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Steric conditions for donor–acceptor interactions in C_{60} complexes with planar organic donors

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Abstract

Charge transfer complexes of fullerene C_{60} with planar donors of tetrathiafulvalene, dithiadiazafulvalene and pyranylidene family were investigated by IR- and UV-VIS-NIR spectroscopy. The analysis of IR and X-ray data shows that the charge transfer complexes of fullerene with the planar donors are involved in polarization interactions of van der Waals type. Charge transfer is very weak in these compounds and is hindered by unfavourable steric factors. As a result, the CT rate does not correlate with the ionization potential of the donor; the charge transfer absorption bands are very weak too. © 1998 Elsevier Science B.V. All rights reserved

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1. Introduction

Compounds derived from fullerene C_{60} are intensively investigated because of their physical properties [1–3]. Up to now, various C_{60} -based materials have been synthesized, among them charge transfer (CT) complexes [4–13] and anion-radical salts [14]. Many CT complexes of C_{60} are obtained with planar donors of the tetrathiafulvalene [15], pyranylidene [16] or dithiadiazafulvalene [17] family. It is known that the CT complexes and radical cation salts of these donors with strong π -acceptors or inorganic anions show very interesting electron transport properties; some of them give evidence for superconductivity [15,18,19].

As a rule, π -donors and π -acceptors studied have a planar shape. Therefore, the donor-acceptor interaction in their CT complexes occurs without any steric hindrances: donor and acceptor molecules are able to approach quite close to each other and their (HOMO-LUMO) molecular orbitals can effectively overlap. In this case, the charge transfer rate δ is mainly dependent on the ionization potential (I_p) of the donor and electron affinity (E_a) of the acceptor. The exceptions are only some donors, e.g. hexaethyl- or hexa-tretbutylbenzene [20] with spacers which prevent a close approach of acceptor molecules.

Fullerenes consist of hexagonal and pentagonal rings which form a practically spherical surface of the molecule [1]. That is different from other planar π -acceptors. The shape of the t_{1u} (LUMO) molecular orbital of C₆₀ is also close to spherical. Therefore, a

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close approach of the donor and fullerene molecules, and parallel arrangements of their molecular orbitals for an effective overlapping, are mainly defined by steric compatibility between the shape of donor and fullerene molecules.

Electron affinity of C₆₀ is rather small, a relative value of adiabatic E_a obtained by CT absorption energies $(h\nu_{\rm CT})$ or the reversible redox potentials in a solution is approximately 2.16 eV [4], but $E_a = 2.65 \text{ eV}$ in a gas phase [21]. It is found [4] that the electron acceptability of C_{60} is comparable to that of weak electron acceptors s-tetracyanobenzene, 2,5dibromo-p-xyloquinone or 2,3-dichloro-1,4-naphthoquinone. The C₆₀ molecule possesses a very high polarizability (~85 A³) [22], therefore, the contribution of van der Waals polarization interaction is substantially higher for C_{60} than other π -acceptors. This work reports the study of C₆₀ complexes with planar donors of a wide ionization potential range by IR- and UV-VIS-NIR spectroscopies. The equation for the estimation of the CT rate in C₆₀ complexes is derived and the CT rate in the complexes investigated is evaluated. The intensity of CT bands in the VIS-NIR range is discussed. The IR-spectra of donor molecules in some C_{60} complexes were studied. These data were compared with the results of X-ray analysis. Possible mechanisms for steric hindrances for charge transfer are considered.

2. CT complexes and the evaluation of the CT rate

According to the Mulliken theory [23], the binding energy of CT complexes is defined by van der Waals forces: coulombic, exchange, polarization interaction energies, and by the CT interaction [23–25]. For the complexes consisting of neutral components without large dipole moments, the polarization interaction is a basic factor. It depends on polarizability of donor and acceptor molecules, and strongly depends on the intermolecular distance (1/r6) between them.

Another type of interaction in these complexes is defined by charge transfer between the donor and acceptor. The dependence of the CT degree (δ) on I_p of the donor, E_a of the acceptor, Madelung energy E_c , and the overlapping integral (S_{01}) is quite well described by the equation for the complexes in their ground state [24]:

$$\delta^{1/2} = c(S_{01}) / (I_{\rm p} - E_{\rm a} - E_{\rm c}) \tag{1}$$

where c is a constant.

