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Donor–acceptor interaction of fullerene C_{60} with triptycene in molecular complex TPC·C_{60}

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Abstract

A molecular complex of fullerene C_{60} with triptycene, TPC·C_{60} is obtained. The complex has a three-dimensional packing of C_{60} molecules. According to the IR spectra, the freezing of free rotation of C_{60} molecules in the complex is maintained up to 360 K. The XP-spectra of TPC·C_{60} show the suppression of $\pi-\pi^*$ transitions of TPC phenylene rings. The separation of C_{60} molecules by TPC ones in TPC·C_{60} results in low intensity of the C_{60} transitions in the 420–500 nm range in an optical spectrum. This absorption is assumed as that attributed to intermolecular transitions between adjacent C_{60} molecules.

Keywords: Molecular complexes; Fullerenes; Crystal structure; Donor–acceptor interaction; Infrared and UV–VIS-spectroscopy; Photoelectron spectroscopy

1. Introduction

Fullerenes as π-acceptors form donor–acceptor complexes with different types of organic and organometallic donors such as substituted tetrathiafulvalenes [1–4], tetraphenylpyranylidene [5], hexamethoxytriphenylene [6], metal containing tetraphenylporphines [7,8] and others [2,9]. The donors with the concave shape are of special interest. Few complexes of C_{60} with such donors are known, namely, the complexes with semi-spherical molecules (cyclotriveratrylene [10] and tetramethyldibenzo-[*b*,*i*][1,4,8,11]-tetraazacyclo-tetradecinenickel (II) [11]), and the molecules with a 'double butterfly' shape (*trans*-9,9′-bis(telluraxanthenyl) [12] and dianthracene [13]). The shapes of these donor molecules conform to the spherical shape of the C_{60} one providing multiple Van der Waals contacts between donor and C_{60} molecules in these complexes [12–13]. The TPC molecule consists of three phenyl rings with an angle of 120° between each pair of rings (see Fig. 1) and also corresponds to the C_{60} sphere.

In this paper, we report the synthesis, thermogravimetry, X-ray photoelectron spectra, IR and optical absorption spectra for single crystals of the C_{60} molecular complex with triptycene, TPC·C_{60}. The crystal structure of the complex is described and some peculiarities of the donor–acceptor interaction of C_{60} with triptycene in the complex are discussed.

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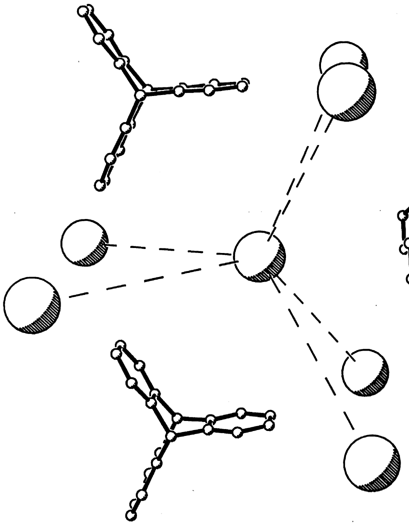

Fig. 1. The mutual orientation of TPC and C_{60} molecules in TPC·C_{60}. The C_{60} molecules are marked by spheres.

2. Experimental

TPC was purchased at Aldrich (98%). The crystals of TPC·C_{60} were obtained by evaporation of C_{60} and TPC benzene solution under argon. The TPC·C_{60} crystals were washed by ether and dried in air. The crystals appear as elongated pyramids with the 20% yield. The composition of the complex was determined from the X-ray analysis.

The IR spectra were measured for C_{60} and TPC in KBr pellets and for TPC·C_{60} single crystals. X-ray photoelectron (XP) spectra were excited by Mg-Kα-radiation (h$\nu = 1253.6$ eV). The reflectance spectra of TPC·C_{60} and C_{60} single crystals were measured with a two-beam specrtoreflectometer in the 250–1100 nm range. The absorption spectra were derived by the Kramers–Kronig transformation of the reflectance spectra. To make this transformation possible, we extrapolated the reflectance spectra as a constant to a low-energy range and as a sum of C_{60} oscillators to a high-energy range suggesting that a major part of intensity of the complex excitations are contributed by C_{60} molecules.

