Solvent Molecules in Crystalline C$_{60}$

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A set of samples C$_{60}$(cr) was prepared and studied using X-ray diffraction analysis, ^{1}H NMR, differential scanning calorimetry (DSC), and gas adsorption methods for elucidating the state of residual solvents in C$_{60}$. The solvent molecules were found to be adsorbed at interfaces of the microcrystals of C$_{60}$(cr); "sintering" of the microcrystals on heating is assumed to be responsible for entrapping some of the solvent molecules in the sample. This may explain the difficulty of removal of the solvents from fullerene samples. The disappearance of the orientational phase transition in DSC curves of mechanically treated samples was interpreted in terms of space defects in the crystals of C$_{60}$.

1. Introduction

Extraction and chromatographic separation of individual fullerenes are the necessary stages of the fullerene synthesis.[1] In both stages, fullerenes are dissolved in a suitable solvent (usually aromatic) or in a solvent mixture. Fullerite (crystalline fullerene) is obtained after crystallization from the corresponding solution. Crystals prepared by such a technique are used as the starting material for further investigations. The resulting product is usually washed with nonaromatic solvent (ether, hexane) and further annealed in a vacuum or purified by sublimation to remove solvent molecules from fullerite. However, it was shown that residual solvent remains in solid C$_{60}$ even after vacuum treatment of the samples of C$_{60}$ at elevated temperatures.[2] So far, the question of why solvent cannot be completely removed from polycrystalline C$_{60}$ has been unanswered.

The aim of this work is to determine the amount and status of hydrogen-containing components in the samples of fullerite C$_{60}$ prepared under various crystallization conditions and thermally treated afterward. The samples were characterized using X-ray diffraction analysis, ^{1}H NMR spectroscopy, differential scanning calorimetry (DSC), and gas adsorption.

2. Experimental Section

Six series of the samples prepared by different procedures were studied in this work.

2.a. Series A (Crystallization from Benzene). Sample A1 was obtained by quick (2 h) vacuum evaporation of the saturated benzene solution of C$_{60}$. Sample A2 was slowly (2 months) crystallized from benzene solution with a seed.

2.b. Series B (Crystallization from Toluene). Sample B1 was obtained by vacuum evaporation of toluene solution, washed with hexane, and air-dried at 120 °C. Sample B2 was obtained by heating sample B1 at 350 °C for 5.5 h under dynamic vacuum (0.1 Pa). Sample B3 was obtained by heating sample B2 at 380 °C for 5 h under dynamic vacuum (0.1 Pa).

2.c. Series C (Crystals of C$_{60}$ Grown from Toluene Solution). Sample C1 was slowly (2 months) crystallized from

toluene solution with a seed. Sample C2 (crystals (3 × 1 × 0.5 mm)) was slowly (6 months) crystallized from toluene solution without a seed.

2.d. Series D (Polycrystalline C$_{60}$ Grown from Toluene Solution). Sample D1 was obtained by vacuum evaporation (3 L/h) of toluene solution. The formed crystals (0.5 × 0.5 × 0.2 mm) were filtered off, 4-fold washed with hexane, and dried under vacuum (0.1 Pa) at room temperature. Sample D2 was obtained by heating sample D1 at 380 °C for 5 h under dynamic vacuum (0.1 Pa). Sample D3 was obtained by grinding sample D1 in an agate mortar for 1.5 h (a small amount of ethanol was added) with subsequent heating at 350 °C for 5 h under vacuum (0.1 Pa).

2.e. Series F. Series F was obtained by addition of a large amount of hexane to the saturated xylene solution (100 mL of hexane per 10 mL of solution).

2.f. Series S. Sample S1 (crystals of C$_{60}$ (0.5 × 0.5 × 0.5 mm)) was grown by vacuum sublimation in a gradient furnace.

According to the high-performance liquid chromatography (HPLC) data, the content of higher fullerenes and oxides was less than 0.02% for all the samples obtained; the procedure of the HPLC analysis is thoroughly described in ref 3. The X-ray diffraction (a DRON-3M diffractometer, Co Kα radiation) indicates that all samples have reflections corresponding to the face-centered cubic (fcc) lattice.

