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Molecular complexes of fullerene C_{60} with aromatic hydrocarbons Crystal structures of $(TPE)_2C_{60}$ and DPA·C_{60} ☆

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Abstract

New C_{60} molecular complexes with aromatic hydrocarbons containing flexible phenyl substituents, $(TPE)_2C_{60}$ (TPE = tetraphenylethylene), DPA·C_{60} (DPA = 9,10-diphenylanthracene), and PA·C_{60}·C_6H_6 (PA = 9-phenylanthracene) have been synthesized. Crystal structures of $(TPE)_2C_{60}$ and DPA·C_{60} have been solved. It has been shown that in both structures the layers of the C_{60} molecules alternate with the layers composed of the donor ones. The phenyl substituents of hydrocarbons occupy the cavities formed upon the spherical C_{60} molecules packing in the layer. The IR spectra indicate the complexes to have a neutral ground state, while the UV-Vis spectrum of DPA·C_{60} shows a weak charge transfer band with the maximum at 630 nm.

Keywords: Molecular complexes; Fullerenes; Aromatic hydrocarbons

1. Introduction

Recently a great number of fullerene complexes with various types of donor molecules [1–9], in particular, aromatic solvents as benzene [3,4], toluene [5], *o*-xylene [6] and methyl-substituted naphthalenes [7] have been studied. Nonplanar hydrocarbons, namely, dianthracene and triptycene also form complexes with fullerenes due to steric conformity of their shapes to the spherical surface of the C_{60} molecule [8–10].

Fullerene complexes with aromatic hydrocarbons have various structures, are thermally stable and, therefore, can be promising in intercalation by alkali metals [11]. Intercalation of such complexes by alkali metals can result in fullerene or aromatic hydrocarbon reduction [12] followed by the formation of the $(D^-{\cdot}C_{60}^-{\cdot}nM^+)$ compounds containing both hydrocarbon and fullerene radical anions.

This paper reports the synthesis of the first C_{60} complexes with aromatic hydrocarbons comprising flexible phenyl substituents and a planar anthracene fragment (**2** and **3**), namely, tetraphenylethylene (TPE); 9,10-diphenylanthracene (DPA); and 9-phenylanthracene (PA) $(TPE)_2{\cdot}C_{60}$ (**1**), DPA·C_{60} (**2**) and PA·C_{60}·C_6H_6 (**3**). Crystal structures of $(TPE)_2C_{60}$ and DPA·C_{60} were solved. IR- and UV-Vis spectra of the complexes were studied.

2. Experiment

Fullerene C_{60} of 99.5% purity grade was used. Benzene was distilled over sodium in argon atmosphere. The complexes were prepared by evaporating benzene solution containing C_{60} and an appropriate donor at a 1:3 ratio during a week in argon atmosphere. The solvent was decanted from the resulting crystals before precipitating the excess of the donor. Compounds **1** and **2** crystallize as prisms with the 80 and 70% yield, respectively. Crystals of **3** were prepared as plates with the 90% yield.

The IR spectra were registered by a "Perkin Elmer 1725X" spectrophotometer using KBr pellets in the 400–7000 cm^{-1} range. Thermogravimetric (TG) analysis was performed using a "Q-1000" derivatograph and quartz bowls in the argon flow at 298–1273 K.

Crystal data for **1**: $C_{112}H_{40}$, M = 1385.50, monoclinic, space group *C2/m*. The unit cell parameters are: $a =$

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10.4757(7) Å, $b = 32.920(2)$ Å, $c = 10.3173(7)$ Å, $\beta = 118.224(2)^\circ$, $V = 3135.0(4)$ Å^3, $Z = 8$, $D_c = 1.468$ g cm^{-3}.

Crystal data for **2**: $C_{86}H_{18}$, M = 1051.09, monoclinic, space group $C2/c$. The unit cell parameters are: $a = 25.207(2)$ Å, $b = 9.8028(6)$ Å, $c = 17.461(1)$ Å, $\beta = 94.077(1)^\circ$, $V = 4303.7(5)$ Å^3, $Z = 4$, $D_c = 1.622$ g cm^{-3}.

The X-ray data for **1** and **2** were collected at 90 K using a Bruker SMART1000 CCD diffractometer installed at a rotating anode source (Mo Kα radiation), and equipped with an Oxford Cryosystems nitrogen gas-flow apparatus. The data were collected by the rotation method with 0.3° frame-width (ω scan) and 20 s exposure time per frame. They were integrated, scaled, sorted and averaged using the SMART software package of programs [13].

