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Synthetic Metals 88 (1997) 225–230

SYNTHETIC METALS

Electronic absorption spectra of the C_{60} complexes with some organic donors

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Received 19 August 1996; revised 20 January 1997; accepted 28 February 1997

Abstract

Electronic absorption spectroscopy was used to study the electron processes in the complexes of fullerene with organic donors (9,9′-bis-*trans*-(telluraxanthenyl), tetranitride tetrasulfur, 2,2′,6,6′-tetraphenyldipyranilydene, tetramethylenedithiodimethyl-tetrathiafulvalene and 2,2′-ethanediylidene bis(4,5-ethylenedithio-1,3-dithiole)). Changes in the electronic absorption spectrum of the fullerene have been investigated and discussed for C_{60} complexes with organic donors of various molecular structure and electron-donor properties. The charge transfer between electron donor and C_{60} has been observed only for the donor molecules having relatively low first oxidation potentials, thus capable of cation-radical formation. The spectral changes were correlated with the donor properties of the organic molecules forming the complexes with the fullerene.

Keywords: Fullerenes and derivatives; C_{60} complex; Electronic spectroscopy; Charge transfer

1. Introduction

Fullerenes, the new molecular building blocks, give us a possibility to synthesize various new materials with interesting properties. The existence of a superconducting state in alkali-metal-doped C_{60} [1] and a molecular ferromagnetism [2] attracted the particular interest of experimentalists and theoreticians in the field of organic solid-state physics. However, C_{60} clathrates and C_{60} complexes form the largest group of the fullerene-derived compounds. The clathrates have been prepared with various solvents [3–5]. Very weak intermolecular interactions of the van der Waals type are typical for this kind of material. Charge transfer (CT) complexes with electron donors have been reported so far [6–12]. Fully ionic CT complexes of C_{60} have been prepared with strong electron donors, such as Cr(TPP) [6], amine TDAE [7] and (Ph_4P) cations [4,12]. Many of them are just insulators, but exhibit interesting magnetic properties. Most often insulating neutral CT complexes have been prepared [8–11]. Their physical properties are mainly determined by conformation and physicochemical properties of organic donor molecules. Various methods have been applied for the studies of their properties; sometimes electronic spectroscopy has been used for characterization of the C_{60} complexes [13–17].

The presence of a CT band (in the visible or UV spectral ranges) as a signature of the formation of a (D–A) complex has been known for a long time [18]. The CT band in the complexes of C_{60} with various electron donors occurs usually between 800 and 1000 nm [19]. Localization of this band depends on the redox potential (E_D) of the donor and should shift towards higher energies with increasing E_D. Usually, other information is not obtained from the electronic spectra. Fullerene bands prevail in the electronic spectrum of C_{60} complexes; the electronic spectra of donors are usually much weaker. This is why the electron spectra can be used for characterization of the electronic state of C_{60} in the complexes and for the assessment of the electronic states in complexes and those in a free C_{60} molecule. However, the changes of the electronic bands of C_{60} caused by complex formation are small because the van der Waals interactions cannot influence strongly the electronic states of the C_{60} molecule. The electronic spectrum of C_{60} consists of strong absorption bands between 200 and 400 nm, which are identified with electric dipole-allowed transitions between occupied (bonding) and empty (antibonding) molecular orbitals (either the $h_u \rightarrow t_{1g}$ transition or the $h_g \rightarrow t_{1u}$ transition). A weak absorption band is seen also in the region 400–630 nm; it is identified as the forbidden electron transition between the h_u HOMO level

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0379-6779/97/$17.00
PII S0379-6779(97)03858-7