Static ^{1}H NMR (200.13 MHz) spectra were recorded on a Bruker AC-200 spectrometer at room temperature, a correction being made for blank experiments with an empty ampule. The spectra of the samples exhibit one or two lines with width at half-maximum amplitude $\Delta\nu_{1/2}$ = 300−2400 Hz (except for the spectrum of sample D3 revealing $\Delta\nu_{1/2}$ = 5500 Hz) and chemical shifts 0−10 ppm (Figure 1). These line widths allow one to assign signals in the static ^{1}H NMR spectra to the type of proton, aromatic (6−9 ppm) or aliphatic and water/OH (1−4 ppm).

The concentration of protons in the samples of C$_{60}$ was determined from the integral intensities in the static ^{1}H NMR spectra, with naphthalene solution in CCl$_4$ (0.0115 mol/l) being used as an external standard.

Magic-angle spinning (MAS) ^{1}H NMR was found to be the most informative for studying the nature of the hydrogen-

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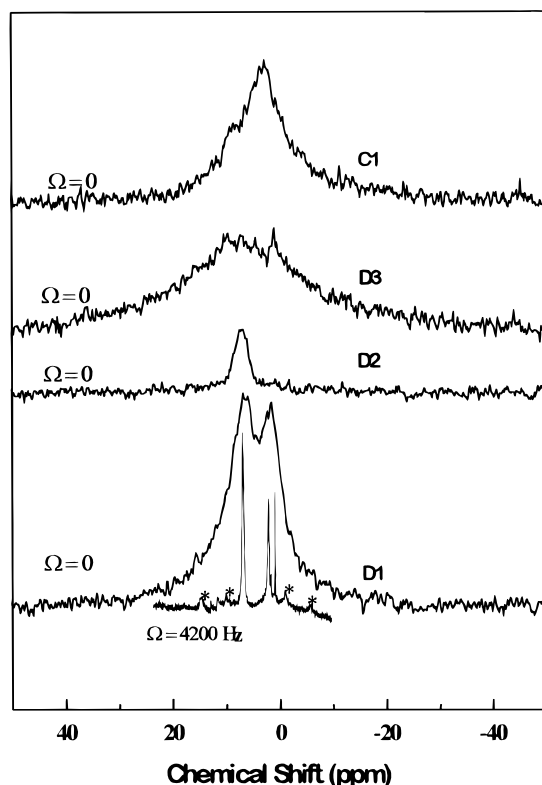
Figure 1. Static ^{1}H NMR spectra for C1, D1, D2, and D3 samples and MAS (Ω = 4200 Hz) ^{1}H NMR spectrum for D1: (i) asterisk denotes sideband from rotation; (ii) two peaks at 7.05 and 2.27 ppm are assigned to the remaining toluene molecules, and one peak at 1.01 ppm is assigned to OH/H$_2$O.

TABLE 1: Concentration of Hydrogen-Containing Impurities in C$_{60}$ Samples

sample	molar ratio H/C$_{60}$	sample	molar ratio H/C$_{60}$
A1	5.0	B3	0.025
A2	0.72	D1	0.21
C1	0.46	D2	0.033
C2	10.6	D3	0.24
B1	0.051	F	0.33
B2	0.025	S1	impurities < 0.005

containing components. The MAS ^{1}H NMR spectra of the samples were recorded on a Bruker MSL-300.

Calorimetric study was carried out with a DSC-7 Perkin-Elmer differential scanning calorimeter in the temperature range 230−298 K.

3. Results and Discussion

3.a. X-ray Diffraction Analysis. The XRD data indicate that all samples have an fcc lattice both before and after heat treatment. The lattice constants for some samples are as follows: C1, 14.121(5) Å; D1, 14.125(7) Å; D2, 14.134(5) Å; S1, 14.119(8) Å.

3.b. ^{1}H NMR. The data on the quantitative determination of the hydrogen-containing impurities in the studied fullerene samples are listed in Table 1. The uncertainty of these data is ±10%. No ^{1}H NMR signal was detected above the background in the spectrum of sample S1, although the accumulation time was significantly prolonged (1024 counts instead of 64 as normally). According to the sensitivity of the spectrometer used, 0.005 mol of protons per mole of C$_{60}$ (or 0.008 wt % of toluene) were estimated as a higher limit for this sample. On the basis

of these data, S1 may be considered nearly free of hydrogen-containing impurities.