It is found that the Madelung energy $E_{\rm c}$ is approximately constant $\sim 3.0 \pm 0.3$ eV [24] for the CT complexes consisting of neutral components, thus the CT rate is dependent on the $(I_p - E_a)$ difference and to a great extent on the overlapping integral (S_{01}) . Charge transfer is possible only if S_{01} is not equal to zero. The value of S_{01} is a function of the overlapping integral for boundary molecular (HOMO-LUMO) orbitals (S_{DA}) of the donor and acceptor. The maximal overlapping of these orbitals in the complexes of π -donor with π -acceptors is possible at their parallel mutual arrangement [24], to which a more effective CT corresponds. Charge transfer from the donor to the acceptor manifests itself as an absorption in the VIS-NIR range. The intensity of the bands associated with charge transfer is also dependent on the overlapping of donor and acceptor HOMO-LUMO orbitals. The decrease of the overlapping due to unfavourable steric factors results in the decrease in the intensities of CT bands [24,25].

There are different methods for the determination of the CT rate: X-ray analysis which enables the determination of the CT rate from the changes in the bond lengths [26], the method of dipole moments [25], and the Tanaka method which is based on the determination of the oscillator strength of the electron transition associated with charge transfer in the VIS-NIR range [27], and others [24,25]. All these methods can be used for the evaluation of the CT rate only for single crystals with known crystal structures. Raman scattering [28] and IR-spectroscopy [29-31] are considered to be good techniques for the estimation of the CT rate even on powdered samples [30,31] or in solutions [32]. There is a simple relation between the electron density on a certain bond and its force constant [32]. This results in a linear dependence on the force constant (k) and the squares of the frequency (ν^2) of some vibrational modes of the donor or acceptor molecules on the CT rate. This linear dependence is described by the following equation:

$$\delta = \Delta k / (k(1 - k_1/k)) \tag{2}$$

Table 1

provided that

$$2(\nu_0 - \nu_N)/\nu_0 \cong \Delta k/k \tag{3}$$

[24,32] and k is approximately proportional to ν^2 , the following equation is derived:

$$\delta = 2\Delta \nu / (\nu_0 (1 - \nu_1^2 / \nu_0^2)) \tag{4}$$

where ν_0 is the mode frequency measured for a neutral molecule, ν_1 is the frequency of the same mode of the anion or cation radical, and $\Delta \nu$ is the difference between the mode frequency for a neutral molecule and the corresponding frequency of the CT complex (ν_N). The attribution for k_0 , k_1 , Δk corresponds to those for ν_0 , ν_1 and $\Delta \nu$, respectively.

All the above-mentioned dependences can also be used in the consideration of C₆₀ CT complexes. Charge transfer to C₆₀ leads to linear frequency changes and to the linear increase of the square root of oscillator strength versus the degree of CT for two $[F_{1u}(2) \text{ and } F_{1u}(4)]$ IR active modes of the fullerene [33,34] at 576 and 1429 cm⁻¹, respectively. The IR measurements of C₆₀ doped by alkali metal (A_x C₆₀ phases where x = 1, 3, 4 and 6), and anion radical salts of C_{60} show the maximal changes for the $F_{1u}(4)$ mode. The frequencies shifted from 1429 cm⁻¹ for $C_{60}(0)$ to 1390–1394 cm⁻¹ for C₆₀(– 1), and the square root of oscillator strength increases from $64 \pm 5 \text{ cm}^{-1}$ for $C_{60}(0)$ to 152 ± 40 cm⁻¹ for $C_{60}(-1)$ [35–38]. Therefore, this mode is more suitable for the determination of the CT rate in C_{60} complexes than other C_{60} modes. Some deviation from the linearity of the frequency shifts of the $F_{1u}(4)$ mode versus the degree of CT were observed only for strong ionization of C₆₀ $(A_x C_{60} \text{ phases with } x > 3)$. Therefore, the correlation is quite linear for CT complexes with $\delta < 1$. Thus, for a uniform charge distribution over the C₆₀ molecule and for $\delta < 1$, Eq. (4) is valid. In the case of the F_{1u}(4) mode of C₆₀, ν_0 is 1429 cm⁻¹, $\Delta \nu$ is the difference between 1429 cm⁻¹ and the corresponding frequency in the CT complex of fullerene, and ν_1 is the frequency of the same mode of the monoanion $C_{60}(-1)$. Table 1 shows the frequencies of the $F_{1u}(4)$ mode of $C_{60}(-1)$ in its various salts. By assuming the value of ν_1 to be 1394 cm⁻¹, an approximate relation can be derived:

 $\delta = 0.028 \Delta \nu \tag{5}$

The approximate degree of CT can be evaluated by

Frequencies of the F_{1u} (4) mode in the C_{60} monoanion-radical salts

Salt	Frequency (cm ⁻¹)
Rb C ₆₀ (single crystal)	1392 [35]
Rb C ₆₀ (thin film)	1393 [36]
(Ph ₄ P) ₂ C ₆₀ Cl (single crystal)	1394 [37]
(Ph ₄ P) ₂ C ₆₀ I	1394 [38]
(Ph ₄ As) ₂) C ₆₀ Cl (single crystal)	1390 [37]

using this equation directly from the frequency shift. It should be noted that the noticeable changes in the force constant of the bond under study begin with a CT rate more than 0.03.

3. Experimental

Single crystals of the CT complexes were grown by a slow evaporation from a solution of C_{60} and donors in different solvents. The (TMDTDM-TTF)₂C₆₀(CS₂)₃, (BEDO-TTF)₂C₆₀, (EDT-TTF)₂C₆₀CS₂, DTDAF(C₆₀)₂CS₂ and TPDP(C₆₀)₂(CS₂)₄ complexes were grown from carbon disulphde (CS₂), TBT(C₆₀)₂ and BNDY·C₆₀ were prepared in toluene, and the rest of the complexes were obtained in benzene. The preparation procedure of CT complexes as single crystals is described in detail elsewhere [5–10,39].

The single crystals of TPDP(C_{60})₂(CS₂)₄ [5,6] and (TMDTDM-TTF)₂C₆₀ (CS₂)₃ [7,10] appear as cubes. Small black crystals were obtained as rhombic plates for (TBT-TTF)₂C₆₀ [8], (EDT-TTF)₂C₆₀·CS₂ [10], DTDAF(C₆₀)₂CS₂ [39] and BEDO-TTF·C₆₀C₆H₆ [8], whereas the crystals of (PhMeTTF)₂C₆₀C₆H₆ and (PhTTF)₂C₆₀·C₆H₆ are prismatic [8]. The crystals of EDY-BEDT-DT·C₆₀·C₆H₆ [9] and EDT-TTF·C₆₀·C₆H₆ [10] were grown as black needles. Small crystals of (BEDO-TTF)₂C₆₀ (4,8] were obtained as polyhedrons, BNDY·C₆₀ crystals [8] were rhombic plates, and DBTTF·C₆₀·C₆H₆ was crystallized as small cubes [8].

Room temperature IR transmission spectra of single crystals were registered with a FT-IR Perkin Elmer 1725 X spectrometer equipped with an IR microscope and a narrow band MCT detector in the $700-3200 \text{ cm}^{-1}$ range. The crystals were mounted on a KBr plate and a surface 0.1 mm in diameter was selected for the measurements. The spectra of the

complexes and the donors were also recorded in KBr pellets containing dispersed samples, with a typical concentration of 1:1000 in the 400–3200 cm⁻¹ range. Assuming the 1 cm⁻¹ accuracy for the wave-number, one could evaluate the parameter δ from Eq. (5) with an accuracy of \pm 0.03.

Electron absorption spectra of C_{60} complexes were measured with Lambda 19 Perkin Elmer UV-VIS-NIR spectrometer at room temperature. All spectra were recorded in KBr pellets containing dispersed samples, with a typical concentration of 1:4000 within 220–2000 nm spectral range.

4. Results and discussion

The donor molecules are shown in the Scheme 1 and their characteristics are presented in Table 2. All these donors with conjugated π -electron systems are planar in their ground state or slightly deviate from planarity. Adiabatic ionization potentials (I_p^{ad}) for TTF derivatives are calculated from a linear function of the first redox potential (E_{ox}^1) versus I_p^{ad} [40]. Such a function is also used for other classes of donor molecules [41]. The calculated I_p^{ad} values are only approximate due to some deviation from this linear function. Such deviations are associated with the differences in solvation energies of some donor molecules and are observed, e.g. for tetrathiafulvalene and teraselena-fulvalene molecules [40,41]. I_p^{ad} of the donors changes within 5.7–7.1 eV.

