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THERMAL STABILITY OF C_{60}-METHYLNAPHTHALENES SOLVATES

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Abstract

The crystalline solvates containing fullerenes and (di)methylnaphthalenes were investigated by thermal analyses and X-ray diffraction methods. It was found that C_{60} with (di)methylnaphthalenes forms two types of stable solvates: either at the molar ratio 1:2 decomposing at temperatures close to 100°C or at 1:1 molar ratio decomposing in the temperature range 120–214°C. Crystalline lattice and thermal stability of the solvates depends on the structure of the solvent molecules. The strong solute-solvent interaction is also manifested by the modification of the C_{60} absorption spectra in solution. The results are discussed using semiempirical quantum chemistry methods.

Keywords: C_{60}-methylnaphthalenes, thermal stability

Introduction

High density of π-electron on the C_{60} fullerene cage leads to a strong interaction between fullerenes with organic solvents rich in π-electron. This interaction distorts distribution of electrons on C_{60} and is observed as an activation of electronic transitions in ultraviolet and visible ranges [1]. It may be expected, that in the solid solvates the proximity of both components results in substantial deformation of the molecules and an overlap of molecular orbitals, which in turn might result in a charge transfer or in closing of the energy gap. We searched for such solvents which form crystallites with C_{60} because it allowed us to determine positions of molecules in the lattice.

We used the following solvents for our experiments: 1-methylnaphthalene (1-MNAP) and dimethylnaphthalenes (DMNAP: 1,3-DMNAP, 1,4-DMNAP and 1,7-DMNAP). These solvents strongly modify the C_{60} absorption spectra in solutions. Such a strong influence on the C_{60} absorption probably arises from the coincidence of three absorption bands in methylnaphthalenes in the region of

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250–340 nm (which were labelled by Clar [2] as α, *p* and β) with C_{60} bands labelled by Leach *et al.* [3] as C, D and E. According to Gallagher *et al.* [1], presence of absorption bands at similar wavelengths in different types of molecules promotes intermolecular interaction. Because the intensity and position of the α and *p* bands depend on the structure of the DMNAP isomers, one can hope to find such an isomer or a derivative, which most strongly interacts with C_{60}.

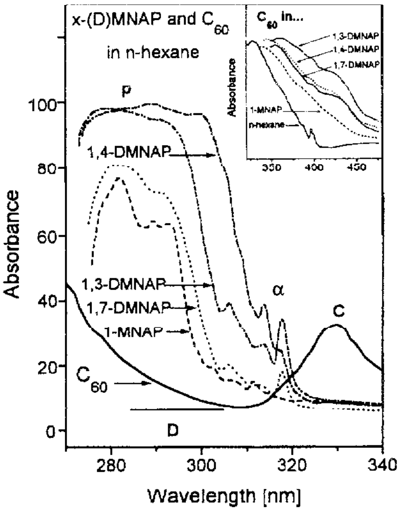

Fig. 1 Absorption spectra of (D)MNAPs and C_{60} in *n*-hexane. The insert presents the absorption spectra of C_{60} dissolvent in (D)MNAP and in *n*-hexane

The absorption spectra of C_{60} dissolved in (D)MNAP is compared in Fig. 1 with the absorption of C_{60} dissolved in *n*-hexane, close to the first electronic transitions in fullerene. We have computed the energy levels and electronic transitions in a complex consisting of one C_{60} and one (D)MNAP in order to illustrate the influence of the solvent molecule on C_{60} simulating to some extent situation in the solution. The calculation were started with optimising both molecules using the semiempirical AM1 model, which well reproduces fullerenes and DMNAP geometry giving the 5–6 and 6–6 bonds lengths in C_{60} equal to 0.1464 and 0.1385 nm respectively. For these calculations one can use alternatively PM3 semiempirical quantum chemistry model because both methods return the same bond lengths in molecules discussed here. In the next step ZINDO/S model [4] was used to calculate the electronic transitions. Comparison of the electronic transitions calculated for the isolated C_{60}, C_{60}:1,4-DMNAP complex and measured absorption of C_{60} in *n*-hexane solution is shown in Fig. 2. Within this picture, skeletons of both molecules retain their symmetries and all changes in the optical transitions result solely from a small distortion of the charge distribution on the molecules.