The static ^{1}H NMR spectra of samples C1, D1, D2, and D3 are shown in Figure 1. For illustration, the high-resolution MAS ^{1}H NMR spectrum of sample D1 is also presented in this figure.

As seen from Figure 1, the static ^{1}H NMR spectra of samples C1, D1, and D2 show rather narrow lines ($\Delta\nu_{1/2}$ < 2400 Hz), thus indicating a fair mobility of the solvent molecules in the samples. The MAS ^{1}H NMR spectrum of D1 reveals several lines. Based on the literature data on the spectrum of toluene in carbon tetrachloride,[4] the lines at 7.05 ppm (intensity 55%) and 2.27 ppm (intensity 32%) were assigned to toluene. The agreement of the measured chemical shifts with those occurring in the spectrum of toluene in solution may be thought of as another evidence for the "free" behavior of the solvent molecules in sample D1. As for the static ^{1}H NMR spectrum of D3, it exhibits a significantly broader line as compared with the spectra of other samples. From the aforesaid, broadening of the line may be assumed as an indication of immobility of the solvent molecules in this sample. We have no reasonable explanation for the peculiarity of the spectrum of D3, but one can suggest that traces of ethanol, which was used on preparing sample D3, may be responsible for the line broadening; according to the data,[5] the molecules of ethanol can be involved in a stronger interaction with C$_{60}$ molecules than aromatic solvents.

Thus, the ^{1}H NMR data give the evidence that the prolonged vacuum heating of the samples fails to remove completely solvent molecules from fullerite; this is in agreement with the earlier data.[2] On the other hand, the chemical interaction between the solvent molecules and C$_{60}$ was found to be rather weak.

3.c. Adsorption Experiments. The data presented in Table 1 indicate that essential weight loss of the samples occurs upon vacuum heating, whereas the lattice constant of C$_{60}$(cr) remains unaffected. Based on these facts and taking into account a weak interaction of the solvent molecules with C$_{60}$, one may suggest that the solvent molecules are not incorporated into the crystal lattice but tend to be adsorbed at the surface of the microcrystals comprising the crystals of C$_{60}$.

The adsorbed phase is assumed to be a liquidlike one.[6] If this is true, removal of the adsorbed solvent should result in an increase of the specific surface area of a sample. To verify this hypothesis, the following experiments were carried out.

The sample of C$_{60}$ (4.13870 g) previously washed with *n*-hexane was kept in a vacuum for 3 h at room temperature. The weight loss was found to be 0.00735 g. The specific surface area determined by the BET method at liquid nitrogen temperature, with N$_2$ as an adsorbate, was equal to 2.8 m^2/g. After heat treatment (380 °C, dynamic vacuum 0.1 Pa, 5 h), the weight loss and specific surface increase to 0.07490 g and to 3.2 m^2/g, respectively. Further heating at 300 °C for 6 h under dynamic vacuum leads to the weight loss of 0.00670 g, while the specific surface area of the sample remains virtually unchanged, 3.1 m^2/g.

The data obtained may be interpreted as follows. The solvent molecules desorb from the interface of the microcrystals on heating the sample, and the BET measurements indicate an increase in specific surface area. However, upon prolonged heating, there is a possibility for the microcrystals to be "sintered"; in this case, some of the solvent molecules can be entrapped into cavities inside the sintered microcrystals. As a result, the surface of the microcrystals partially turns inaccessible for adsorption of nitrogen, and the BET experiment shows no change in the specific surface area of the sample. It should be

TABLE 2: Characteristics of the Orientational Phase Transition[a]

cooling rate (deg/min)	sample D1		sample D2		sample S1		sample C1	
	ΔH	$-T$ (°C)	ΔH	$-T$ (°C)	ΔH	$-T$ (°C)	ΔH	$-T$ (°C)
0.5	5.93	20.4	5.47	24.8	8.02	18.3	7.02	14.8
1.0	5.75	20.3	6.76	25.5	7.71	18.4	6.85	15.1
2.0	6.56	20.3	5.60	24.3	7.97	18.8	8.21	15.3
5.0	6.85	21.7	6.43	25.0	8.00	19.0	7.62	15.3
10	7.65	26.1	6.74	30.9	8.10	23.2	8.15	20.1