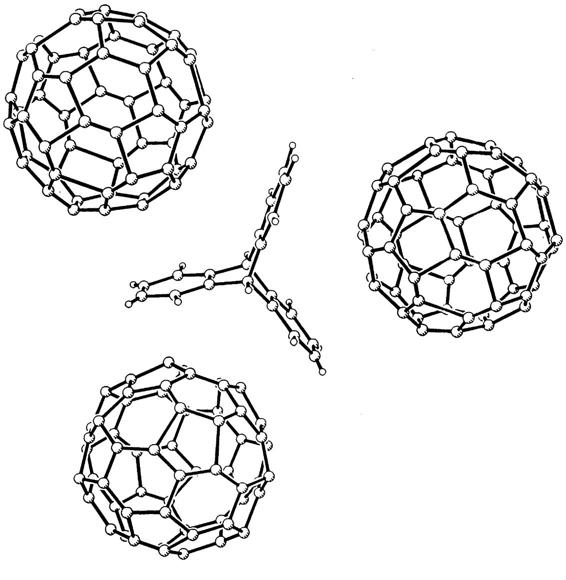

Fig. 2. The coordination of one TPC molecule with three fullerene C_{60} ones in the crystal structure of TPC·C_{60}.

3. Results and discussion

TPC·C_{60} has the following unit cell parameters: tetragonal, space group $I_{4(1)}$/amd, $a = 13.296(9)$ Å, $c = 46.37(5)$ Å, $V = 8200(10)$ Å^3, $z = 8$ [14].

The mutual orientation of TPC and fullerene molecules in TPC·C_{60} are shown in Fig. 1. Each fullerene molecule has six closest fullerene neighbors in an approximately trigonal prismatic arrangement with 10.17 Å distances between the centers of the C_{60} spheres. This distance is close to the Van der Waals diameter of the fullerene molecule (10.18 Å) but is essentially larger than that in C_{60} crystals (10.02 Å [15]). Thus fullerene molecules form a unique three-dimensional framework. Each C_{60} molecule is also surrounded by three TPC molecules arranged in the vertices of an equilateral triangle.

Triptycene molecules form chains in the cavities of the fullerene framework. Each triptycene molecule has Van der Waals contacts with three fullerene molecules (see Fig. 2) retaining its initial geometry.

Thermogravimetry revealed a partial decomposition of TPC beginning with 575 K (21.7% loss of mass), i.e. the same temperature as the decomposition temperature of the individual donor. The loss of mass, which began at 875 K, is due to the C_{60} sublimation.

The IR spectrum of TPC·C_{60} is a superposition of those of C_{60} and TPC (Fig. 3). The most intensive absorption bands of TPC at 741, 797, 1164, and 1456 cm^{-1} are shifted by 2–4 cm^{-1} relatively to their position in the spectrum of individual TPC. Nevertheless, the shifts of the absorption bands are observed for C–H vibrations of phenyl rings at 3000–3100 cm^{-1} (up to 6 cm^{-1}) and for tertiary C–H vibrations at the 2950–2980 cm^{-1} (up to 20 cm^{-1}) (Fig. 3a). Apparently, the C–H vibrations of TPC are especially sensitive to coordination with C_{60}.

The C_{60} bands also reflect the interaction with TPC. The $F_{1u}(3)$ mode of C_{60} at 1182 cm^{-1} is wider (7 cm^{-1}) than that in the IR spectrum of the C_{60} crystals. It is most probably due to the disorder of C_{60} molecules in the TPC·C_{60} crystals.

It is known [16] that IR-active F_{1u} modes of C_{60} are threefold degenerated and the lowering of C_{60} symmetry results in the appearance of two or three components instead of a single band. The $F_{1u}(4)$ band is especially sensitive to these changes. A multi-component $F_{1u}(4)$ mode was observed in the spectrum of C_{60} crystals at temperatures lower than the temperature of the orientational phase transition (255 K) [16] and for C_{60} complexes with amines at room temperature [17]. This fact is explained by the lowering of local symmetry of C_{60} due to the transition from free to freezing rachet rotation of C_{60} molecules [16].

The $F_{1u}(4)$ mode for TPC·C_{60} is split into two components with the maxima at 1425 and 1431 cm^{-1} (Fig. 3b). This splitting is also observed even at high temperature (360 K). In the case of TPC·C_{60}, the splitting of the $F_{1u}(4)$ mode is also associated with the lowering of local symmetry of C_{60} at the freezing of free rotation of C_{60} molecules due to the intermolecular interaction with TPC molecules. The temperature at which the freezing rachet rotation of C_{60} molecules remains in TPC·C_{60} is higher than that for C_{60} crystals [12] and some other C_{60} complexes [18]. The correspondence of the shapes of TPC and C_{60} molecules obviously promote the formation of multiple C(TPC)–C(C_{60}) Van der Waals contacts.

