J. Chem. Research (S),
1997, 442–443
J. Chem. Research (M),
1997, 2647–2664

Molecular Complex of C_{60} with the Concave Aromatic Donor Dianthracene: Synthesis, Crystal Structure and Some Properties

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A new molecular complex dianthracene C_{60} $(C_6H_6)_3$, with a layered structure and a strong van der Waals interaction which is favoured by the concave donor molecule, is obtained by diffusion methods.

Fullerene C_{60} is able to form charge transfer (CT) complexes[1,3,7,8] basically with a weak CT degree owing to its being a weak acceptor.[3] The interactions in these complexes are van der Waals interactions. The planarity of π-donors is less preferential for the coordination with spherical fullerene molecules since steric compatibility between C_{60} and the donor molecules is needed for effective van der Waals interaction. Possibly donors with an initially concave shape correspond to C_{60} spheres well and can form complexes with stronger van der Waals interactions between the components. Such donors are cyclotriveratrylene[7] and *trans*-9,9′-bis-(telluraxanthenyl) (BTX).[8] Dianthracene also has a 'concave' shape and was chosen for preparing the C_{60} complex.

Here we report the synthesis, crystal structure and some characteristics of the new C_{60} molecular complex DAN C_{60} $(C_6H_6)_3$ with the donor dianthracene (DAN).†

DAN C_{60} $(C_6H_6)_3$ (**1**) was prepared by the filtration of DAN and C_{60} benzene solutions (1 mmol dm^{-3} and 0.1 mmol dm^{-3} respectively) into one flask (DAN:C_{60} = 1:1) and evaporation down to 50 ml by heating. The solution became colourless after standing overnight and a polycrystalline precipitate was formed with a quantitative yield. Fullerene C_{70} does not form a crystalline complex with DAN even after complete evaporation of the benzene solution.

High-quality single crystals of **1** were obtained by a diffusion method from saturated benzene solutions of C_{60} and DAN during 2 months and were washed with benzene.

IR spectroscopy of **1** showed that the frequencies of the absorption bands attributed to C_{60} remained practically unchanged with respect to the individual C_{60} which showed an absence of a noticeable CT. The shifts of the DAN main absorption bands with respect to an individual donor in the 400–1500 cm^{-1} range do not exceed 2 cm^{-1} but the positions of the C—H absorption bands have larger shifts (1–6 cm^{-1}).

There are absorption bands attributed to the basic electron transition of C_{60} at 265, 342 and a shoulder at 450 nm in the UV–VIS–NIR optical absorption spectrum of **1**. The electron transition of DAN (the absorption band maximum is less than 220 nm in any individual donor) was not observed. No charge transfer band was found in the 500–1000 nm range.

C1s X-ray photoelectron spectra of **1**, C_{60}, and DAN are presented in Fig. 1. The satellite structure which can be represented by two peaks (P_1 and P_2) was observed in all spectra to the side of higher binding energy from the P_0 peak. In the case of DAN the distance between P_0 and the most intensive satellite peak P_1 is equal to 6.6 eV. This satellite peak originates from the excitation of $\pi \rightarrow \pi^*$ transitions in the phenyl rings. For satellite structures of C_{60} and **1** the intensity is substantially larger and the distances between the P_0 and P_1 peaks are smaller than those in the spectrum of DAN. All these facts testify that the natures of the satellites are different for DAN and for C_{60} and **1**. The $\pi \rightarrow \pi^*$ transitions which are characteristic of DAN phenyl rings were not manifested in the spectrum of **1**. This is obviously associated with the strong interaction of the π-electrons of the C_{60} and the DAN phenyl rings.

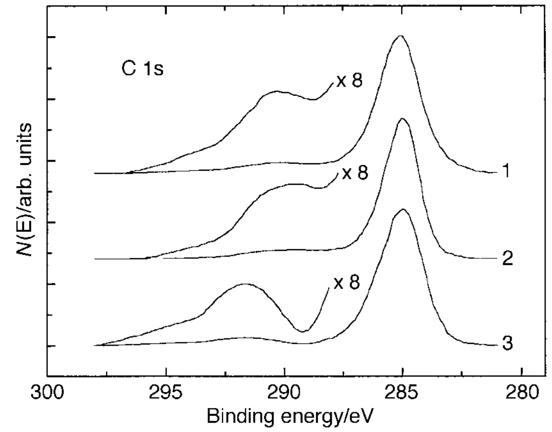

Fig. 1 C1s X-ray photoelectron spectra of **1** (1), C_{60} (2) and DAN (3)

The thermogravimetry revealed that the benzene is removed from the complex crystals starting at 425 K. A partial decomposition of DAN was observed from 605 K, and the loss of mass after 1075 K is due to C_{60} sublimation.

Single crystal X-ray diffraction data showed that the fullerene, dianthracene and three solvent molecules reside in special positions on the symmetry plane. The projection of the crystal structure along the *b* axis is shown in Fig. 2. A mutual orientation of the DAN and C_{60} molecules is shown in Fig. 3.

The C_{60} molecules are arranged in layers lying in the *ab* plane. The closest distance between the centres of the fullerene spheres is along the *ab* diagonal and is equal to 10.08 Å. However, the layer arrangement is far from being hexagonal dense packing. The centre–centre distances along the *a* and *b* axes are much larger and are equal to 13.260 and 15.117 Å, respectively. The concave shape of the DAN molecules allows its efficient packing with the C_{60} spheroids. Thus, each 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 C(C_{60})–C(DAN) intermolecular contacts (~3.4 Å) shown in Fig. 3 are close to the sum of the van der Waals radii of sp^2 carbon atoms (3.35 Å).[18]

Two-thirds of the C_6H_6 molecules on the symmetry plane fill the gaps in the slack layers of the DAN molecules. One third of the benzene molecules are incorporated in voids of layers of fullerene molecules.