[a] ΔH, enthalpy in J/g; T (°C), onset temperature of the phase transition. The uncertainty in ΔH determination did not exceed 4%. The uncertainty in temperature measurements did not exceed 0.5 deg.

noted that "sintering" of the molecular crystals at elevated temperatures is well-known from the literature.[7,8]

3.d. DSC Data. It is known that parameters of the orientational phase transition of solid C_{60} (260 K) are highly sensitive to residual solvent,[2] degree of crystallinity,[9] particle size,[10] unidentified defects,[11] hydrostatic pressure,[12,13] intercalated gases,[14,15] and stacking faults.[16] With this in mind, we carried out the DSC experiments on samples with fairly high (C1, D1) and low (D2, S1) contents of solvents. Parameters of the orientational phase transition were determined as a function of the scan rate (Table 2) because according to refs 17 and 18 kinetics of the phase transition in C_{60} is the most sensitive to prehistory of the samples. The data obtained for D1 and D2 are in close agreement regardless of a difference in the solvent content in these samples but obviously different from the data for C1 and S1. Indeed, the T_{on} and ΔH values for the first pair of samples are lower compared with those for the second pair. In addition, a correlation between the ΔH values and scan rate is clearly seen for samples D1 and D2; to a lesser degree the correlation is observed for C1 but not observed for S1.

Inasmuch as residual solvents cannot be responsible for such results, it is worthy of note that samples D1 and D2 were prepared under nonequilibrium conditions, whereas the conditions for preparing C1 and S1 may be considered as being nearly equilibrium. Taking this into account, one may suggest that crystals of samples D1 and D2 are far from being perfect and have a significantly higher density of space defects than crystals in C1 and S1. Consequently, the fraction of C_{60} molecules located on the defects in D1 and D2 is larger compared with those in C1 and S1. It is believed that molecules located on defects are in other orientational states than isotropic rotation. This is supported by broadening of the line at 143.4 ppm in static ^{13}C NMR spectrum of a mechanically treated sample of C_{60}, as was demonstrated in our earlier experiments.[19,20]

The decrease in the transition enthalpy due to the decrease in the fraction of freely oriented molecules follows from the simple thermodynamic model of the phase transition in C_{60}(cr) suggested in ref 21. According to this model, the decrease in the fraction of freely oriented molecules will cause the change in the internal energy of the crystal and the decrease in the enthalpy of the phase transition.

In this context, it is of special interest to discuss the properties of sample D3 because mechanical treatment should increase the density of space defects in the crystals of C_{60}. According to the DSC data,[10,22] mechanical treatment of samples of C_{60} increases the temperature interval of the first-order phase transition up to its disappearance. Indeed, in our experiments with D3 no phase transition was seen in the DSC curve.

The following explanation for this result can be offered. It is well established that the C_{60} molecules that are characterized by orientationally disordered rotation in the high-temperature phase ($T > 260$ K) change the nature of their rotation and are engaged into correlated group reorientations in the low-temperature phase. Space defects are likely to disrupt this ideal picture by dividing the phase into numerous regions where local phase transitions take place independently, thus smearing the phase transition in DSC experiments.

4. Conclusions

The results of the study of the series of C_{60} samples prepared by various methods allowed us to draw the following conclusions.

(1) The molecules of solvent are not incorporated into the crystal lattice of C_{60}, but rather are adsorbed at the interfaces of microcrystals.

(2) "Sintering" of the microcrystals upon heating is assumed to be responsible for entrapping some of the solvent molecules in the sample. This may be the reason solvents cannot be completely removed by vacuum heating of samples of C_{60} and only sublimation makes it possible to obtain virtually solvent-free materials.

(3) Disappearance of the orientational phase transition in DSC curves of mechanically treated samples was observed as earlier, with the nature of this effect being explained in terms of the space defects in the crystals of C_{60}.

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