Optical absorption spectra of TPC·C_{60} and C_{60} single crystals are shown in Fig. 4. The absorption spectrum of TPC in KBr pellets showed that its absorption bands lie at the wavelengths less than 250 nm, therefore the absorption in the measured range is attributed to C_{60}. The two most intensive bands at 265 and 345 nm are the same as for C_{60} crystals, however, the absorption at 420–500 nm (3.0–2.5 eV) shows considerably lower intensity. The absorption in this range is attributed to dipole-forbidden HOMO–LUMO transition in one C_{60} molecule [19] or intermolecular HOMO–LUMO transitions between adjacent C_{60} molecules [20].

The distances between the centres of C_{60} molecules in TPC·C_{60} (10.17 Å) are larger than that in C_{60} crystals (10.02 Å), due to the separation of the C_{60} molecules by TPC ones. In this case, the overlapping

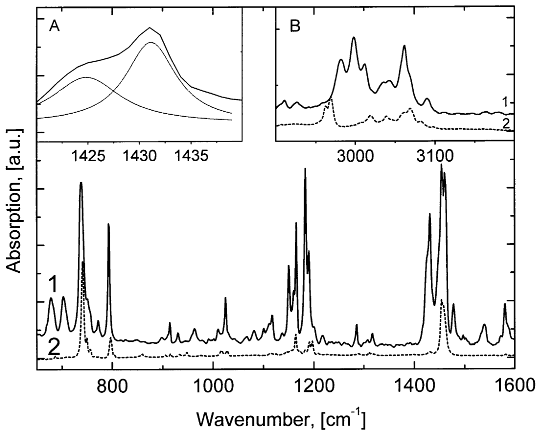

Fig. 3. IR spectra of TPC·C_{60} (1) and TPC (2) single crystals in the 650–1600 cm^{-1} range. (a). IR vibration bands of C–H bonds of donor in TPC·C_{60} (1) and in pure TPC (2) at 2900–3200 cm^{-1}. (b). The C_{60} $F_{1u}(4)$ mode in the TPC·C_{60} complex.

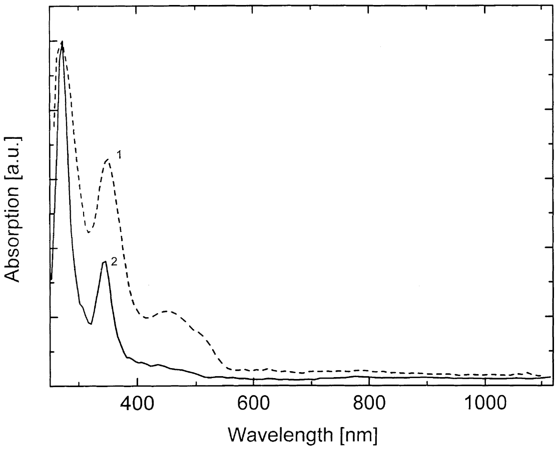

Fig. 4. Optical absorption spectra of TPC·C_{60} (2) and C_{60} (1) single crystals.

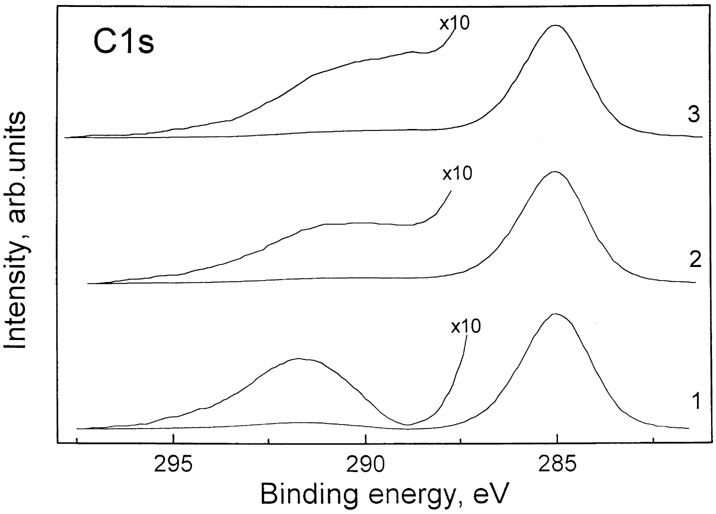

Fig. 5. X-ray photoelectron C1s spectra of TPC (1), TPC·C_{60} (2) and solid C_{60} (3).