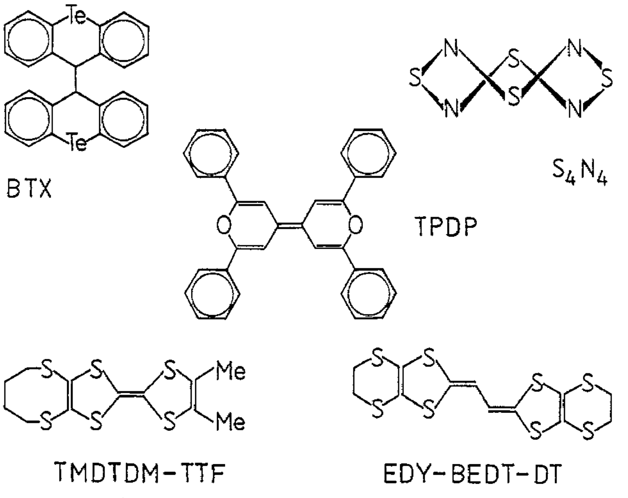
with H_u symmetry and the one-electron t_{1u} LUMO level with T_{1u} symmetry [20]. A significantly enhanced absorption in this region, when compared with that in solution, may be attributed to stronger intermolecular interactions which distort the symmetry and, as a result, enhance forbidden transitions. This is why the broad absorption band often detected around 450 nm has been assigned to C_{60} aggregation [21,22]. It is known that the electronic spectra of C_{60} in solutions and in the van der Waals crystals are nearly the same, except for small frequency shifts and broadening of the bands observed in the solids.

The C_{60} molecules crystallize into a cubic structure (f.c.c.) with a nearest-neighbour C_{60}–C_{60} distance of 10.02 Å [23]. Taking into account π-electrons of the carbon atoms, the diameter of the C_{60} molecule should be 10.18 Å. This is why a partial covering of the π orbitals and a weak van der Waals interaction are possible in the solid fulleride. In the complexes with various donor molecules, the bonding of the fullerenes increases. The donor can be coordinated by C_{60} with the π–π interaction with its aromatic substituents or with the π–n interaction with heteroatoms of the donor. These interactions hinder the fullerene rotation. This is why the transition from C_{60} solution to a fullerite, the crystalline form of C_{60}, and the transition from the fullerite to a C_{60} complex, should give similar changes in the electron spectra.

The aim of our paper is an investigation of the complex formation on the electronic absorption spectra of C_{60}. The C_{60} complexes with various electron-donor molecules, which coordinate C_{60} in different ways, have been chosen for the study.

2. Experimental

Donor molecules chosen for complexation with C_{60} are shown in the following scheme:



where 9,9′-bis-*trans*-(telluraxanthenyl) is abbreviated as BTX, tetranitride tetrasulfur as S_4N_4 (redox potentials of both BTX and S_4N_4 are unknown because the donors are probably unstable to electrochemical oxidation), 2,2′,6,6′-tetraphenyldipyranilydene as TPDP (first redox potential $E_{1/2} = +0.15$ eV, second potential is $+0.47$ eV, both measured in acetonitrile) [24], tetramethylenedithiodimethyl–tetrathiafulvalene as TMDTDM–TTF (first redox potential $E_{1/2} = +0.39$ eV, second potential is $+0.72$ eV, both measured in acetonitrile) [25], and 2,2′-ethanediylidene bis(4,5-ethylenedithio-1,3-dithiole) as EDY–BEDT–DT (first redox potential $E_{1/2} = +0.41$ eV, second potential is 0.64 eV, both measured in acetonitrile) [25].

Redox potential values change according to the order: TPDP > TMDTDM–TTF > EDY–BEDT–TTF > BTX, S_4N_4. Thus, TPDP is the strongest donor.

$BTX \cdot C_{60} \cdot CS_2$ (**I**) complex was prepared from a CS_2 solution of stoichiometric quantities of C_{60} and BTX. The complex is triclinic with $a = 10.309$ Å, $b = 10.988(3)$ Å, $c = 12.011$ Å, $\alpha = 85.20(2)°$, $\beta = 71.85(1)°$, $\gamma = 79.82(2)°$, $V = 1271.91$ Å^3, $P\bar{1}$, $Z = 1$. The details of the complex preparation are given elsewhere [26].

$BTX \cdot C_{60}$ (**II**) complex was grown from saturated solutions of C_{60} and BTX (molar amounts) in a mixed solvent (1:3) of 1,2-dichloroethane and toluene. Small black crystals in the form of plates were obtained. The compound formula was confirmed by thermal gravimetric analysis (TGA); there is no evidence of the solvent in the crystals [26].

