 20 ps correlation time at 273 K, and the best fit to the data gives a 15 ps correlation time at room temperature. The C$_{60}$ ^{13}C resonance of the C$_{60}$/*p*-bromocalix[4]arene propyl ether cocrystal appeared as a single sharp peak at all temperatures of this work, even at 130 K. The 1.1 kHz magic-angle sample spinning produced no spinning sidebands at any temperature, which is further evidence of the presence of fast molecular motion occurring at all temperatures.

The activation energy of crystals of pure C$_{60}$ has been measured previously by solid-state NMR, with one group[3] finding 4.0 ± 0.9 kJ/mol and the other[4] reporting 5.8 ± 0.5 kJ/mol for the fcc crystal structure. Others, using neutron scattering experiments, found an activation energy of 3.4 ± 1.5

kJ/mol for pure fcc C_{60}.[14] Our measurement of 5.6 kJ/mol for C_{60} in the C_{60}/p-bromocalix[4]arene propyl ether cocrystal lies within the various values reported for pure fcc C_{60} and adds support to the model of the C_{60} motion being fast isotropic reorientation. As noted by others,[4] the correlation time of C_{60} dissolved in tetrachloroethane is 15.5 ps at 283 K, and the correlation time expected for free molecular rotation of C_{60} in the gas phase is 3.1 ps at 283 K. The correlation time of C_{60} at room temperature for pure C_{60} has been determined previously by two groups, with one[3] finding 12 ps and the other[4] finding 9.1 ps. We find the correlation time of C_{60} in the C_{60}/p-bromocalix[4]arene propyl ether cocrystal at room temperature to be 15 ps, which is comparable to that found in pure C_{60} at room temperature. The correlation time of C_{60} in the C_{60}/p-bromocalix[4]arene propyl ether cocrystal is also comparable to that in solution and only modestly longer than that expected for an unhindered rotor in the gas phase.

The correlation time can be used to obtain the rotational diffusion constant, D. During a time Δt, the mean-square angle of rotation about each of the three independent axes for a system described by isotropic rotation is $\langle \theta_i^2 \rangle = 2D\Delta t$.[4] The rotational diffusion constant is related to the correlation time by $\tau = 1/6D$.[4] Hence, at room temperature the rotational diffusion constant is $11 \times 10^9 \text{ s}^{-1}$ for C_{60} in the C_{60}/p-bromocalix[4]arene propyl ether cocrystal.

In conclusion, the C_{60} molecules in the C_{60}/p-bromocalix[4]-arene propyl ether cocrystal undergo fast isotropic reorientation similar to the motion found in fcc crystals of pure C_{60}. The p-bromocalix[4]arene propyl ether molecules of the cocrystal provide little hindrance to the motion of the fullerene molecules. The nature of the C_{60} molecular motions in pure crystals of C_{60} changes from isotropic motion to discrete jumps between symmetry equivalent orientations at a temperature of 249 K. In fact, at 130 K the motions of pure crystalline C_{60} are so slow as to yield a full CSA powder pattern.[3] However, the molecular dynamics of C_{60} in the C_{60}/p-bromocalix[4]arene propyl ether cocrystal appear to remain as rapid isotropic reorientation down to at least 130 K.

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