

ARTICLES

Solid-State NMR Studies of Fullerene C₆₀/Benzene Solvates

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Stable van der Waals-bonded C₆₀/benzene solvates were prepared using a novel crystallization technique. Solid-state NMR measurements on highly crystalline solvate under liquid benzene show that there is very little interaction between benzene and the C₆₀ molecules and that the rotation of C₆₀ at room temperature is not hindered. The magnetization transfer between benzene protons and local C₆₀ molecules is highly inefficient. Three benzene species have been found in the solvate: two, nearly freely mobile, in wide and narrow porous structures, and the third constrained by C₆₀ molecules in lattice defects. Premelting of deuterated benzene within the C₆₀ solvate has been observed at $T_m - 10.5$ K.

Introduction

It is well established that pure crystalline fullerene C₆₀ is a molecular rotor at room temperature.^{1,2} Fullerene C₆₀ readily forms solid solvates with a variety of host solvents including benzene,^{3–5} *n*-pentane,⁶ hexane,⁷ *n*-heptane,⁸ and CS₂.⁹ While large faceted polyhedral crystals can be successfully grown, these solvate crystals are generally not air stable and rapidly lose solvent by evaporation. This process leads to X-ray diffraction (XRD) patterns with diffuse bands as a result of a substantial degree of disorder in the crystal structure.¹⁰

The study of C₆₀/benzene solvates by solid-state NMR is of particular interest since it may make it possible to examine the interaction of aromatic systems in a model van der Waals-bonded environment, and both C₆₀ and benzene give unique well-separated single ¹³C NMR resonances with all the protons in the benzene molecule being equivalent.

The room-temperature crystal structure of C₆₀/benzene solvates has not been established. Low-temperature single-crystal

XRD studies indicate two possible crystal structures: C₆₀ in an approximately hexagonal close-packed arrangement³ or an approximately cubic close-packed arrangement^{4,5} separated by benzene molecules, both structures being stoichiometric with composition of C₆₀·4C₆H₆. The relevance of these low-temperature XRD studies to the room-temperature structure needs to be tested. The application of solid-state NMR to this solvate system could provide an insight into the molecular arrangements of the two species at room temperature via monitoring the individual magnetic environments and nature of molecular motion.

An early attempt to grow C₆₀ solvate crystals from benzene was reported by Maniwa et al.,¹¹ but very little benzene was retained in the lattice after removal to air. The C₆₀/*n*-pentane system⁶ and C₆₀/CH₂I₂/C₆H₆ cocrystals¹² have been studied by NMR. To our knowledge there has been no solid-state NMR study of a stable C₆₀/benzene solvate, although the work of Geiser et al.¹² is of relevance. Their proton-decoupled ¹³C magic-angle-spinning (MAS) NMR spectrum shows sharp resonances at 146.7, 133.1, and 35 ppm corresponding to carbons from C₆₀, C₆H₆, and CH₂I₂, respectively. XRD reveals that the benzene molecule is held by van der Waals interactions between one carbon atom of the benzene molecule and two

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carbons each from two adjacent C_{60} molecules on the either side of the benzene. Although Geiser et al. believe that these interactions are sufficient to "halt the free rotation [of the C_{60}] even at room temperature", an effect reported for C_{60} with intercalated O_2 ,^{13,14} they do not comment on the effect on the molecular reorientation of benzene. Masin et al.¹⁵ concluded that there was no such motional hindrance in their mixed C_{60} - C_{70} /chloroform solvate crystals. The aim of the present work is to address this question to the case of a C_{60} /benzene crystal in terms of motion of the fullerene and that of the intercalated solvent and to provide information on the structure of C_{60} /benzene solvate at ambient temperature.

Experimental Section

Techniques. NMR spectra were acquired on a Chemagnetics CMX-400 spectrometer. MAS rotors were spun in nitrogen gas at ca. 4.5 and 8 kHz. The 1H spectra were recorded at 399.91 MHz (9.4 T) using $2 \mu s$ ($\pi/4$) pulses and 10 s recycle delays. The variable-temperature (123–280 K) 2H spectra were acquired at 61.39 MHz with $2 \mu s$ pulses and 1–6 s recycle delays. ^{13}C NMR spectra were acquired at 100.56 MHz using $1 \mu s$ ($\pi/6$) pulses and 45 s recycle delays. 1H - ^{13}C cross-polarization (CP)/MAS spectra were measured with a $2.8 \mu s$ 1H $\pi/2$ pulse, a single contact optimized contact time of 4 ms and a 10 s recycle delay. The Hartmann-Hahn condition was established using hexamethylbenzene at both MAS rates. 1H and ^{13}C chemical shifts are given in ppm from external tetramethylsilane (TMS). 2H chemical shifts are given from deuterated water. In all variable-temperature experiments 10–15 min was allowed for equilibration after the required temperature was reached.

