ELSEVIER

Synthetic Metals 103 (1999) 2364–2365

SYNTHETIC METALS

C_{60} complexes with dianthracene and triptycene: synthesis and crystal structures.

D.V. Konarev, Y.V. Zubavichus[a], E.F.Valeev[a], Yu. L. Slovokhotov[a], Yu.M. Shul'ga, and R.N. Lyubovskaya*
Institute for Chemical Physics Research RAS, Chernogolovka, 142432, Russia.
[a] *Institute of Organoelement Compounds RAS, 28 Vavilov St., Moscow, 117334, Russia*

Abstract

New molecular complexes of fullerene C_{60} with aromatic hydrocarbons TPC·C_{60} and DAN·$C_{60}(C_6H_6)_3$, were obtained. For the first time a three-dimensional packing of fullerene molecules is observed in TPC·C_{60}. The DAN·$C_{60}(C_6H_6)_3$ complex has a layered structure with alternating sheets of C_{60} and donor molecules. Complexes with strong van der Waals interaction were formed due to the shape concordance between the TPC, DAN and spherical C_{60} molecules. XPS spectroscopy of the complexes showed the suppression of π-π* transitions in TPC and DAN phenyl rings in the complexes due to the donor- C_{60} interaction.

Keywords: Single crystal growth, X-ray diffraction, XPS- spectroscopy, Fullerenes.

1. Introduction.

Fullerenes as π-acceptors form donor-acceptor complexes with different type of organic donors [1-4]. The donors with initially concave shape are of interest for C_{60} complex formation. A few complexes of C_{60} with such donors are known, among them are the complexes with semi-spherical cyclotriveratrylene molecule [5], trans-9,9`-bis (telluraxanthenyl) [6-7] which have a "double butterfly" shape.

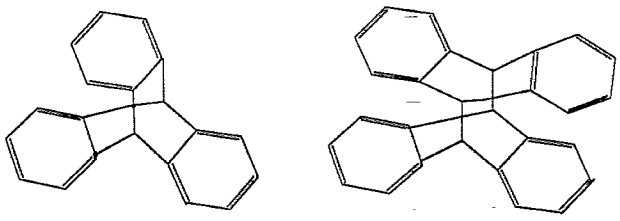
Dianthracene molecule has a "double butterfly" shape, triptycene one is formed by three phenylene rings arranged at an angle of 120° with respect to each other. Thus the shapes of these molecules fit well the shape of C_{60}.

In this paper we report the synthesis of new molecular complexes of C_{60} with triptycene and dianthracene of the TPC·C_{60} and DAN·$C_{60}(C_6H_6)_3$ composition. The crystal structures of the complexes are described. The X-ray photoelectron spectra of the complexes are discussed.

2. Experimental

The crystals of TPC·C_{60} **(1)** were obtained by evaporation from benzene solution containing C_{60} and TPC with 20 % yield. The crystals of **1** have a form of elongated pyramids. High quality DAN·$C_{60}(C_6H_6)_3$ **(2)** single crystals with the shape of flattened oblique bars of approximate 2×4 mm size were obtained by diffusion method from C_{60} and DAN saturated benzene solutions [8]. The composition of the complexes was determined from the X-ray analysis.

The X-ray study of single crystals was carried out with an automatic four-circle Siemens P3 diffractometer at the Centre for X-ray diffraction studies, Institute of Organoelement Compounds, Moscow, Russia. The measurements were performed using graphite-monochromatized Mo-K_α radiation. The structures of **1** and **2** were solved by direct methods using SHELXS-86 and refined using SHELXS-93 program.



TPC DAN

Preliminary lattice parameters of **1** are: $C_{80}H_{14}$, M=974.92, tetragonal, $I4_1/amd$, a=13.296(9), c=46.37(5) Å, V=8200(10) Å^3, z=8, D_c=1.580 g cm^{-3}, F(000)=2958, μ= 0.068 cm^{-1}, T=153K, $2\theta_{max}$=48°; N_{tot}=1769, N_{obs}=1058 (I>2σ). Current value of R_f=0.20.