of HOMO–LUMO of adjacent C_{60} molecules in TPC·C_{60} is weaker than that in C_{60} crystals. Dependence of the intensity of C_{60} absorption at 420–500 nm on the distances between C_{60} molecules testifies that this absorption can be, more likely, attributed to the intermolecular HOMO–LUMO transitions.

The charge transfer band is not detected in the absorption spectrum of TPC·C_{60}. X-ray photoelectron C1s spectra of TPC, TPC·C_{60}, and solid C_{60} are presented in Fig. 5. The satellite structure is observed near photoelectron C1s peak in all the spectra. In the case of TPC, the satellite structure appears as a peak with a well-pronounced maximum. The results of the Gaussian-fit of this satellite peak are given in Table 1. The values of the parameters indicate that this satellite is attributed to the π–π^* transitions in "pseudophenyl" rings (see, for example [21]). In the case of solid C_{60} and TPC·C_{60} the satellite peaks were not well pronounced. Different fits of the spectra with two Gaussians yield somewhat different fitting parameters for the satellite peaks. The averaged results of the fit are presented in Table 1.

Table 1
The Gaussian fitting of C1s spectra of the compounds

Compound	Peak	Area (%)	Width (eV)	Loss-energy (eV)
C_{60}	1	73	1.64	–
	2	27	6.70	3.16
TPC·C_{60}	1	78	1.73	–
	2	22	6.70	3.06
TPC	1	9	1.84	–
	2	09	3.14	6.73

The Gaussian line approximation of the TPC·C_{60} spectrum assumes that the π–π^*-plasmon characteristic of TPC disappears or changes its nature. One could suggest that the loss channel characteristic of TPC is suppressed in TPC·C_{60} due to the TPC and C_{60} intermolecular interaction.

All plasma oscillations of valence electrons are also observed in the XP-spectra. The values of the ($\sigma(\pi)$) plasmon energy [$\hbar\omega_p(\sigma + \pi)$] determined from the XP-spectrum of TPC·C_{60} is equal to 25.8 eV, in accordance with Ref. [21]. The calculation of the energy in terms of the free electron model ($\omega_p = 4\pi n e^2/\mathrm{m})^{1/2}$, where n is valence electron density, e and m are electron charge and mass, respectively) yields 21.3 eV for TPC·C_{60} since n is equal to 0.326 $\mathrm{\AA}^{-3}$ as it follows from the structural data. The value of the δ-parameter [$\delta = 1 - \hbar\omega_p(\text{theory})/\hbar\omega_p(\text{expt})$] for TPC·$C_{60}$ is equal to 0.18. For solid C_{60} δ is also equal to 0.18 [3]. This evidences that ($\sigma(\pi)$ plasmon of TPC·C_{60} is delocalized to the same extent as in the case of solid C_{60}.

4. Conclusions

A complex of fullerene C_{60} with triptycene was obtained here. Due to weak donor properties of TPC (its first ionization potential is 7.89 eV [22]) noticeable charge transfer in TPC·C_{60} is absent and this compound may be attributed to molecular complexes. The complex is formed mainly by polarization Van der Waals forces. The intermolecular interaction of C_{60} with TPC results in the freezing of free rotation of C_{60} molecules in a crystal even at high temperature (360 K). The interaction with C_{60} manifested itself in considerable changes in the positions of vibrations of C–H bonds. The XP spectra of TPC·C_{60} demonstrate the suppression of the $\pi \rightarrow \pi^*$ transitions of phenylene rings characteristic of TPC are suppressed. A considerable lowering of the intensity of C_{60} transitions in the 420–500 nm range is observed in optical absorption spectra due to the increase of the C_{60}–C_{60} distances in the complex relatively to C_{60} crystals. The dependence of the intensity of these transitions on the distances between the C_{60} molecules allows these transitions to be attributed to intermolecular HOMO–LUMO transitions between adjacent C_{60} molecules. All these features seem to be typical for other C_{60} molecular complexes formed by donor molecules corresponding in shapes to the spherical C_{60} one.

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