The structures were solved by direct methods using SHELXTL NT version 5.10 [14].The least-square refinement on F^2 in the anisotropic approximation for all non-hydrogen atoms was done to: $R_1 = 0.056(1)$ for 2802 observed ($F > 4\sigma(F)$) reflections (4311 unique reflections, 289 parameters) and $wR_2 = 0.147$, final G.O.F. = 0.962 and $R_1 = 0.039(2)$ for 3638 observed (4863 unique reflections, 578 parameters) and $wR_2 = 0.097$, final G.O.F. = 1.03.

3. Results and discussion

In $(TPE)_2C_{60}$ an asymmetric unit contains a half of the TPE molecule and a quarter of the C_{60} one. The TPE molecule resides on the crystallographic twofold axis, whereas fullerene resides both on the twofold axis and the *m*-plane. This makes stoichiometry of the complex as 2TPE:C_{60}. The C_{60} molecules are disordered through rotating by 180° about the twofold axis, with the occupancy of each part being refined to 53/47%.

C_{60} and TPE molecules form layers in the *ac* plane (Fig. 1). Each fullerene molecule has six neighbors in a layer with the distances between the centers equal to 10.48, 10.32 and 10.67 Å. There are no shortened van der Waals contacts between carbon atoms of the C_{60} or TPE molecules in the corresponding layers.

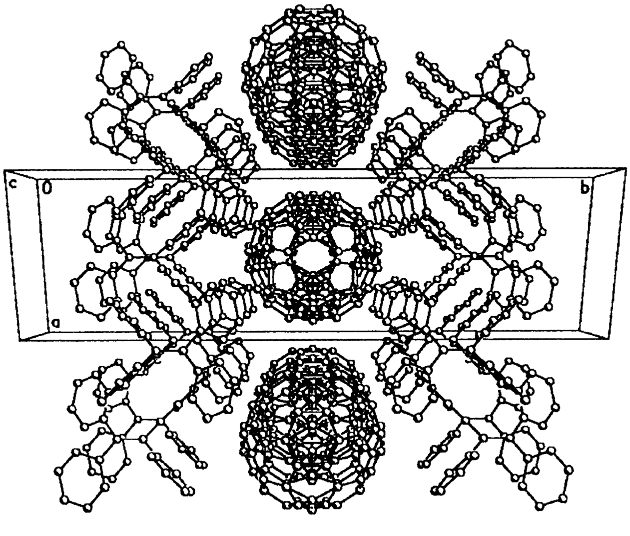

Fig. 1. The projection of the crystal structure of **1** along the *b*-axis.

Phenyl substituents of TPE insert in the cavities formed by the C_{60} spheres in the layer. As this takes place, the phenyl substituents have the π–π contacts with the five to six bond of adjacent fullerene, with the 3.49 Å distance between the center of the phenyl ring and the center of the five to six bond of C_{60}. This results in the formation of shortened van der Waals contacts equal to 3.20–3.42 Å between the TPE molecule and the four adjacent fullerene ones.

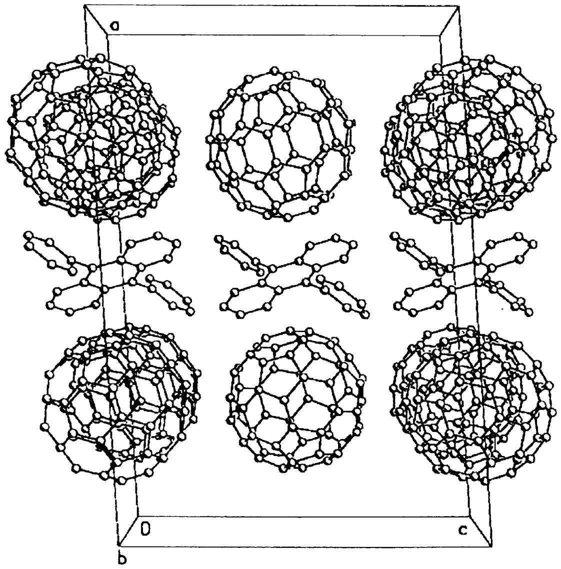

Fig. 2. The projection of the crystal structure of **2** along the *c*-axis.

In DPA·C_{60} fullerene and DPA molecules reside in special positions on the twofold axis. The C_{60} molecules are disordered between two orientations, related by a 60° rotation about the sixfold non-crystallographic axis. The two positions were refined to 60/40% occupancy. The C_{60} molecules form dense packed hexagonal layers in the *bc* plane (Fig. 2). Each C_{60} molecule has six adjacent C_{60} ones inside the layer with the distances between the centers in the 9.80–10.01 Å range.

