Crystal solvate of C_{60} with tricloroethylene, $C_{60} \cdot C_2HCl_3$

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Extraction of fullerenes from carbon soot by trichloroethylene has been studied. We have found that C_{60} forms a solvate with trichloroethylene ($C_{60} \cdot C_2HCl_3$: a = 31.31(1); b = 10.156(4); c = 10.146(4) Å; V = 3228.6 Å^3, Z = 4, d_{calc} = 1.752 g cm^{-3}, orthorhombic symmetry). Its thermal stability has been studied using TG and DSC. A phase transition of the first order at 167 K has been detected.

Key words: fullerene C_{60}; extraction; thermal stability; TG; DSC; phase transitions.

Selection of solvents for C_{60} and other fullerenes is of considerable interest both in connection with the preparation of fullerene crystals and the study of their structure and physicochemical properties and in connection with the search for selective solvents to extract fullerenes from carbon soot.[1] Toluene and benzene are among the most often used solvents for C_{60}. They form solvates, some of which are isolated as single crystals.[2—4] It is also known that C_{60} gives clathrate-type molecular compounds with many other solvents.[5—7]

Although the stoichiometry and the structure of some of these clathrates have been established, the role of guest molecules in stabilizing these structures is still unclear.[8] The formation of C_{60} solvates sometimes results in suppression of the orientational disorder characteristic of pure C_{60}.[9]

The present work reports data on the preparation of crystals of the solvate of C_{60} with trichhloroethane and studies of their properties by X-ray diffraction, TG, and DSC.

Experimental

Fullerene-containing soot was obtained according to methods used by Kratschmer[10] on an experimental set described earlier.[11] C_{60} was extracted from the soot by toluene followed by column chromatography on graphite (40 × 600 mm, a 20 : 80 mixture of toluene : hexane as the eluent). After the solvent was distilled on a rotary evaporator, the powder of C_{60} was washed with ether and dried at 623 K *in vacuo* for 2 h. The purity of C_{60} was determined by electron spectroscopy (Specord M-40) and HPLC (microcolumn Milichrom-2 chromatograph, UV-detector, λ = 330 nm, a 120×2 mm Silasorb-diol steel column, average particle diameter 9 μm, column capacity 4700 theoretical plates with respect to anthracene, dry hexane as the eluent). IR spectra as KBr pellets were recorded on a Specord M-80 spectrometer.

$C_{60} \cdot C_2HCl_3$ solvate. Pure C_{60} (>98.5 %, 25 mg) was dissolved in 20 mL of trichloroethylene (TCE) with heating (~75 °C). The hot solution was filtered, the mother liquor was cooled to ~20 °C at a rate of ~10 °C h^{-1}, and the solvent was slowly evaporated for 3 to 4 days. The crystals obtained were filtered off (black prisms up to 3 mm in length, Fig. 1), washed with alcohol, and dried *in vacuo* at ~20 °C. Found (%): C, 87.55; H, 0.09; Cl, 12.52. $C_{62}HCl_3$. Calculated (%): C, 87.39; H, 0.12; Cl, 12,49. IR spectrum (ν/cm^{-1}): C_{60}, 527, 577, 1180, 1429; C_2HCl_3, 628, 777, 838, 925.

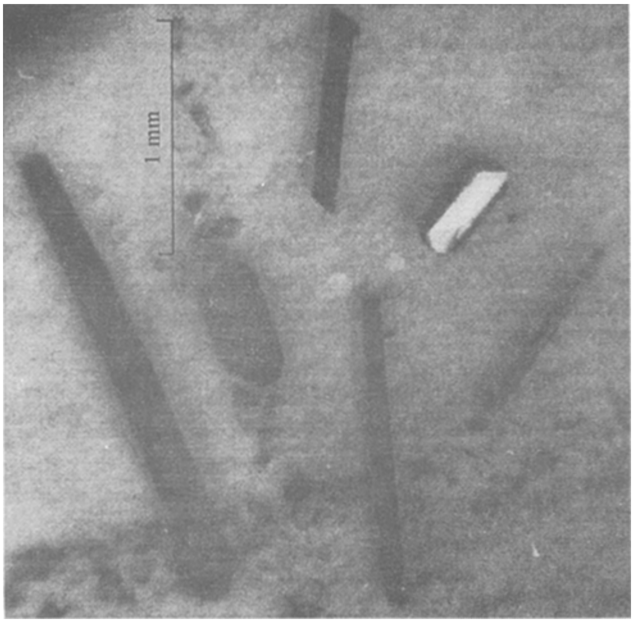

Fig. 1. Crystals of $C_{60} \cdot C_2HCl_3$.