Crystal data for **2** are: $C_{106}H_{38}$, *M*=1311.36, monoclinic, *Cm*, *a*=13.260(5), *b*=15.177(4), *c*=15.764(5) Å, β=110.97(2)°, *V*=2962(2) Å^3, *Z*=2, D_c=1.470 g cm^{-3}, F(000)=1188.0, μ=0.074 mm^{-1}, T=293 K, $2\theta_{max}$=50.2°; N_{tot}=4775, N_{obs}=2871 (I>2σ). Finally R_f=0.069, R_w=0.189.

X-ray photoelectron spectra (XP) were excited by Mg-K_α-radiation (hν =1253.6 eV).

3. Results and Discussion.

X-ray photoelectron C1s spectra of TPC, TPC·C_{60}, and solid C_{60} are presented in Fig.1. The satellite structures were observed in all spectra to the side of higher binding energies from the main peak. In the case of TPC, the satellite

PII: S0379-6779(98)00705-X

structure appears as a single peak at 6.73 eV with well-defined maximum. This satellite is attributed to the $\pi \rightarrow \pi^*$ transitions in "pseudophenyl" rings . In the case of solid C_{60} and **1**, the satellite peaks were not well resolved. The results of Gaussian fitting for the maximum of satellite peak are 3.16 and 3.06 eV for solid C_{60} and **1**, respectively. All these facts testify that the natures of satellites are different for TPC and for C_{60} and **1**. The $\pi \rightarrow \pi^*$ transitions characteristic of TPC were not observed in the spectrum of the complex. It is obviously associated with the interaction of π-electrons of C_{60} and TPC phenyl rings. The similar effect was observed for the DAN·$C_{60}(C_6H_6)_3$ complex.

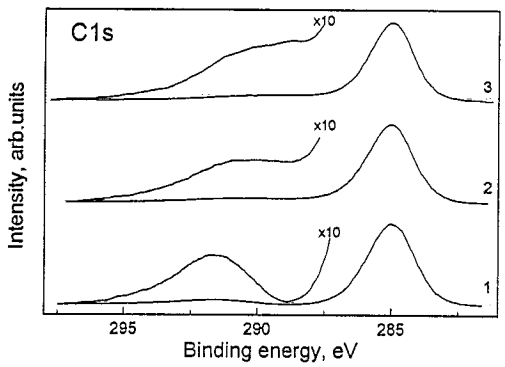


Fig.1. X-ray photoelectron C1s spectra of TPC (1), TPC·C_{60} (2) and solid C_{60} (3).

The crystal structure of TPC·C_{60} was solved with high resulting R-factor due to disorder of fullerene molecules. Therefore we present only a general view of C_{60} and TPC molecules packing in the crystal.

The centres of both triptycene and fullerene molecules occupy positions with the C_{2v} point symmetry. Fullerene molecules form a unique three-dimensional framework. Each fullerene molecule has six closest fullerene neighbours in an approximately trigonal prismatic arrangement with 10.17 Å distances between them. It is close to van der Waals radius of fullerene molecule (10.18 Å). Triptycene molecules form chains along *a* and *b* axes in the cavities of the fullerene cluster packing. Each triptycene molecule has van der Waals contacts with three fullerene molecules. The crystal packing of the TPC·C_{60} complex is schematically presented in Fig.2.

In the crystal structure of DAN·$C_{60}(C_6H_6)_3$ [8] fullerene, dianthracene and three solvent molecules reside in positions on the symmetry plane.

The C_{60} molecules are arranged in layers lying in the *ab* plane. The shortest distance between the centres of fullerene spheres in **2** is along the *ab* diagonal and is equal to 10.08 Å, being close to that in C_{60} (10.02 Å) [9]. A concave shape of DAN molecule allows its efficient packing with C_{60} spheroids. Thus, every C_{60} molecule is sandwiched between two DAN molecules which form two-dimensional layers parallel to the *ab* plane. The whole packing pattern may be described as alternating sheets made up of C_{60} and DAN molecules. The shortest intermolecular contacts C(C_{60})-C(DAN) (~3.4Å) are close to the sum of van der Waals radii of sp^2 carbon atoms (3.35 Å).