$(S_4N_4)_{1.33} \cdot C_{60} \cdot (C_6H_6)_{0.66}$ (**III**) was obtained from S_4N_4 saturated solution in benzene. The single crystals grew in the form of plates [27]. The unit cell parameters are: $a = 29.449(6)$ Å, $b = 17.009(3)$ Å, $c = 24.127(3)$ Å, $\alpha = \beta = 114.017(21)°$, $V = 11039(3)$ Å^3, $Z = 8$ [28].

$S_4N_4 \cdot C_{60}$ (**IV**) was grown from a solution of a four-fold excess of S_4N_4 in toluene. The black single crystals grew in the form of rhombic plates with a yield of 90%. Elemental analysis and TGA show the absence of the solvent in the crystals and suggest the compound formula: $S_4N_4 \cdot C_{60}$ [27].

$TPDP \cdot (C_{60})_2 \cdot (CS_2)_4$ (**V**) was grown from a stoichiometric solution of C_{60} and TPDP in CS_2. The single crystals show a form of cuboids [29]. The unit cell parameters are: $a = 13.050(3)$ Å, $b = 15.510(4)$ Å, $c = 22.010$ Å, $\alpha = 102.87(2)°$, $V = 4343.0$ Å^3, $Z = 2$ [30].

$(TMDTDM\text{–}TTF)_2 \cdot C_{60} \cdot 3CS_2$ (**VI**) was prepared from the molar solution of C_{60} and TMDTDM–TTF in CS_2. The single crystals grew in the form of black cuboids. A composition of the single crystals was evaluated from X-ray analysis. The compound is monoclinic with $a = 15.174(3)$ Å, $b = 13.313(3)$ Å, $c = 16.762(3)$ Å, $\beta = 103.17(3)°$, $V = 3297.06$ Å^3, $Z = 2$ [31].

$(EDY\text{–}BEDT\text{–}DT) \cdot C_{60} \cdot C_6H_6$ (**VII**) was grown from the stoichiometric solution of C_{60} and EDY–BEDT–DT in benzene. The single crystals grew in the form of black needles. The compound has a layered structure with alternating sheets of C_{60} and CS_2 and donor molecules.

Electronic absorption spectra of the fullerene, C_{60}, and its complexes with various donor molecules were measured with a Perkin-Elmer UV–VIS–NIR Lambda 19 spectrometer. All the spectra were recorded in KBr pellets containing dispersed samples with typical concentration 1:2000, at room temperature; the spectral range was from 240 to 1200 nm. The spectra (shown later in Figs. 2–6) are normalized in relation to the amplitude of the strongest electronic band of C_{60} at about 264 nm. With this choice of coordinates, an immediate comparison of the spectra of various complexes and pure C_{60} becomes possible.

3. Structural peculiarities

The BTX molecules consist of two non-planar telluraxanthene fragments in a 'double butterfly' conformation [32]. This is why BTX can coordinate by Te atoms and phenyl rings with C_{60} in both the **I** and **II** complexes (Fig. 1(A)). In complex **I** the CS_2 molecules coordinate the fullerene as well. There are no shortened C_{60}–C_{60} intermolecular contacts [33]. TGA shows that **I** loses 5.5% of its mass in the 200–230 °C range, which corresponds to the removal of CS_2 from the complex. The temperature of the donor decomposition in complexes **I** and **II** is about 30 °C higher than the temperature of the decomposition of the free BTX [26].

The tetranitride tetrasulfur molecules in complexes **III** and **IV** occur in the 'crown' form. The complexes show a layered structure: the close-packed layers of C_{60} alternate with layers containing S_4N_4 and C_6H_6 molecules. The coordination of S_4N_4 with C_{60} is possible because of lone electron pairs on the nitrogen atoms [28]. TGA shows that the temperature of S_4N_4 decomposition is higher in **IV** than in **III** by 20 °C. It suggests the stronger coordination of the donor in the complex without solvent molecules [27].