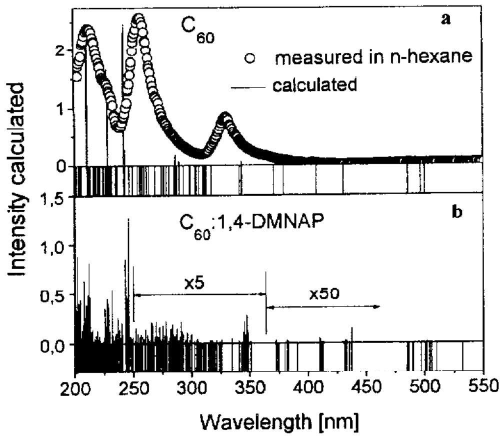

Fig. 2 Comparison of C_{60} absorption measured in *n*-hexane with position and intensity of singlet electronic transitions calculated within the terms of ZINDO/S model for isolated C_{60} (a) and C_{60}:1,4-DMNAP complex (b)

Thermal and structural analyses

The powder samples were prepared by grinding of the C_{60} powder with small amount of respective solvent. As it was found during the thermodynamic experiments (TG, DSC), C_{60} forms crystalline solvates with dimethylnaphthalenes (DMNAP) of either 1:1 or 1:2 molar ratio, their crystalline structure was determined by the X-ray powder diffraction measurements. The stability at elevated temperatures and composition of crystalline samples were analysed with the DuPont 1090 Thermal Analyser. The decomposition of the 1:1 solvates begins above 120–220°C, and of the 1:2 solvates above 80–110°C. The two steps of the process can be observed either by the DSC or TG methods (Figs 3 and 4). Both steps are best resolved in the case of C_{60} $(1,4\text{-DMNAP})_2$ solvate (Fig. 4). In the first sharp transition at 112°C one of 1,4-DMNAP molecule is released, then, as it is proved by the X-ray diffraction, the solvate adopts another crystalline structure. In the second step with a peak at 214°C, the second molecule is freed. Between these two minima there is a broad minimum due to the evaporation of the solvent molecules released in the first transition. The enthalpy change of the decomposition exceeds evaporation enthalpy of the pure solvent. The lattice stabilisation energy of the solid phase of 1:1 solvate can be evaluated from the difference of the respective enthalpies, it is of the order of E_s=0.2eV/(C_{60}·(D)MNAP). The parameters determined from the thermal processes in all investigated solvates are listed in Tables 1 and 2.

Because the structural data were obtained from the powder X-ray diffraction therefore we were unable to determine unambiguously the unit cell, we may only

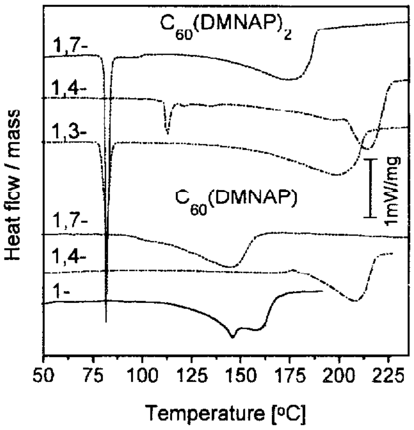

Fig. 3 Heat flow during decomposition of $C_{60}((D)MNAP)_2$ and $C_{60}(D)MNAP$ sample

