Synthesis and crystal structure of a new molecular complex of fullerene C_{70}, $4BNDY \cdot 3C_{70} \cdot 4C_6H_6$ (BNDY is binaphtho[1,8-*d*,*e*]-1,3-dithiin-2-ylidene)

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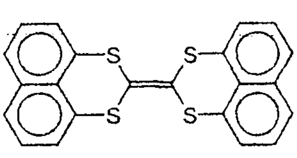
A new C_{70}-based molecular complex $4BNDY \cdot 3C_{70} \cdot 4C_6H_6$ (**1**) (BNDY is binaphtho[1,8-*d*.*e*]-1,3-dithiin-2-ylidene) was prepared, and its full X-ray diffraction study at room temperature was performed. The C_{70} molecules in crystal **1** are ordered in different ways, and their ordering depends on van der Waals interactions between them and nonplanar BNDY molecules in the boat conformation. The neighboring BNDY molecules in the structure are bound to each other by π—π interactions.

Key words: fullerene, C_{70}, molecular complexes, synthesis, X-ray diffraction analysis, crystal structure, intermolecular interactions.

Compounds of fullerenes C_{60} and C_{70} have recently attracted great attention due to their discovered superconductivity[1,2] and ferromagnetism.[3] Although C_{60} and C_{70} are similar in structure, the properties of their related compounds differ significantly. For example, superconductors M_3C_{60} (M_3 = K_3, Rb_3, Rb_2Cs, Rb_2Tl, Na_2Cs, and Na_2Rb) are formed when fullerene C_{60} is doped by alkali metals, whereas the doping of C_{70} results in the formation of M_4C_{70} salts possessing only metallic conductivity.[2] For example, the $TDAE \cdot C_{60}$ salt (TDAE is tetrakis(dimethylamino)ethylene) exhibits ferromagnetic properties at low temperatures, whereas the similar salt $TDAE \cdot C_{70}$ is paramagnetic.[4]

It is more difficult to synthesize C_{70}-based compounds; therefore, they are much less studied than C_{60} derivatives. Now crystal structures are known for about 90 compounds based on C_{60} and only about ten crystal structures are known for C_{70}-based compounds; for them the most X-ray structural experiments were carried out at low temperatures, for example, X-ray analysis of $(S_8)_6C_{70}$[5] and $BTX \cdot C_{70}(CS_2)_{0.5}$ (BTX is *trans*-9,9'-bis(telluraxanthenyl)).[6]

Donor-acceptor fullerene complexes with conducting molecular chains or dimeric layers of donor molecules are of special interest as electroconducting compounds.[7] Such chains or layers can probably be obtained using large donor molecules comparable in size with fullerene molecules. The organic donor binaphtho[1,8-*d*,*e*]-1,3-dithiin-2-ylidene (BNDY)[8] satisfies this requirement and can form complexes with fullerenes.



BNDY

In this work, we consider the method for synthesis, crystal structure, and IR and UV spectra of the new C_{70}-based molecular complex $4BNDY \cdot 3C_{70} \cdot 4C_6H_6$ (**1**).

Experimental

IR spectra of C_{70}, BNDY, and complex **1** were recorded on a Perkin—Elmer 1725 X spectrometer, and electronic absorption spectra were recorded on a Lambda 19 Perkin—Elmer UV-VIS-NIR spectrometer in KBr pellets (1 : 1000 and 1 : 4000, respectively).

C_{70}-Fullerene(binaphtho[1,8-*d*,*e*]-1,3-dithiin-2-ylidene)-benzene solvate (1) was obtained by evaporation of a benzene solution containing C_{70} (20 mg, 0.024 mmol) and BNDY (10 mg, 0.025 mmol; synthesized by the previously described procedure[8]) in an argon atmosphere for 5 days. Crystals of the complex (rectangular black plates) were washed with ether and dried in air to obtain the complex in 70% yield. Found (%): C, 85.76; H, 1.74; S, 10.82. $C_{322}H_{72}S_{16}$. Calculated (%): C, 86.96; H, 1.70; S, 11.43.

X-ray structural study of complex 1. The main crystallographic parameters: $C_{322}H_{72}S_{16}$, M = 4453.07, tetragonal unit cell, $a = b = 21.203(3)$ Å, $c = 20.734(4)$ Å, $V = 9321(3)$ Å^3, space group $P4_2mc$, $Z = 2$, $d_{calc} = 1.586$ g cm^{-3}, $F(000) = 4496$, sample size 0.34×0.25×0.15 mm, μ(Cu-Kα) = 2.328 mm^{-1}.