The XRD patterns were recorded on a Philips PW1710 automated powder diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV, 40 mA), 0.02° step size, and 1 s step time.

Sample Preparation. The ^{13}C MAS NMR spectrum of highly pure parent solid C_{60} consists of a single Lorentzian line at 144.0 ppm with 1.8 Hz line width. No upshifted secondary resonances corresponding to intercalated oxygen as reported by Assink et al.¹³ were found even with fast recycle times (< 1 s) used to reveal rapidly relaxing species. The intercalated organic residue in the source C_{60} was less than 0.05 wt % (as determined by quantitative 1H NMR measurements). Protonated benzene ($> 99\%$ pure) was distilled prior to use, and further purified by fractional crystallization close to its melting point. Deuterated benzene (Aldrich 99.5%) was used as received.

Preliminary tests confirmed the instability of C_{60} /benzene solvates in air due to solvent loss. Although precipitated C_{60} /benzene solvates can be prepared by slow solvent evaporation of saturated C_{60} /benzene solutions,^{3,4} this method is unsuitable given the high cost of deuterated benzene. A new closed volume crystallization technique was developed in which a filtered saturated solution (ca. 1 mg of C_{60} /mL of benzene) was cooled from room temperature to close to the freezing point of benzene. Under these conditions the solubility of C_{60} in benzene falls dramatically and large faceted translucent cherry-red solvate crystals can be grown within hours. The aim of this procedure is to create a *pure* van der Waals-bonded environment with uniform magnetic environment at a molecular level over extended crystal volumes. The crystals were recovered by pipetting them from solution and were found to exhibit strong optical activity toward plane-polarized white light. Following recovery, the product was stored in sealed vials in a refrigerator under a C_{60} /benzene solution to prevent crystal resolution or redistribution of intercalated solvent due to thermal effects. For samples containing deuterated benzene the crystallization flask was warmed and further C_{60} dissolved. We

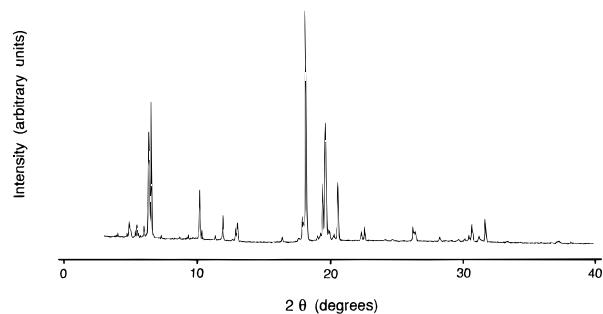


Figure 1. Powder XRD pattern of C_{60} /benzene solvate acquired at room temperature in an atmosphere saturated with benzene vapor.

note that the presence of small amounts of C_{70} and C_{60} derivatives in solution greatly inhibits this process, and the technique cannot be applied to purify C_{60} .

To prevent degradation of the sample crystallinity during measurement, solid-state NMR measurements were conducted in a rotor containing a minimum of additional C_{60} /benzene liquid. We have ensured that the liquid did not spin out under the influence of the very considerable centrifugal force (ca. 300 kilogravities) at the maximum spinning rate of 8 kHz. NMR measurements were typically performed with the sample at 17–20 °C. Some slight sample heating is inevitably caused by high-power 1H decoupling, but we have no evidence to suggest that the samples were exposed to high enough temperatures to disrupt the solvate lattice significantly.

Methods of obtaining well-resolved XRD powder patterns of the C_{60} /benzene solvates were also investigated. The crystallinity of the solvate could be preserved intact for the duration of the measurement (ca. 1 h) by creating a vapor well around the solvate crystals using tissues saturated with benzene.

Results

X-ray Diffraction. The line widths in the XRD pattern of the C_{60} /benzene solvate (Figure 1) are typically 0.06° , indicating very high crystallinity. The clean powder pattern indicates the structure with long-range order. No line positions coincide with those from solvent-free pure C_{60} . No attempt has been made to determine the room-temperature structure from the powder pattern at this stage, and the noncentrosymmetric structure evidenced by optical activity makes this task particularly difficult.