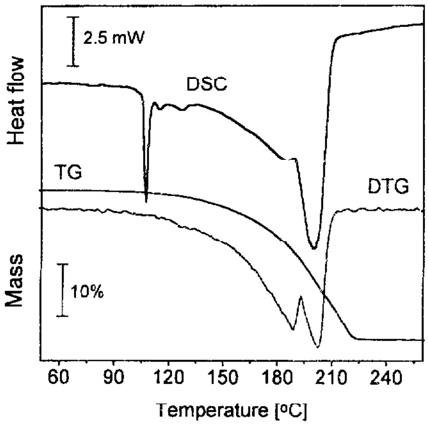

Fig. 4 DSC, TG and DTG curves for crystalline samples of $C_{60}(1,4\text{-}DMNAP)_2$

propose possible arrangement of molecules in the lattice. The powder diffraction patterns were indexed with the use of the TREOR program. According to these results all the solvates crystallise in a triclinic lattice differing slightly in lattice constants and angles. The unit cell of $C_{60}(D)MNAP$ solvates contains 2 fullerenes and 2 (D)MNAPs.

The unit cell of the 1:2 solvates is similar but contains two additional solvent molecules. In the 1:2 lattice, each fullerene has its six not equivalent C_{60} neighbours and eight DMNAP neighbours. Small differences in the shape of the solvent molecules are responsible for variation of the parameters of the lattice.

Table 1 Data of thermal decomposition of C_{60}(D)MNAP

C_{60}(D)MNAP	Decomposition 1:1	
	T/°C	ΔH^r
1-MNAP	145	79.2
1,3-DMNAP	120	77.7
1,4-DMNAP	214	76.1
1,7-DMNAP	143	72. 8

Table 2 Data of thermal decomposition of $C_{60}(DMNAP)_2$

$C_{60}(DMNAP)_2$	Transition: 1:2 → 1:1		Evaporation of released DMNAP	
	T_1/°C	ΔH	T_2/°C	ΔH^r
1,3-DMNAP	81	12.8	199	67.6
1,4-DMNAP	112	8.3	199	61.5
1,7-DMNAP	81	16.2	175	60.0

We used the molecular mechanic model MM2 [5] in order to optimise structure of the molecules in the lattice determined by the X-ray diffraction. The optimisation procedure leads to a deformation and rotation of DMNAP molecules from their original orientation. Probably the decomposition of the 1:2 solvates, which occurs at so low temperatures as such a sharp well-defined endothermal effect is induced by relaxation of the strained solvent molecules.

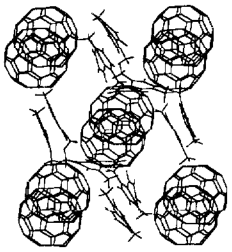

Fig. 5 Proposed arrangement of molecules in the unit cell of $C_{60}(1,4\text{-}DMNAP)_2$ solvates optimized with the MM2 model

We also evaluated the influence of dense packing of molecules on the molecular energy levels in the 1:2 solvates using semiempirical quantum chemistry method ZINDO/S. According to those results, the molecular orbitals extend over the whole complex, the HOMO-LUMO gap decreases by 2.5 eV relatively to the isolated C_{60} and charge is shifted towards fullerene, which in the case of $C_{60}(1,4\text{-}DMNAP)_2$

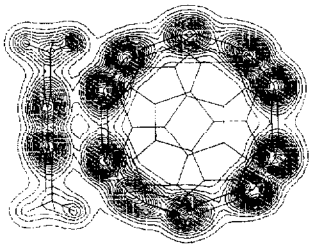

Fig. 6 Isosurfaces of charge distribution over the C_{60}:1,4-DMNAP complex

acquires a negative charge of up to 0.6 e. Illustaration of the charge distribution is shown in Fig. 6. It ought to be mentioned here, that the charge shift is very sensitive to the relative position of both molecules and calculated for larger complex may differ from the value given above.

Conclusions

The fullerene with (di)methylnaphthalenes forms two types of stable solvates: the 1:2 decomposing at low temperatures and the 1:1 that decompose at higher temperatures. Small differences in the structure of the solvent molecules influence crystalline lattice and thermal stability of the solvates. Probably the strong solute solvent interaction observed in ultraviolet and visible light promotes crystallisation of C_{60}(D)MNAP and very dense packing of the molecules. It leads to deformation of molecules affecting the energy of molecular orbitals and to lowering of the HOMO-LUMO energy gap.

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