The experiment was carried out on a KM-4 KUMA DIFFRACTION automated four-circle diffractometer, $\omega/2\theta$-scan mode, Cu-Kα radiation, a graphite monochromator, 4381 independent reflections, 1140 of which had intensities $I > 2\sigma(I)$, $2\theta_{max} = 160.18°$. X-ray absorption in the crystal was not applied.

The crystal structure of **1** was solved by direct methods and subsequent Fourier syntheses by the SHELX86[9] and SHELXL93[10] programs. The space group $P4_2/nmc$ corresponded best to systematic quenchings of reflections for crystal **1**. First an attempt was made to solve the structure in this group. Atoms of the BNDY molecules and atoms of one

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independent fullerene C_{70} molecule were localized, the latter being arranged on axis 4_2, which does not contradict C_{70} — D_{5h} symmetry for this unit cell. However, the second independent fullerene C_{70} molecule in this space group should be located on the $\bar{4}$ axis, which is impermissible for the symmetry of fullerene. Therefore, we considered several other space groups which were also appropriate in quenchings. As a result, only in the $P4_2mc$ group did we find the main structural motif and finally refined the atom positions in complex **1**. The unit cell of **1** contains three independent C_{70} molecules with crystallographic symmetry *mm*, four BNDY molecules, and four C_6H_6 molecules with symmetry *m*. Testing of the structure by the PLATON program[11] showed that the sites of the BNDY and C_6H_6 molecules can be described in the $P4_2/nmc$ group, and those of C_{70} can be described only in the noncentrosymmetrical group $P4_2mc$.

The structure was refined by the least-squares method in the anisotropic approximation for all nonhydrogen atoms using the SHELXL93 program complex. The final value of the R factor is 0.090 (by $|F|$ for the observed reflections), $wR = 0.165$ (by $|F|$ for all reflections). Hydrogen atoms were not localized. Since the body of experimental data was restricted, the bond lengths in C_{70} and C_6H_6 molecules were located during refinement. All calculations were performed on a Pentium-100 PC.

The bond lengths, angles, and coordinates of atoms in structure **1** were deposited in the Cambridge Structural Data Bank.

Results and Discussion

A fragment of crystal structure **1** is presented in Fig. 1. The unit cell of crystal **1** contains three C_{70} molecules with symmetry *mm* (*i.e.*, 1/4 molecule is an independent part of each fullerene C_{70}). Two C_{70} molecules (**A** and **B**) are localized on axis 4_2, and one C_{70} molecule (**C**) is localized on axis *2*. Two types of chains of C_{70} molecules are arranged along axis *c* in the crystal. In chains of the first type formed by C_{70} molecules and passing through the center of the cell (molecule **A**) and the origin of coordinates (**B**), C_{70} molecules are arranged in the sequence **A**—**A'**—**A''**... (Fig. 2) or **B**—**B'**—**B''**. In these chains, nonplanar BNDY molecules coordinate with C_{70} molecules (see Fig. 2). In chains of the second type, passing through the middles of edges of the unit cell (**C**), the C_{70} molecules alternate with benzene molecules. The BNDY molecules do not "cover" the C_{70} molecules, because the naphthalene fragments deviate from the fullerene edges (Fig. 3). This mutual arrangement of the C_{70} and BNDY molecules results in a stronger disordering of the carbon atoms of fullerene in these chains as compared to that in the chains of the first type. This is expressed by many satellite peaks near the sites of the carbon atoms of the **C** molecules of fullerene in the difference Fourier synthesis at the final stage of refinement.

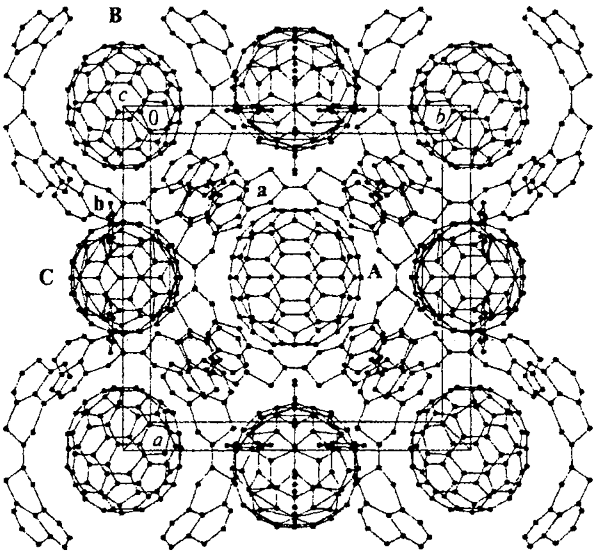

Fig. 1. Fragment of the crystal structure of **1** (for simplicity only some molecules of the complex are shown on the projection of the structure). **A**, **B**, and **C** are C_{70} molecules; **a** and **b** are two independent BNDY molecules (see text).