In complex **V** (Fig. 1(B)) the molecule of TPDP coordinates the fullerene by the phenyl rings. It is known from the X-ray crystal structure of the TPDP compounds that the phenyls decline from the plane of the dipyranilydene skeleton [34]. The solvent molecules are also strongly coordinated to C_{60} [30]. The temperature of the CS_2 removal from the complex is shifted to higher temperatures (120–200 °C).

Compound **VI** shows a layered structure. The acceptor layers are separated by the layers of the donor dimers in conformation 'head–tail'. The donor molecule is bent and coordinates four sulfur atoms with C_{60}. The distances between these atoms and the carbons of the fullerene are shorter than the sum of their van der Waals radii. The solvent molecules occur at two different sites: in the fullerene layers with short distances S (solvent)–C (fullerene) and between donor and C_{60} layers. In the second site, the molecules are weakly coordinated — this is suggested by the low value of the solvent release temperature, about 80 °C [31].

The EDY–BEDT–DT donor shows a similar molecular structure to the structure of BEDT–TTF and it coordinates the C_{60} in compound **VII** by the n–π interaction with sulfur atoms.

Thus, the complexes of C_{60} presented here show various structural properties — this is why they could also differ in the electronic structure.

4. Results

The electronic spectrum of pristine, very pure C_{60} in the KBr matrix is shown in all the figures of this paper as solid lines. This spectrum is useful for discussion of the spectra of the complexes. The C_{60} spectrum can be divided into arbitrary regions. The first one, between 240 and 400 nm, contains the