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The unit cell parameters and the intensities of 2058 independent reflections (250 with $I > 2\sigma(I)$) for the $C_{60} \cdot C_2HCl_3$ crystal were measured on a four-circle automatic KM-4 KUMA DIFFRACTION diffractometer at room temperature (monochromatic Mo-Kα radiation, ω/2θ scan technique). The low-temperature X-ray diffraction experiments were carried out on a semiautomatic three-circle DAR-UM diffractometer.

The calorimetric experiments were carried out on a "Mettler" DSC-30 differential scanning calorimeter (Switzerland).

The calorimeter was temperature calibrated with the following materials: hexane, water, gallium, indium, *p*-nitrotoluene, lead, zinc. Five scannings for each were made in aluminum crucibles under an argon atmosphere at the rate of 10 K min^{-1}. The sample weight was 13.650±0.002 mg. Samples heated from 103 to 298 K.

Thermogravimetric analysis was performed on "Mettler" thermobalances (Switzerland) under an argon atmosphere, in the temperature range 308—1223 K at a heating rate of 25 K min^{-1}.

Results and Discussion

The study of the extraction of fullerenes from carbon soot by different solvents showed that in the case of trichloroethylene the extract contained considerable amounts of TCE (>12 %), which could be removed by annealing the extract *in vacuo* at 623 K (Table 1). This was confirmed by the elemental analyses for Cl and by the IR spectra before and after annealing. The IR spectrum of the nonannealed extract shows bands of TCE. C_{60} gives rather a stable solvate with TCE, which is probably in agreement with the somewhat higher selectivity of TCE to C_{60} compared with toluene and benzene (see Table 1).

During slow evaporation of the solution of C_{60} in TCE, $C_{60} \cdot C_2HCl_3$ crystals (see Fig. 1) with rhombic symmetry are formed. Table 2 gives their unit cell parameters at 296 and 198 K. When the temperature is decreased further (below 198 K), significant changes in the intensities of the control reflections, *hkl* (14.1.0) and (15.1.0), are observed. At 163 K these changes become maximum and the crystal symmetry is changed.

These results indicate that the phase transition is a first order transition and agree with the DSC data. Figure 2 gives a typical calorimetric curve of the $C_{60} \cdot C_2HCl_3$ crystals.

Table 1. Comparative characteristics (%) of the extracting ability of benzene, toluene and TCE with respect to C_{60}

Solvent	The yield of extract after treatment with ether	Amount of C_{60} in the extract	Loss of the extract upon annealing
Benzene	9.3	85.0	3.2
Toluene	11.6	85.0	3.9
TCE[a]	19.2	89.3	12.7

[a] The solubility of C_{60} in TCE is 1.48 mg mL^{-1} and is close to that in benzene.

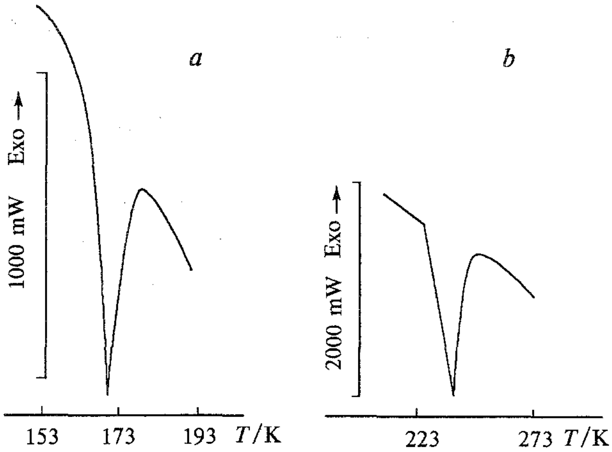

Fig. 2. DSC curves for the initial $C_{60} \cdot C_2HCl_3$ crystals (*a*) and the crystals preheated at 673 K to the constant weight (*b*).