^{13}C NMR of Protonated Solvate. The static proton-decoupled ^{13}C NMR spectrum of the solvate (Figure 2a) contains two sharp lines at 143.67 and 128.65 ppm, corresponding to C_{60} and benzene, respectively. The full width at half-maximum (fwhm) of the C_{60} line (184 Hz) is comparable to that for pure (oxygen-free) C_{60} (200–220 Hz). The fwhm of the line from intercalated benzene is ca. 177 Hz, compared with 23 Hz measured for liquid benzene in a saturated C_{60} /benzene solution (no spinning). This shows that chemical shift anisotropies of both the C_{60} and benzene are almost completely motional averaged, although the majority of the benzene in the solvate is *not* incorporated as a rigidly constrained species or a freely diffusing liquid. The very similar widths of the chemical shift anisotropy (CSA) patterns for benzene and C_{60} indicate that motional averaging is nearly equally efficient and the rotational correlation times similar. The line width also indicates that benzene does not hinder the motion of C_{60} compared to a pure C_{60} phase.

In the proton-decoupled ^{13}C spectrum with MAS at 4.5 kHz both lines sharpen considerably to fwhm of less than 20 Hz and are unsplit (Figure 2b). This confirms the absence of multiple magnetic environments in the solvate, which is

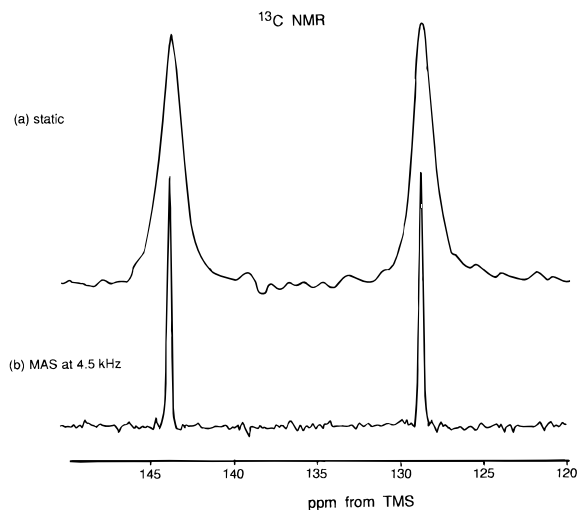


Figure 2. ¹³C NMR spectra of C₆₀/benzene solvate with proton decoupling: (a) static sample; (b) with MAS at 4.5 kHz.

TABLE 1: ¹³C NMR Chemical Shifts of C₆₀ and Benzene in Pure and Solvated States (Measured with MAS at 4.5 kHz)

species	isotropic chemical shift (ppm)
pure C ₆₀	144.00
C ₆₀ in solvate	143.67
bulk benzene in solvate	128.65
pure liquid benzene	128.43

consistent with the XRD result. However, upon prolonged (> 1 h) spinning at 8 kHz C₆₀ lines split irreversibly, which is probably caused by the centrifugal forces leading to the disruption of the solvate structure and the creation of multiple magnetic environments in C₆₀. This effect thus reflects the limit of the van der Waals forces which bind the solvate together. Absolute chemical shifts in Table 1 show that the presence of benzene in the solvate leads to a small (0.33 ppm) additive shielding to the C₆₀ isotropic chemical shift, while the effect of the benzene is smaller with a net deshielding of 0.22 ppm compared to the free liquid.

¹H NMR. The room-temperature ¹H spectrum of benzene in the static sample of C₆₀/benzene solvate under minimal excess liquid (Figure 3a) consists of a very broad asymmetric multi-component line with fwhm ≈ 80 Hz. The ¹H spectrum with MAS at 4.6 kHz is clearly resolved into three superimposed components (Figure 3b). The spectrum can be further sharpened by spinning at 8 kHz (Figure 3c). However, prolonged spinning at this rate results in a poorly resolved ¹H spectrum due to disruption of the solvate lattice. The deconvoluted parameters for MAS at 8 kHz (Table 2) show three distinct proton resonances: one very sharp from the free liquid benzene and two from the solvate (one very broad (line B) and one quite sharp (line S)). Integrated intensities give an approximate proton ratio of B:S = 19.3:1. Figure 3c indicates that the fraction of free liquid benzene in the rotor is likely to be less than 15% of the total benzene.

