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# New molecular complexes of $C_{60}$ and $C_{70}$ with BMPP: synthesis and crystal structure

A.L. Litvinov,*[a] D.V. Konarev,[a] R.N. Lyubovskaya,[a] B.P. Tarasov,[a] I.S. Neretin,[b] Yu.L. Slovokhotov[b]

[a] *Institute of Problems of Chemical Physics RAS, 142432 Chernogolovka, Russia.*
[b] *Institute of Organoelement Compounds RAS, 28 Vavilov St., 117334 Moscow, Russia*

**Abstract**

New molecular complexes of fullerenes $C_{60}$ and $C_{70}$ with organic donor 4-benzoyl-3-methyl-1-phenyl-2-pyrazoline-5-one (BMPP): BMPP·$C_{60}$ and $(BMPP)_2C_{70}(C_6H_6)_{0.5}$ were obtained. The crystal structure of BMPP·$C_{60}$ was determined. The complex has a three-dimensional packing of fullerene molecules in which each fullerene molecule has six adjacent $C_{60}$ ones. The conformationally flexible BMPP molecule forms Van der Waals contacts with the spherical $C_{60}$ molecule by nitrogen atoms and phenyl groups. The data of IR-spectroscopy indicate a neutral ground state for the complexes. BMPP·$C_{60}$ shows luminescence similar to $C_{60}$ luminescence.

*Keywords:* Single crystal growth, X-ray diffraction, Luminescence , Fullerenes.

## 1. Introduction

Fullerenes form donor-acceptor complexes with different organic donors [1-3]. The donor molecules must either have a concave shape such as dianthracene and BTX or be flexible [3]. In the latter case the promising donors are chelating molecules. 4-Benzoyl-3-methyl-1-phenyl-2-pyrazoline-5-one (BMPP) is an example of such type of

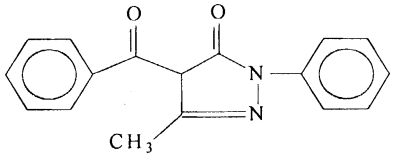


**Fig.1.** 4-Benzoyl-3-methyl-1-phenyl-2-pyrazoline-5-one

molecules [4]. Due to the presence of ketone groups and sterical flexibility, BMPP forms stable compounds with $Ca^{2+}$, $Sr^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Mn^{2+}$ and other metals [5]. We used the chelate-forming molecule BMPP to prepare the complexes with fullerenes.

This paper presents the data on the synthesis, crystal structure and some properties for new molecular complexes of $C_{60}$ and $C_{70}$ with BMPP. Luminescent properties of BMPP·$C_{60}$ are discussed.

## 2. Experimental

IR spectra were registered with a «Perkin Elmer 1725X» spectrophotometer in the 400-3200 $cm^{-1}$ range. Thermogravimetric analysis was carried out with a «Q-1000» derivatograph in the argon flow. The luminescent spectrum of BMPP·$C_{60}$ was measured in KBr pellets at laser excitation (514 nm and 100 K).

$C_{60}$ and $C_{70}$ of 99% grade were used. Benzene was distilled over Na under argon.

The complexes of $C_{60}$ and $C_{70}$ with BMPP (Fig. 1) were obtained by evaporation of benzene solution containing a BMPP and $C_{60}(C_{70})$ at a 8:1 (15:1) molar ratio. Crystals were washed with ether. The complexes were obtained with a 90% yield. BMPP·$C_{60}$ (1) and $(BMPP)_2C_{70}(C_6H_6)_{0.5}$ (2) were formed as elongated prisms and black plates,

*Corresponding author. Fax: (096) 515-35-88; E-mail: litvin@cat.icp.ac.ru


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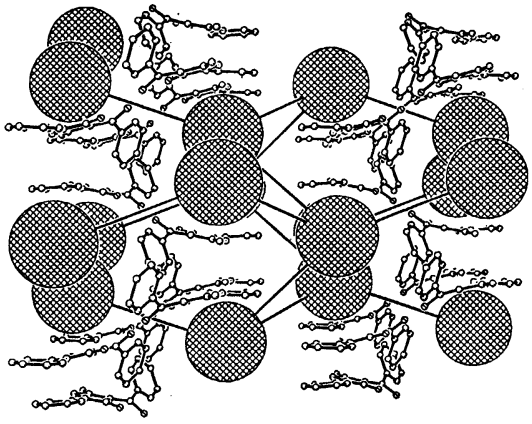

**Fig. 2.** Packing of $C_{60}$ molecules in BMPP·$C_{60}$; BMPP molecules are located in channels of $C_{60}$ packing.

respectively. The composition of the complexes was determined by elemental and thermogravimetric analyses.