Hence new molecular complexes of C_{60} with aromatic hydrocarbons, TPC and DAN, were obtained. The close

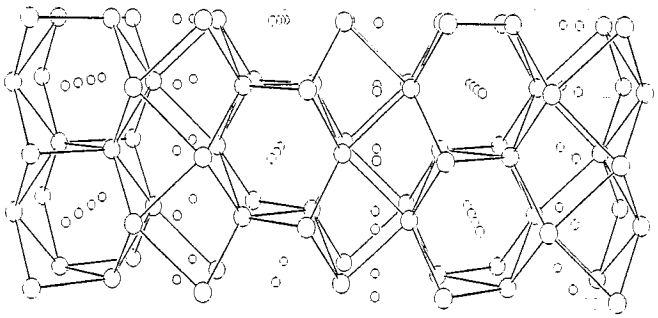


Fig.2. The crystal packing of the TPC·C_{60} complex. C_{60} and TPC molecules are marked by large and small spheres, respectively.

approach of donor molecules to C_{60} ones is possible due to the shape concordance of a spherical C_{60} molecule and concave donor ones. As a result, the complex with a strong van der Waals interaction was obtained. The XPS-spectra of the complexes demonstrate that the $\pi \rightarrow \pi^*$ transitions of phenyl rings characteristic of donors are suppressed. For the first time we obtained the C_{60} complex with an organic donor which has the three-dimensional packing of fullerene molecules, and the shortest distance between the centres of fullerene spheres close to van der Waals radius of C_{60}.

Acknowledgements

The work is supported by Russian program "Fullerenes and atomic clusters" and Pirelli Cavi S. p. A..

References

[1] A. Izuoka, T. Tachikawa, T. Sugawara, Y. Suzuki, M. Konno, Y.Saito, and H. Shinohara, *J.Chem.Soc., Chem.Comm.*, (1992) 1472

[2] G. Saito, T. Teramoto, A. Otsuka, Y. Sugita, T. Ban, M.Kusunoki, and K.- I. Sakaguchi, *Synth. Met.*, **64** (1994) 359

[3] D. V. Konarev, Y.V. Zubavichus, Yu. L. Slovokhotov, Yu. M. Shul'ga, V. N. Semkin, N. V. Drichko, and R.N.Lyubovskaya, *Synth.Met.*, **92** (1998) 1

[4] D.V. Konarev, E.F. Valeev, Yu. L. Slovokhotov, and R.N. Lyubovskaya, *J.Phys.Chem.Solids*, **58** (1997) 1865

[5] J.W. Steed, P.C. Junk, J.L. Atwood, M.J. Barnes, C.L.Raston, and R.S.Burkhalter, *J. Am.Chem.Soc*, **116** (1994) 10346

[6] D.V. Konarev, R.N. Lyubovskaya, Yu.M. Shul'ga, O.S. Roschupkina, M.G. Kaplunov, I.N.Kremenskaya, L.P. Rozenberg, S.S. Khasanov, and R.P.Shibaeva, *Mendeleev Commun.*, (1996) 3

[7] D.V. Konarev, R.N. Lyubovskaya, O.S. Roschupkina, Yu.M. Shul'ga, M.G. Kaplunov, I.N. Kremenskaya, L.P. Rozenberg, S.S. Hasanov, and R.P. Shibaeva. *Molecular Materials*, **8**, 1996, 79-82.

[8] D.V. Konarev, E.F. Valeev, Yu.L. Slovokhotov, Yu.M.Shul'ga, and R.N. Lyubovskaya, *J.Chem. Res.* (S), (1997) 442

[9] P.W. Stephens, L. Mihaly, P.L. Lee, R.L.Whetten, S.M. Huang, R. Kaner, F. Diederich, and K.Holczer, *Nature*, **351** (1991) 632.