The presence of a distinct endothermic peak in the temperature range 157—174.5 K unambiguously attests to a phase transition. The temperature of the peak maximum is 167 K; the transition heat is ΔH = 2.75±0.6 J g^{-1}. The phase transition is obviously connected with the orientational ordering of the C_{60} molecules in the crystal solvate, as is the case for the crystals of pure C_{60} and some other C_{60} solvates of the clathrate type. However, compared with pure C_{60}, the transition to $C_{60} \cdot C_2HCl_3$ occurs at a lower temperature (250 and 167 K, respectively). Probably it is due to the orientational disorder that the $C_{60} \cdot C_2HCl_3$ crystals gave a small number of observed reflections in the X-ray diffraction experiment, which did not allow us to solve their structure.

We also studied the stability of the $C_{60} \cdot C_2HCl_3$ crystals at elevated temperatures, 308—1223 K, by the thermogravimetric method (Fig. 3). The TG and DTG curves show two temperature intervals where the sample loses weight. The first one (379.3—523 K, Δm = 14.97 %) corresponds to complete removal of TCE from the crystals, which is confirmed by microanalysis and IR spectroscopy data. The IR spectrum of the sample preheated to 673 K only shows the bands of pure C_{60}. The second temperature interval (992.8—1223 K, Δm = 81.9 %) corresponds to the process of C_{60} sublimation.

The sample preheated to 673 K to remove TCE was analyzed on a calorimeter. It should be noted that after

Table 2. Unit cell parameters of the rhombic $C_{60} \cdot C_2HCl_3$ crystals at different temperatures

Parameter	296 K	198 K
a/Å	31.33(1)	31.210(7)
b/Å	10.155(4)	10.077(3)
c/Å	10.146(3)	10.087(3)
V/Å^3	3228.6	3172.4
Z	4	4
d_{calc}/g cm^{-3}	1.752	1.783

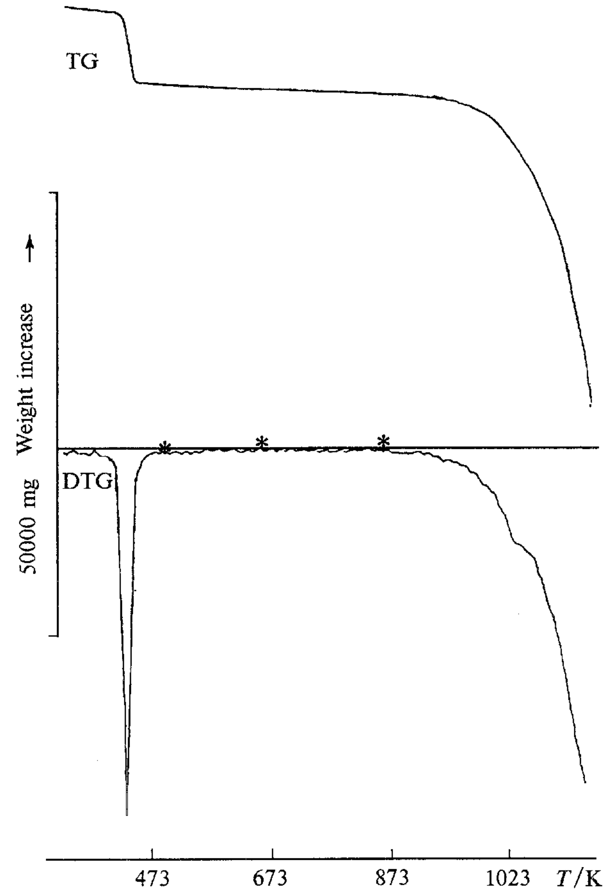

Fig. 3. TG and DTG curves for the $C_{60} \cdot C_2HCl_3$ crystals.

thermal pretreatment the crystals lose their lustre and their surface becomes porous, although they retain their initial shape.The calorimetric curve (see Fig. 2) shows an endothermic peak in the temperature range 223—253 K. The peak maximum corresponds to 240 K and the enthalpy change $\Delta H = 4.8\pm0.6$ J g^{-1}. The phase transition is broader and its temperature and ΔH are lower than for the pure cubic C_{60} crystals. After removal of TCE, the samples become strongly disordered and do not give any reflections on Lauegrams unlike the initial solvate crystals. The presence of considerable disorder in the thus-obtained C_{60} samples obviously leads to broadening of the phase transition temperature range and changes in its characteristics.

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