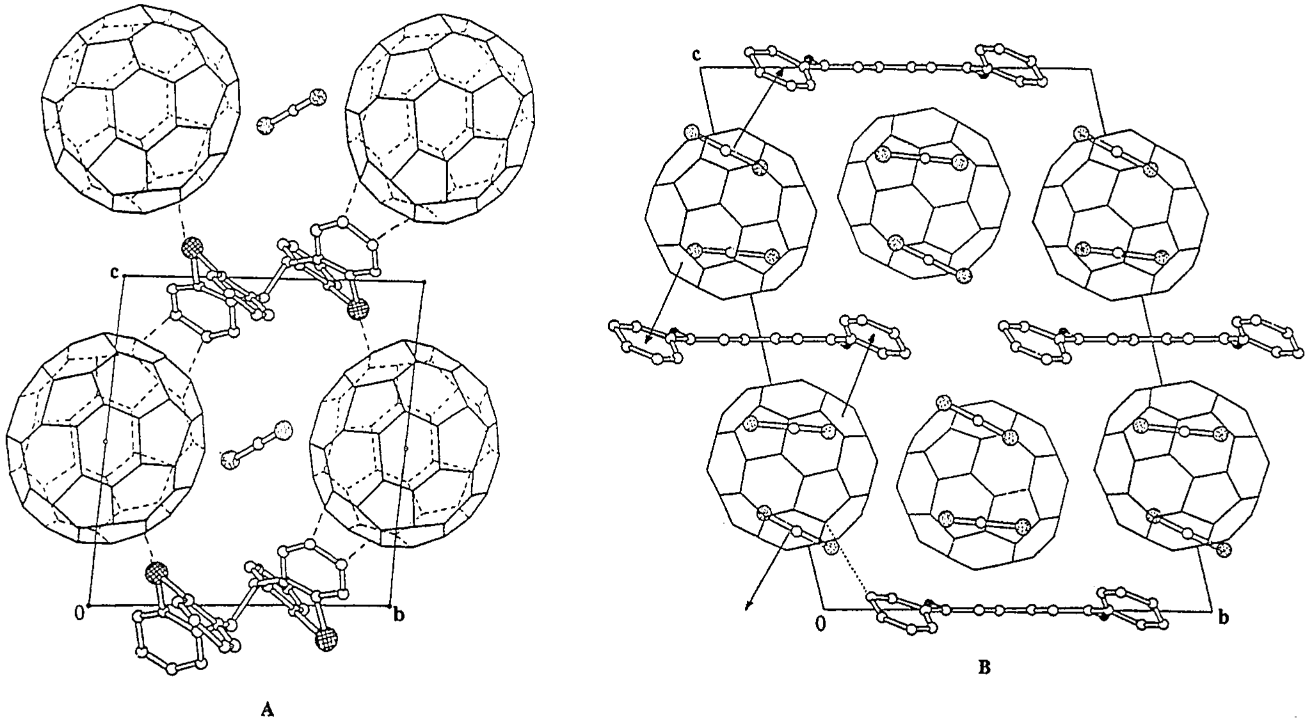


Fig. 1. Projection of the crystal structure along the *a* direction for (A) BTX·C_{60}·CS_2 (**I**) [33] and (B) TPDP·$(C_{60})_2$·$(CS_2)_4$ (**V**) [30].

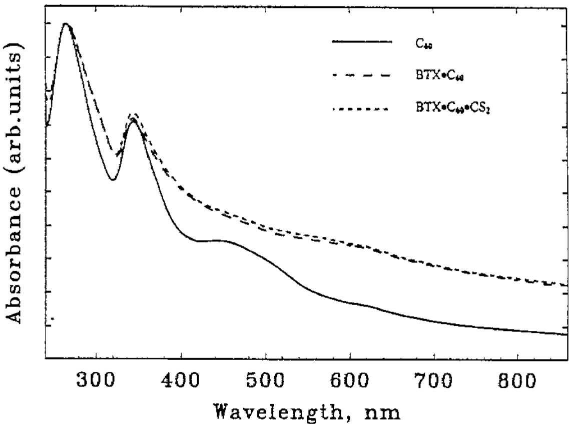


Fig. 2. Electronic absorption of C_{60}, BTX·C_{60}·CS_2 (**I**) and BTX·C_{60} (**II**) in KBr pellets.

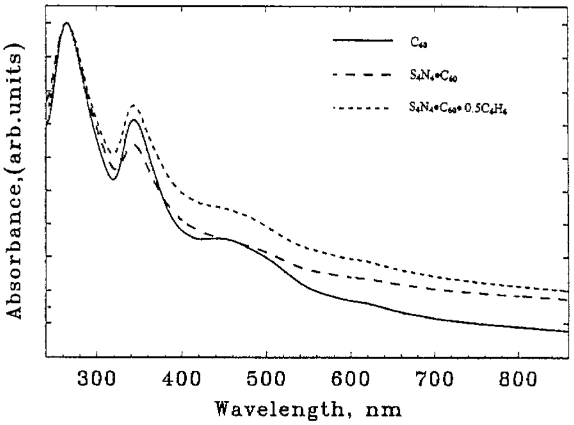


Fig. 3. Electronic absorption of C_{60}, $(S_4N_4)_{1.33}$·C_{60}·$(C_6H_6)_{0.66}$ (**III**) and S_4N_4·C_{60} (**IV**) in KBr pellets.

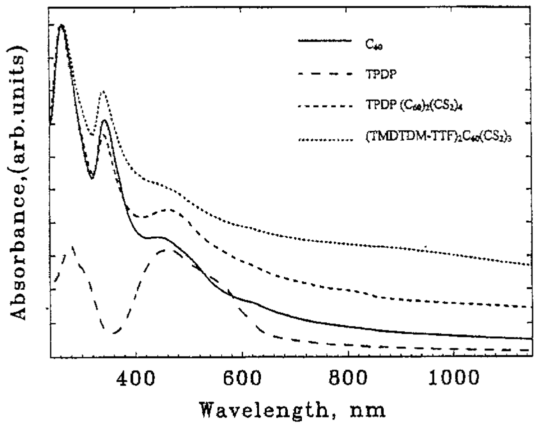


Fig. 4. Electronic absorption of C_{60}, TPDP, TPDP·$(C_{60})_2$·$(CS_2)_4$ (**V**) and $(TMDTDM{-}TTF)_2$·C_{60}·$3CS_2$ (**VI**) in KBr pellets.

dipole-allowed electronic transitions with maxima at 264 and 343 nm. In the next range, between 400 and 650 nm, weak but very broad bands, representing dipole forbidden modes, are observed at about 455 and 620 nm; the former should be assigned to C_{60} aggregates. The localization of these bands has been found by a double differentiation of the spectra.