¹H-¹³C CP/MAS NMR. The line at 129.6 ppm with spinning sidebands in the ¹H-¹³C CP/MAS spectrum of the solvate (Figure 4) comes from a motionally hindered benzene species. The intensity of the line from C₆₀ is very low, indicating that little direct magnetization transfer from benzene protons to C₆₀. This again points to no substantial rotational hindering of the C₆₀. The narrow line at 128.7 ppm comes from mobile benzene in the solvate (*not* from free liquid benzene) since measurements using a 1 ms contact time gave a huge attenuation of this line relative to the broad CP benzene center

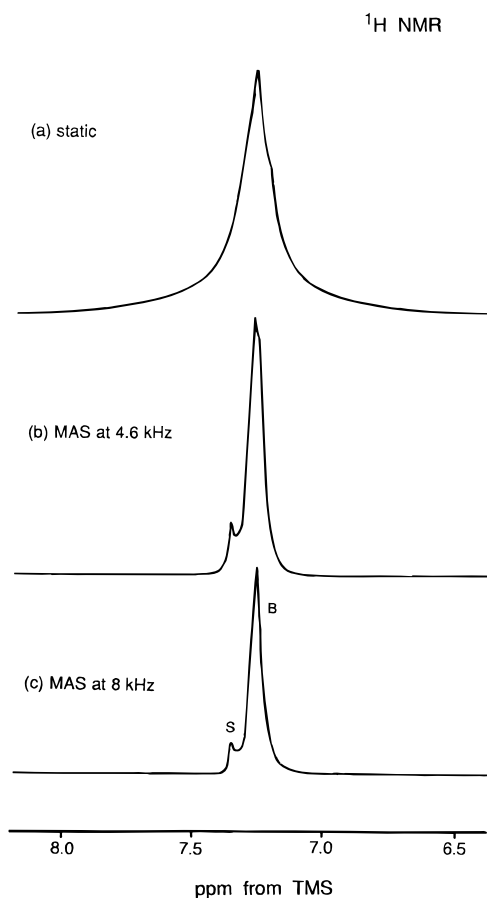


Figure 3. ¹H NMR spectra of C₆₀/benzene solvate: (a) static spectrum; (b) with MAS at 4.6 kHz; (c) with MAS at 8 kHz.

TABLE 2: Deconvoluted Parameters of ¹H MAS NMR Spectra for C₆₀/Benzene Solvate (Measured with MAS at 8 kHz)

species	chemical shift (ppm)	fwhm (Hz)
broad line (B)	7.23	40.5
free liquid benzene	7.27	7.6
sharp line (S)	7.36	7.4

band. We believe that this is a residual effect caused by a distribution of velocities of the molecular motion.

The magnitude of the chemical shift anisotropy of the hindered benzene was estimated by modeling the sideband pattern following the method of Herzfeld and Berger.¹⁶ The best data fit is shown in Figure 4b. The analysis yielded a CSA width of 16.5 ± 0.5 kHz with an asymmetry parameter of 0.1 ± 0.1, corresponding to nearly axial symmetry. This implies that the restricted benzene molecules are likely to be constrained to rotation around the C₆ hexad axis.

²H NMR. The solvate prepared with deuterated benzene was examined by ²H NMR. Static and MAS ¹³C NMR measurements of the deuterated solvate gave very similar results to those shown in Figure 2. Figure 5 shows a series of narrow-band ²H spectra near 0 Hz under static and MAS conditions for the nearly isotropic benzene in the solvate at 280 K. In comparison to liquid deuterated benzene, the static ²H spectrum of deuterated benzene within the solvate reveals a slightly upshifted broadened line. At 4.4 kHz MAS rate, the broadened line splits into one major line at 87 Hz and one small line at -25 Hz with intensity ratio of ca. 24:1. This is consistent with the ¹H result for protonated solvate. The ²H results again point to the presence of two distinct intercalated benzene species in the solvate undergoing isotropic motion.