A relatively high *R*-factor value reached (0.069) and a significant variance in C—C bond lengths (1.04–1.84 Å) indi-

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†Systematic name: 5,6,11,12-tetrahydro-5,12[1′,2′]:6,11[1″,2″]-dibenzenodibenzo[*a*,*e*]cyclooctene.

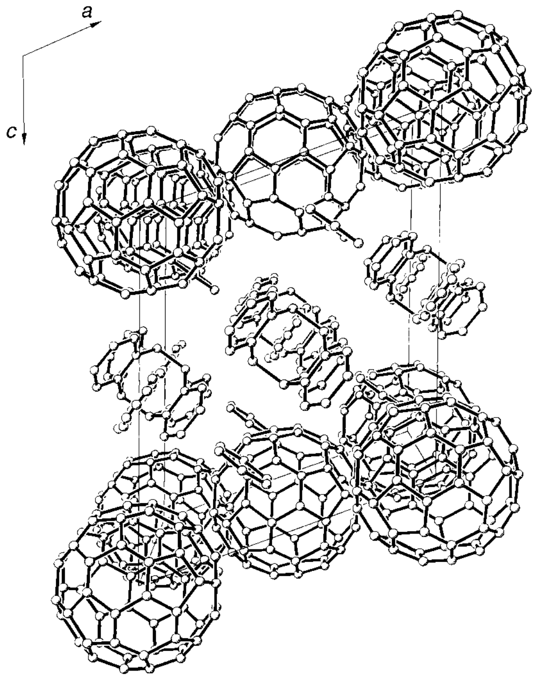

Fig. 2 Projection of the crystal structure along the *b* axis

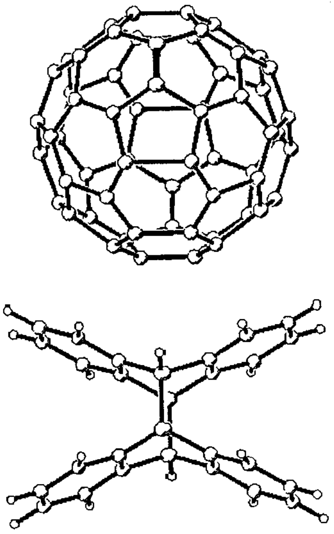

Fig. 3 A mutual orientation of DAN and C_{60} molecules

cate some degree of disorder of the fullerene molecules in this compound. This disorder was not later clarified from the difference electron density map.

Therefore **1** is to be considered as a van der Waals compound without noticeable charge transfer. This is associated with the weak donor properties of DAN and the weak acceptor properties of fullerene. The interaction is mainly of van der Waals character and is realized through the polarization interaction of C_{60} and DAN molecules. The close approach of the donor to C_{60} is attained due to the correspondence of a spherical C_{60} molecule and a concave donor one. As a result, a complex with close contacts and a strong interaction between its components was obtained. The strong interaction results in a quantitative formation of **1** in solution. The unique ability of this donor to form a complex with C_{60} which is quantitatively precipitated from even dilute benzene solutions can be used to isolate C_{60} from different mixtures. The elongated shape of C_{70} does not allow formation of a complex with DAN. This can therefore be used as a method for the partial separation of C_{60} from C_{70}. Fullerene C_{60} is easily isolated from the complex by its dissolution in hot toluene.

Crystal Data for **1**.—$C_{106}H_{38}$, $M = 1311.36$, $F(000) = 1188.0$, monoclinic, $a = 13.260(5)$, $b = 15.177(4)$, $c = 15.764(5)$ Å, $\beta = 110.97(2)°$, $V = 2926(2)$ Å^3, space group Cm, $Z = 2$, $D_c = 1.470$ g cm^{-3}, $\mu(\mathrm{MoK}\alpha) = 0.74$ cm^{-1}. The experimental data were collected at room temperature on a Siemens P3 diffractometer using a graphite monochromator with MoKα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods using SHEHLXS-86 and refined using SHELXL-93 with anisotropic thermal parameters for all atoms. All hydrogen atoms were located on the difference Fourier map and added to the refinement with fixed positional and thermal parameters. The final R value was 0.069 ($R_w = 0.189$). The estimated standard deviations for the geometrical parameters involving non-hydrogen atoms lie within the following ranges: in dianthracene molecules bond lengths 0.010–0.017 Å; bond angles 0.60–0.91°, in C_6H_6 and C_{60} molecules bond lengths 0.02–0.05 Å; bond angles 1–5°.

We thank Dr V. N. Semkin and Dr A. Graja for help with IR and UV–VIS spectra investigations and Dr B. P. Tarasov for thermogravimetric analysis. This work was supported by the Foundation of Intellectual Collaboration in the framework of the Russian Programme ‘Fullerenes and Atomic Clusters’ (grants 95087 and 94018).

Techniques used: X-ray diffraction, IR, UV–VIS–NIR, X-ray photoelectron spectroscopy, thermogravimetric analysis

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Table 1: Crystal data and structure refinement for **1**

Table 2: Atomic coordinates and equivalent isotropic displacement parameters for **1**

Table 3: Bond lengths and angles for **1**

Appendix: Anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters for **1**

Received, 8th July 1997; Accepted, 27th August 1997
Paper E/7/04862I

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