The C_{60} layers alternate with those composed of the DPA molecules. The donor layer consists of chains formed by the DPA molecules, the molecules from the adjacent chains being turned with respect to each other, the angle between the C7–C8 bonds (between the anthracene skeleton and the phenyl substituents) of the neighboring molecules is 80.1°. Inside the DPA chain there is one $C \cdots C$ shortened contact (3.47 Å) between the carbons of phenyl substituents. Each DPA molecule forms shortened van der Waals contacts with the four C_{60} ones. Outer edges of the anthracene skeleton form van der Waals contacts with hexagons of the two C_{60} molecules from the adjacent layers with the shortest $C \cdots C$ distances of 3.26–3.64 Å. The π-interaction between DPA and C_{60} is evidenced by a small value of the dihedral angle (4.4°) between the phenylene groups of DPA and C_{60} hexagons.

The phenyl substituents of DPA also form shortened van der Waals contacts ($C\cdots C = 3.41-3.50$ Å) with hexagons of the two other C_{60} molecules. However, the overlapping of the π-orbitals of the phenyl substituents of DPA and C_{60} is insignificant because of an unparallel arrangement of these fragments with respect to each other.

The DPA geometry remains almost unchanged in the complex as compared to the DPA geometry in neat crystals [15].

According to the TG data the complexes start to decompose at temperatures higher than 370 °C for **1** and 450 °C for **2** that indicates their high thermal stability. Compound **3** starts to decompose even at 150 °C because of the presence of a solvent in the compound.

The IR spectra of **1**–**3** exhibit absorption bands (AB) of the starting donors, fullerene C_{60} and AB of benzene in **3**. AB of the donors remain almost unchanged at complex formation (the maximal shifts of AB do not exceed 2 cm^{-1}). Thus, the IR spectra together with the X-ray data indicate the retention of initial geometry of hydrocarbons in the complexes with fullerenes. AB of C_{60} are not shifted in the complexes with respect to the starting one and the resulting compounds can be attributed to the complexes with neutral ground states.

The UV-Vis spectra of **1**–**3** are a superposition of the spectra of starting C_{60} and the corresponding donors. The spectrum of **2** exhibits also a wide weak AB in the visible range which is absent in the spectra of parent DPA and C_{60}. To discriminate this band correctly we subtracted the normalized spectra of DPA and C_{60} from that of **2**. This band can be attributed to charge transfer from DPA to C_{60} (CTB) on absorption of light quantum. The presence of this band in the spectrum of the complex may be evidence of the overlapping of the DPA and C_{60} π-orbitals. However, the energy of charge transfer corresponding to the maximum of CTB (630 nm, 1.97 eV) is too high for charge transfer to be realized in the ground state.

4. Conclusion

New C_{60} complexes with aromatic hydrocarbons were obtained. The complexes are composed of the C_{60} and aromatic hydrocarbon layers bound by the shortened van der Waals contacts between C_{60} and the phenyl substituents of DPA and TPE or the phenylene groups of the planar anthracene fragment of DPA. The structure of **2** can be presented in the whole as that of the parent C_{60} separated into layers by the layers of the DPA molecules. Complex formation is attained due to the phenyl groups of the DPA molecules inserted in the cavities formed by the spherical C_{60} molecules. Such type of packing enables even flat DPA molecule to form shortened van der Waals contacts with the spherical C_{60} ones with the minimal $C(\text{donar})\cdots C(C_{60})$ distance of 3.26 Å. These contacts are comparable with the similar $C\cdots C$ distances in the C_{60} complexes with concave aromatic hydrocarbons. For example, the C_{60} complexes with triptycene and dianthracene have the shortest $C\cdots C$ distances in the 3.27–3.35 Å range [8,10].

In $(ET{\cdot}I_3)C_{60}$, where ET is bis(ethylenedithio)tetrathiafulvalene the flat ET^{+} cations and the linear I_3^{-} anions also occupy the cavities in the C_{60} layer [16]. Therefore, this new type of packing is evidently characteristic of C_{60} complexes comprising flat molecules.

1 and **2** are examples of high thermally stable layered complexes the neutral state of which may be changed by doping. It has recently been shown, that two-dimensional insulating organic molecular crystals of anthracene, tetracene, pentacene [18] and fullerenes [17], become metallic and superconducting through charge injection. Organic layered semiconductors formed by van der Waals forces could provide more latitude for device engineering and open a new field of research [17,18].

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