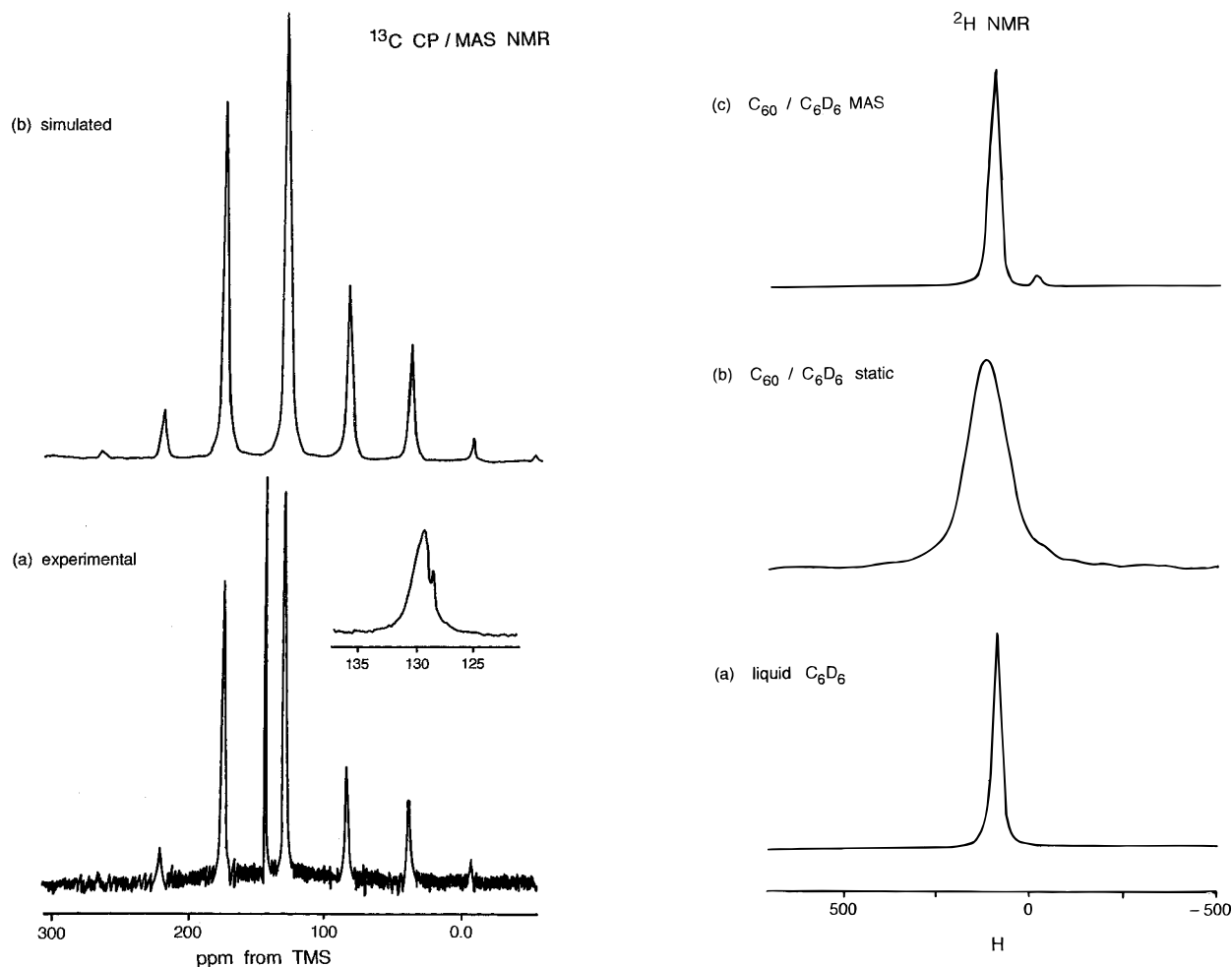


Figure 4. ^1H - ^{13}C CP/MAS NMR spectrum of C_{60} /benzene solvate. Calculated sideband pattern is also shown.

The static wide-band ^2H spectrum for the solvate at 280 K (Figure 6a) shows that a proportion of the benzene is undertaking motion about the hexad axis, indicating a constraint of the motion of the benzene molecule. The small peaks near the main peaks are part of the powder pattern. This result is consistent with the ^{13}C CP measurements. The amount of constrained benzene constitutes only a few percent of the total.

To study the effect of temperature on the behavior of the benzene within the solvate, the crystals were washed three times with fresh C_{60} -saturated *protonated* benzene to remove the excess deuterated benzene. Surprisingly, virtually *all* the deuterated benzene was washed out, leaving just the constrained benzene species. A small residual “isotropic” line is almost certainly due to incomplete washing (Figure 6b). The ^1H spectrum measured with MAS at 4.4 kHz, in order to confirm that the solvate is essentially intact, was fully consistent with that from the solvate prepared directly with protonated benzene (not shown). This indicates that protonated benzene has replaced deuterated benzene within the internal structure of the solvate. The result shows that the solvate forms an open structure containing channels of molecular dimension to account for the observed isotropic chemical shifts at 87 and -25 Hz.