Fig. 2 shows, apart from the above-mentioned spectrum of C_{60}, the spectra of **I** and **II**. It is shown that the band at 455 nm disappears in the spectra of both complexes of BTX, with and without the solvent. This testifies that the C_{60} aggregates disappear in the presence of the electron donors. Instead of the aggregates the fullerene molecules form the CT complex with the BTX donor. On the other hand, the absorption bands at 264 and 343 nm are broadened, which suggests that the complex formation does not affect the electronic states of C_{60} significantly, but the relevant energy levels are broadened. A small shift of the band at 620 nm (to 617 nm) can also be detected.

The electronic spectra of **III** and **IV** are shown in Fig. 3. The bands of C_{60} in the complexes are broadened in comparison with the bands of pristine C_{60}, whereas the absorption bands around 450 nm are strongly reduced. The CT band is not detectable in the complexes **I–IV**, however. It seems that the absence of CT band in the C_{60} complexes with BTX or S_4N_4 confirms their inability to form ion-radicals because of their high first oxidation potentials. Of course, the band typical for a monoanion $C_{60}{}^{1-}$ (usually about 1080 nm) is absent in all investigated complexes.

Electronic absorption spectra of **V**, **VI** and **VII** are shown in Figs. 4 and 5. A weak, but very broad band at about 810 nm has been observed in the C_{60} complex with TPDP (Fig. 4). This feature can be attributed to a CT band; it seems reasonable because the oxidation potential of TPDP is relatively low and this donor forms ion-radicals. This is why the CT process is possible between TPDP and C_{60}. The band of 620 nm, typical for the pristine C_{60}, is shifted a little more down to 614 nm. A distinct band at 452 nm should be attributed to the absorption of the donor centered at 453 nm (the band of the pristine donor TPDP is shown also in Fig. 4). One can notice some broadening of the allowed C_{60} bands, in particular the band at 343 nm.

The CT band at about 900 nm is shown in the electronic spectrum of **VI** (Fig. 4). The donor TMDTDM–TTF is also able to form ion-radicals. A weak band at about 621 nm, typical for the pristine C_{60}, is shifted down to 613 cm^{-1} in the spectrum of the complex. It seems that the band at 343 nm is also shifted down to 340 nm; this band and the band at 264 nm are broadened.

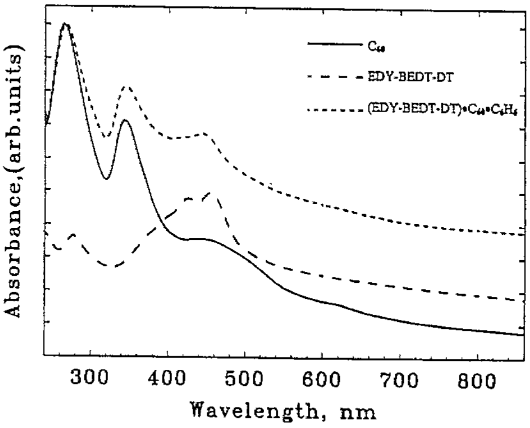


Fig. 5. Electronic absorption of C_{60}, EDY–BEDT–DT and (EDY–BEDT–DT)·C_{60}·C_6H_6 (**VII**) in KBr pellets.

The bands of complex **VII** (Fig. 5) are also broadened and shifted but slightly. At 444 nm the band of the donor is observed; this band also coincides with the weak feature of C_{60} aggregates centered at about 455 nm. On the other hand, this band is distinctly shifted by about 11 nm as compared to the donor band.