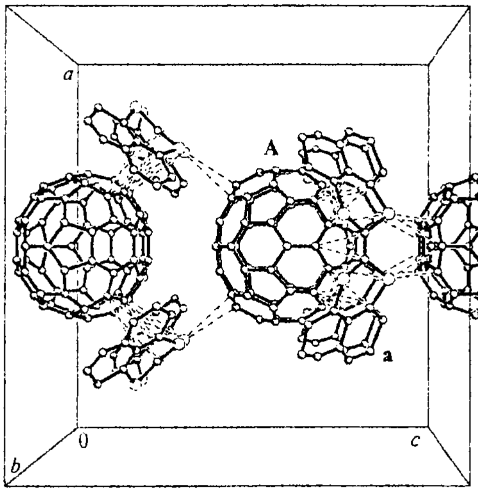

Fig. 2. Arrangement of C_{70} in chains of the first type of structure **1** (shown for **A** molecules only; for **B** molecules, the environment is similar).

In structure **1**, between the BNDY and C_{70} molecules we observed intermolecular contacts of the S...C (3.54—3.61 Å) and C...C (3.17—3.57 Å) types, which

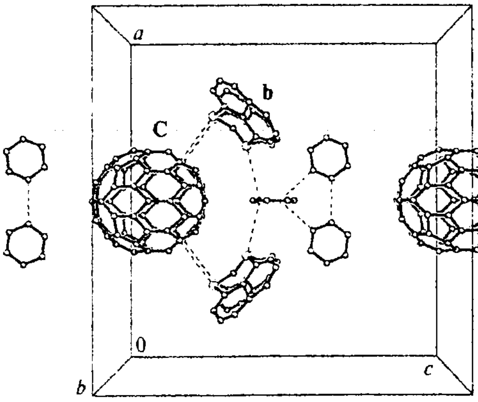

Fig. 3. Arrangement of C_{70} in chains of the second type of structure **1**.

are shorter than the sum of the van der Waals radii of S and C atoms. Each **A** and **B** molecule of fullerene C_{70} is surrounded by four BNDY molecules. Fullerene **C** forms only four intermolecular contacts with the BNDY molecules, and **A** and **B** form 36 and 44 such contacts, respectively. This distribution of the contacts explains the stronger disordering of the carbon atoms in the **C** molecules as compared with those in **A** and **B**.

In structure **1**, the *m* plane passes perpendicularly to the central C=C bonds of two independent BNDY molecules (**a** and **b**). The **a** and **b** BNDY molecules surround the **A** and **B** fullerene molecules, respectively, and form intermolecular contacts with them (see Fig. 2). A considerably lower number of intermolecular contacts was observed for **a** and **b** BNDY with fullerene molecules **C** (see Fig. 3).

The BNDY molecules also form chains arranged in parallel to the *a* and *b* axes (Fig. 4). In these chains, the naphthalene fragments of the adjacent BNDY molecules are linked with each other by van der Waals interactions. The π—π-character of this interaction is indicated by an almost planar arrangement of these fragments (the dihedral angle between their planes is equal to ~3.7°) and the shortened contacts between the atoms of the adjacent BNDY molecules (3.30—3.57 Å), which is less than the sums of the van der Waals radii of the carbon atoms. Thus, π—π-interaction between the donor molecules perhaps takes place in structure **1**, which was observed for the first time, according to our knowledge, for the fullerene complexes. The shortened contacts between the adjacent BNDY molecules in the chains result in the situation that the planes of the BNDY molecule are not parallel to the edges of C_{70} (see Fig. 2). This mutual arrangement weakens the interaction of the π-systems of the BNDY and fullerene molecules and favors disordering of the C_{70} molecules in structure **1**.

Benzene molecules in structure **1** are localized in the *m* planes, and shortened intermolecular distances are observed between them and the **A**, **B**, and **C** fullerene molecules (3.23—3.56 Å) and between the C_6H_6 molecules (2.99—3.58 Å).