Figure 7 shows the spectra of a washed sample at 123 and 268 K on warming. The splittings of the powder pattern, $\nu_Q/2$, where ν_Q is the quadrupole coupling constant, are 70.33 and 67.65 kHz at 123 and 268 K, respectively. The different splittings at the two temperatures are caused by benzene ring wobble and will not be discussed further. The onset of melting of the benzene on warming the sample is reflected in the

appearance of the “isotropic” line. This melting is reproducibly observed at 268 ± 1 K (Figure 7b) and represents the release of residual *deuterated* benzene by melting of *protonated* benzene. We believe that this phenomenon is due to “premelting” of benzene in narrow channels in the solvate which approach the size of single benzene molecules. Premelting of benzene has been observed by ^1H NMR at grain boundaries,¹⁷ although the present depression of $\Delta T_m \approx -10.5$ K is remarkably large. We think this is unlikely to be caused by melting of a solvent contaminant as the protonated benzene was extensively purified prior to use and the melting points of possible organic solvent contaminants are not close to this temperature.

Discussion

This first detailed study of C_{60} /benzene solvates by solid-state NMR has shown unexpected behavior by both the benzene and the C_{60} . A stable C_{60} /benzene solvate was made using a novel method. MAS at 8 kHz was found to cause the deterioration of the quality of the NMR spectrum by disrupting the long-range order in the solvate lattice. The peripheral acceleration of sample is probably close to the limit of van der Waals forces holding the solvate together. The results demonstrate that the presence of the benzene solvent within the C_{60} solvate lattice does not hinder the rotation of the C_{60} . The motion of C_{60} in C_{60} /benzene is similar to that in pure C_{60} crystals.^{1,2} We suggest that three kinds of benzene species are present: (i) a majority of the benzene (B1) resides in a porous environment, the nanometer dimensions of which can accom-

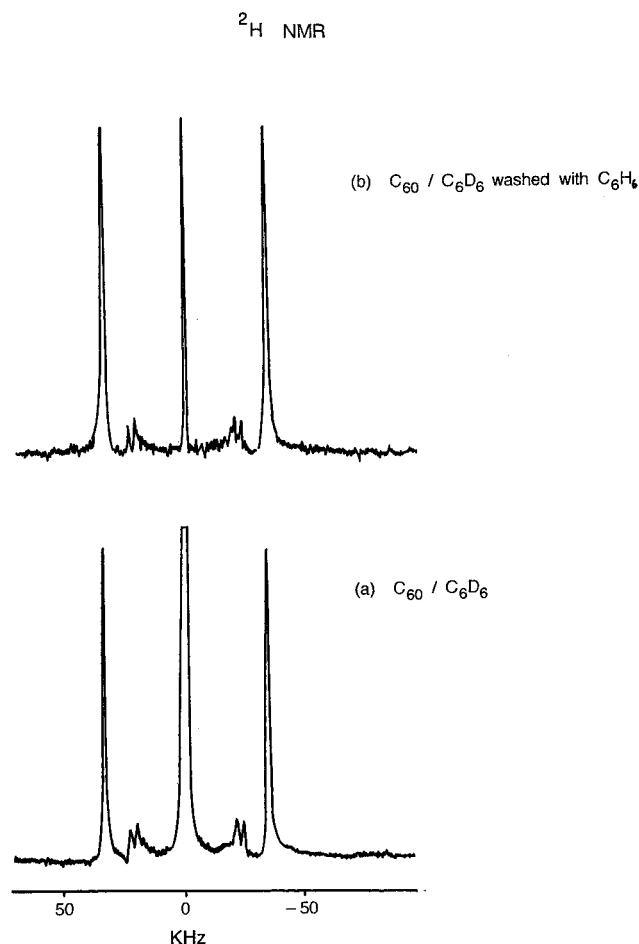


Figure 6. Static ²H NMR spectra: C₆₀/C₆D₆ solvate (a) before and (b) after washing with C₆H₆.

moderate several molecules; (ii) a minor fraction of benzene (B2) resides in a very narrow porous environment in which the benzene molecules are likely to be a freely mobile but essentially isolated species; (iii) another minor fraction (B3) is constrained possibly in the defect sites of the C₆₀ lattice by the C₆₀ molecules.