The crystal data for **1** are: M=998.91, monoclinic, space group $P2_1/c$, a=18.100(4) Å, b=13.158(3) Å, c=19.277(4) Å, β=116.44(3)°, Z=4; V=4111.8 Å$^3$, $D_c$=1.591 g/cm$^3$, T= 293K, 7133 reflections collected, 6431 unique, $R_I$= 0.131, $R_I$ indices based on 2471 reflections with F>4σ.

## 3. Results and Discussion

In the cristal structure of **1** both molecules are located in general positions. **1** has a three-dimensional framework in which each $C_{60}$ molecule is surrounded by six neighbouring $C_{60}$ ones with the distances between the centers equal to 9.99-10.15 Å (Fig. 2). The BMPP molecule coordinates to two $C_{60}$ molecules by nitrogen atoms with the N(BMPP)...C($C_{60}$) distances of 3.18-3.41 Å and by phenyl rings of benzoyl group with the C(BMPP)...C($C_{60}$) distances of 3.43-3.79 Å. The donor molecules are located in the cavities of the fullerene three-dimensional packing. It is interesting that the BMPP molecule is more planar in the complex than in the individual state. The angles of rotation of phenyl and benzoyl groups relatively to the pyrazoline ring are 15.0 and 57.5°, respectively. These angles are 28.3 and 59.9° in the individual state [6].

**1** decomposes in two temperature ranges. Beginning from 360°C, the partial decomposition of donor was observed and the sublimation of $C_{60}$ starts at 600°C, i.e. essentially lower than for pure $C_{60}$ (800°C) [7].

**2** decomposes in three temperature ranges. Beginning at 115°C, benzene is removed. The partial decomposition of donor was observed above 405°C and the sublimation of $C_{70}$ starts at 550°C.

The donor decomposition accompanied by nitrogen evolution seems to break the bonds between fullerene molecules and lowering its sublimation temperature.

The IR-spectra of **1** and **2** are a superposition of the spectra of starting BMPP and fullerenes. The shifts of some absorption bands up to 6 cm$^{-1}$, the redistribution of the intensities and the appearance of some new absorption bands (at 1616 cm$^{-1}$) may be associated with coordination of BMPP to fullerenes and the changes in its initial conformation. The absorption bands of $C_{60}$ and $C_{70}$ are not shifted relatively to starting fullerenes. Thus, noticeable charge transfer is absent in the ground state of the compounds.

Luminescence of **1** is attributed to $C_{60}$ and the position of the two peaks at 730 and 805 nm is close to that of starting $C_{60}$ (732 and 811 nm) [8]. By now there are only few examples of luminescence in $C_{60}$ molecular complexes. For example, in the luminescence spectrum of BTX·$C_{60}$·$CS_2$ the peaks are shifted by 0.16 eV to lower energies relatively to the spectrum of $C_{60}$. That indicates the narrowing of the HOMO-LUMO gap of $C_{60}$ as a result of complex formation [9]. The absence of noticeable changes in the luminescence spectrum of BMPP·$C_{60}$ allows us to conclude that at complex formation the HOMO-LUMO levels of $C_{60}$ remain unchanged relatively to starting $C_{60}$. This may be associated with weaker interaction of donor and fullerene π-systems in BMPP·$C_{60}$ than in BTX·$C_{60}$·$CS_2$.

Hence new molecular complexes of fullerenes $C_{60}$ and $C_{70}$, BMPP·$C_{60}$ and (BMPP)$_2C_{70}(C_6H_6)_{0.5}$ were obtained. The complexes have a neutral ground state according to the data of IR-spectroscopy. BMPP·$C_{60}$ forms an unusual three-dimensional packing of fullerene molecules in which each fullerene molecule has six adjacent $C_{60}$ ones. BMPP coordinates to the spherical $C_{60}$ molecule by nitrogen atoms and phenyl groups. BMPP·$C_{60}$ shows luminescence similar to that of $C_{60}$ without noticeable shifts in the position of the peaks which show only a weak interaction of π-systems of BMPP and $C_{60}$ in the complex.

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