As far as we know, data on the molecular structure of BNDY were not published until the present time. In structure **1**, the BNDY molecules have the boat conformation. The planar central fragments of BNDY consisting of S atoms form dihedral angles with the naphthalene fragments of 28.6° and 30.5° for molecules **a** and **b**, respectively. The C_{70} molecules in structure **1** are oblong: the eccentricities of the cross section of all molecules are approximately equal and amount to 0.88. The distances between the centers of the fullerene molecules in complex **1** differ: the distances of the **A**—**A** or **B**—**B** types are equal to 10.36 Å, and those of the **A**—**C** or **B**—**C** types are 10.60 Å.

Fullerene molecules in crystals of the complexes are often disordered[12] due to their "rotation," which substantially impedes the study of the structures of these compounds. The role of a stabilizing "anchor" in the complexes can be accomplished by conformationally labile donor molecules, which can change their conformation, aligning to the spherical shape of fullerene molecules and preventing their rotation by intermolecular interactions. This ordering has previously been found for several C_{60} complexes: $(BEDT\text{-}TTF)_2C_{60}$ (BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene),[13] TMPD · C_{60} (TMPD is *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine),[14] $(TMTSF)_2C_{60}(C_6H_6)_2$ (TMTSF is tetramethyltetraselenafulvalene).[15] Structure **1** contains C_{70} molecules with different ordering: the **A** and **B** molecules participating in many intermolecular interactions are the most ordered, and the **C** molecules with few of these interactions are less ordered.

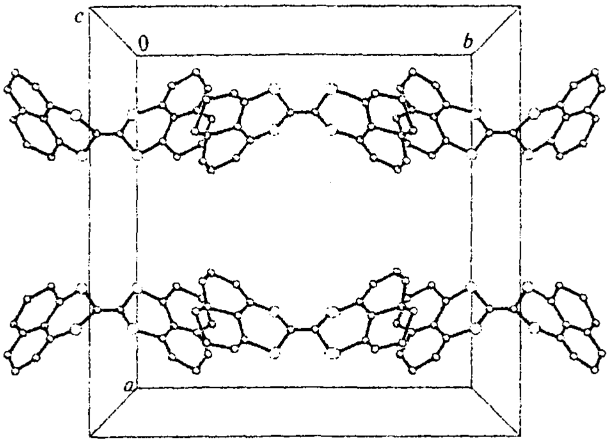

Fig. 4. Chains of BNDY molecules in structure **1** (for simplicity only chains along the *b* axis are shown; chains along the *a* axis are similar).

IR spectra of the starting C_{70}, BNDY, and $4BNDY \cdot 3C_{70} \cdot 4C_6H_6$ complex were studied in the 400—1600 cm^{-1} region. The positions of the main absorption bands (AB) of C_{70} in the spectrum of complex **1** (at 1429, 1133, 795, 674, 642, 578, 565, and 458 cm^{-1}) remain almost unchanged (the shift of AB does not exceed 1 cm^{-1}) relative to that of individual fullerene C_{70}. The absence of shifts of the absorption band of C_{70} at 1430 cm^{-1}, which is the most sensitive to the charge transfer to the C_{70} molecule,[16] indicates that the charge transfer from the donor to the fullerene molecule is absent. The absorption bands of BNDY in the spectrum of complex **1** (at 1551, 1362, 1207, 896, 807, and 752 cm^{-1}) are also close to AB of individual BNDY. Insignificant shifts (to 3 cm^{-1}) of AB in the spectrum of **1** can be associated with a change in the conformation of the donor molecule. The bands at 1477 and 674 cm^{-1} are attributed to benzene, which is present in the composition of the complex.

The electronic absorption spectrum of the complex contains AB at 240, 364, and 490 nm, which are characteristic of the ground electron transitions of C_{70}. The intensity of the absorption bands of BNDY is, evidently, lower than that of AB of C_{70}, and hence, AB of BNDY are not observed in the spectrum. No bands that can be attributed to charge transfer were observed in the 500—2000 nm region.

Thus, according to the data of IR and UV spectroscopy, compound **1** can be attributed to molecular complexes, because it has no noticeable charge transfer in the ground state. This is evidently related to the weak donor properties of BNDY (the first oxidation potential relative to the saturated calomel electrode (SCE) in acetonitrile E_{ox} = +1.14 V[8]) with respect to fullerene C_{70} (the first reduction potential relative to SCE in dichloromethane E_{red} = −0.41 V[17]).

Probably, the complex is formed due to polarization van der Waals forces, which result in partial ordering of the C_{70} molecules. The interaction of the π-systems of the adjacent BNDY molecules in the crystal structure of **1** suggest a future preparation of a related conducting compound by intercalation with strong oxidants.[7]

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