Free diffusional motion of B1 and B2 benzene molecules appears to be hindered, but they are not physically entrapped. However, the motion of B3 benzene is restricted to rotation around its C₆ hexad axis. A simulation of the ¹³C CP sidebands and static ²H spectra proves the motion of B3 benzene. The B3 species exhibits proton magnetization transfer by cross-polarization both to benzene carbons and to the neighboring C₆₀ molecules. However, the ¹³C NMR lines from all three kinds of benzene are at the same chemical shift. We assign lines B and S in the ¹H MAS spectra to B1 and B2 kinds of benzene, respectively. The porous space occupied by several B1 benzene molecules gives rise to multiple magnetic environments and leads to broad lines. The ¹H line of B3 benzene is probably obscured by other resonances. A similar feature is found in the ²H MAS spectrum: the intensity ratio is very close to that of the ¹H spectra. However, deuterated B3 benzene cannot be observed in the ²H spectra, because the intensity of the line is severely reduced by spinning sidebands in the MAS spectrum and overlaps with other lines in the static spectrum.

Upon washing the deuterated solvate with fresh C₆₀-saturated protonated benzene, the B1 benzene species is completely removed as it resides in a relatively wide porous space, and a small part of B2 benzene still remains in the narrow channels. The premelting point found by ²H NMR further supports this conclusion. By contrast, B3 benzene molecules cannot be

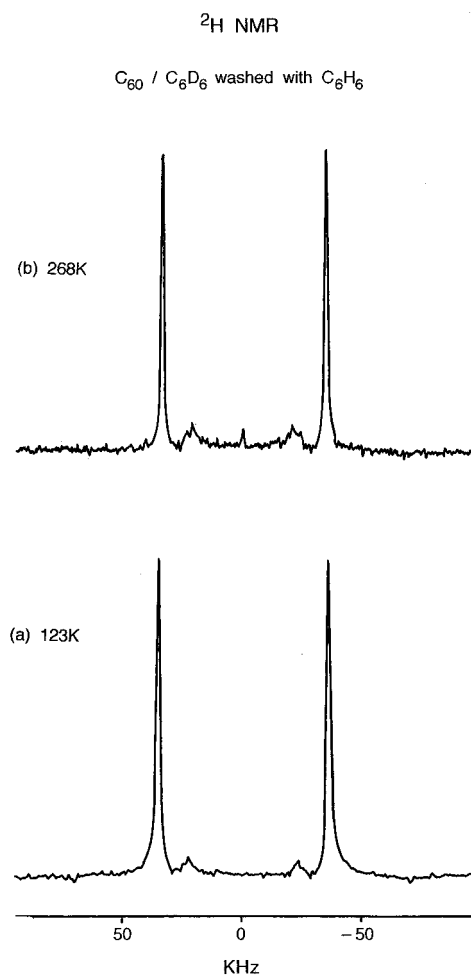


Figure 7. Static ²H NMR spectra: C₆₀/C₆D₆ solvate at (a) 123 K and (b) 268 K on warming.

removed and rotate around their C₆ hexad axes, being constrained by the adjacent C₆₀ molecules.

Our results have implications for the crystal structure of the C₆₀/benzene solvate. It is apparent that multiple magnetic environments exist for the benzene and the structure essentially contains a network of pores of varying dimensions. It has been suggested^{4,5} that the C₆₀/benzene solvate at low temperature consists of disordered one-dimensional columns of C₆₀ with interspersed benzene and this type of structure could qualitatively account for some of the NMR results.

A further consideration arises from the strong optical activity of the solvate crystals. As the majority of intercalated benzene is shown to be readily mobile, no rotation of the plane of polarized light can be generated by the solvent. The published low-temperature structure³⁻⁵ is centrosymmetric and thus not optically active. The room-temperature structure is therefore noncentrosymmetric.

The presence of an isotropic benzoid rotor in C₆₀ powder prepared by crystallization from benzene was previously noted in passing by Maniwa,¹¹ but the effect was too weak to be assigned to benzene rather than some contaminant. From our experience it is likely that major contributors to the previously detected motional hindrance in C₆₀ are due to intercalated solvent contaminants, particularly phthalates.¹⁸

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