5. Discussion

The spectral changes in the absorption of the fullerene, observed after the complex formation, are similar for all the investigated compounds. First of all, a broadening of the dipole-allowed electron transitions at 262 and 343 nm is observed. Moreover, the absorption around 450 nm disappears or is strongly reduced. A comparison of the electronic spectra of the fullerene in the KBr pellet and in solution (Fig. 6) reveals the large broadening of the band about 343 nm in the solid phase. It is caused mainly by the vibrational structure of the electronic states. In the complexes, this band is further broadened (Fig. 6), but this effect is donor dependent. For the complexes with BTX the broadening of the dipole-allowed electronic transition is somewhat larger due to the stronger coordination of C_{60} by the BTX molecules. The 'double butterfly' molecular structure of this donor and physicochemical properties of Te atoms strengthen the coordination and additionally broaden the electronic band.

The large band between 490 and 640 nm seen in pristine C_{60} (see Fig. 6) is also assigned to the transitions between the singlet ground state S_0 and the lowest excited singlet state S_1 [35]; some contribution of the C_{60} aggregates [21,22] is also possible. In the complexes this band is strongly reduced. In the complex with BTX the large absorption of C_{60} is completely invisible. This suggests that the phonon spectrum of the C_{60} molecule is strongly influenced by the intermolecular interactions, and the large band between 490 and 640 nm, activated by vibronic coupling, should be invisible.

It is distinctive that the CT bands have been observed only for C_{60} complexes with TPDP and TMDTDM–TTF (compounds **V** and **VI**). According to Saito et al. [19], the CT band is located between 800 and 900 nm. Both the donors can form cation-radicals with suitable acceptor molecules. Since the fullerene electron affinity is pronounced [36,37], a CT mechanism is conceivable in these complexes. The absence of the CT band for other investigated donors coincides with their inability to form ion-radicals; otherwise, the process like $D + C_{60} \rightarrow D^+ + C_{60}^-$ is not very probable for these donors. It seems that these compounds are weak CT complexes in the meaning of Mulliken's complexes [18]. Their fundamental state is neutral; the induced CT is observed only for the strongest donors TPDP and TMDTSM–TTF. It should be noticed that the C_{60} band at 621 nm is shifted down by several nm in the complexes in which the CT occurs.

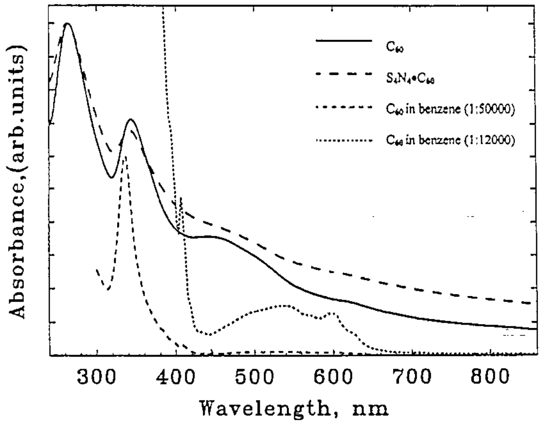


Fig. 6. Electronic absorption of C_{60} and $S_4N_4 \cdot C_{60}$ in KBr pellets and C_{60} in benzene solution of various concentrations: 1:50 000 and 1:12 000.

The absorption bands of the donors are clearly evident in the spectra, with merely insignificant changes of the wavelengths in all the complexes. In compounds **V** and **VII** the donor absorption coincides with the weak absorption of the neutral C_{60}.

6. Conclusions

Some typical changes of the electronic spectrum of fullerene are observed after the complex formation. These changes are correlated with the electron-donor properties of the organic molecules forming the complexes with C_{60}. In particular, a broadening of the electron excitations at 262 and 343 nm is correlated with the nature of the complex and the coordination of C_{60}. Thus, the studies of the electronic spectra in the visible and near-IR regions can give information on the coordination and intermolecular interactions between C_{60} and donors in various complexes. Among other features, it can be evidenced from the disappearance of the large band between 490 and 640 nm, as well as the onset of the CT band.

Acknowledgements

This work was financially supported by the Polish Committee for Scientific Research (Grant No. 7T08A 044 11) and by the Russian program 'Fullerenes and Atomic Clusters'. D.V.K. and V.N.S. acknowledge the Institute of Molecular Physics, P.A.S., Poznań, for its hospitality.

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