Since C_{60} is a weak acceptor, the formation of C_{60} anion radical salts was observed for the donors with E_{ox}^{l} more negative than -0.44 eV or adiabatic I_{p} less than 5.5 eV. TDAE donor forms an anion radical salt with C_{60} and its I_{p}^{ad} is less than 5.36 eV [42]. Thus, the donors used by us are rather weak and can form only CT complexes with C_{60} with the different CT rate. The substantial CT rate was assumed only for stronger donors, i.e. DTDMF and TPDP.

The FT-IR absorption spectrum of the BEDO-TTF·C₆₀·C₆H₆ single crystal is shown in Fig. 1(a); the spectra of the BEDO-TTF·C₆₀·C₆H₆ complex and the donor in KBr pellets are shown in Fig. 1(b) and (c). These spectra are typical for the investigated materials and reflect the effects common for all complexes. First of all, the spectra of the complexes consist of 10s of bands. Two out of four F_{1u} modes,



Scheme 1.

Table 2		
Donors a	nd their	characteristics

Donor	$E_{\rm ox}.1^{*a} ({\rm eV})$	$E_{\rm ox}.2^{\rm b}~({\rm eV})$	$I_{\rm p}~({\rm eV})$	$I_{\rm p} - E_{\rm a}({\rm C}_{60})^{\rm c}({\rm eV})$
2,2'-bi/4-methylthio-3-phenyl-5-methoxy-carbonyl-1,3-thiazolinilidene/,	-0.02 [17]	0.48 [17]	5.74*	3.58
DTDAF				
2,2',6,6'-tetraphenyldipyranilydene, TPDP	0.15 [43]	0.47 [43]	5.80 [16]	3.64
trans-5,5'-diphenyl-4,4'-dimethyltetrathiafulvalene, PhMeTTF	0.34 [44]	0.73 [44]	6.13 ^a	3.97
tetramethylenedithiodimethyl-tetrathiafulvalene, TMDTDM-TTF	0.39 [45]	0.72 [45]	6.20 ^a	4.04
2,2'-ethanediylidene bis (4,5-ethyleneditio-1,3-dithiole), EDY-BEDT-DT	0.41 [45]	0.64 [45]	6.22 ^a	4.06
bis(ethylenedioxy)tetrathiafulvalene,BEDO-TTF	0.42 [4]	-	6.23 ^a	4.07
trans-4,4'-diphenyl-tetrathiafulvalene, PhTTF	0.43 [45]	0.77 [45]*	6.24	4.08
ethylenedithio-tetrathiafulvalene, EDT-TTF	0.44 [4]	-	6.25 ^a	4.09
4,4',5,5'-tetrakis(benzoylthio)tetrathiafulvalene TBT-TTF	0.66 [45]	0.93 [45]	6.46 ^a	4.30
dibenzotetrathiafulvalene, DBTTF	0.62 [45]	0.89 [45]	6.68 [46]	4.52
binaphtho[1,6-d,e]-1,3-dithiin-2-ylidene, BNDY	1.14 [47]	-	7.1 ^a	4.94

^aThe ionization potentials of TTF derivatives estimated from a linear function of the first redox potential versus adiabatic I_p ($I_p^{ad} = 1.13 E_{ox}$. (1) + 5.75 eV) obtained for molecules [39].

^bThe first and second oxidation potentials in acetonitrile.

^cAdiabatic E_a of C₆₀ 2.16 eV [4].

which are IR active in the C_{60} molecule of I_h point group, appear near 1183 cm⁻¹ and 1429 cm⁻¹ absorption peaks; the other two F_{1u} modes which appear around 576 cm⁻¹ and 527 cm⁻¹ can be observed (for technical reasons) only in the spectra of powdered samples in a KBr matrix. There are also numerous bands of donors and solvents used for the crystal growth. It is typical that almost all the bands have frequencies below 1550 cm⁻¹.

The spectra of the complexes also contain numerous bands characteristic of the broken I_h symmetry of the fullerene molecule [Fig. 1(a) and 2(a)].



Fig. 1. FT-IR spectrum of single crystal of BEDO-TTFC₆₀C₆H₆ CT complex (a); that of BEDO-TTFC₆₀C₆H₆ complex in a KBr pellet (b) and that of BEDO-TTF in KBr (c).

The lowering of the molecular symmetry leads to the activation of many silent modes and the appearance of a great number of higher order combination modes in the crystal. This phenomenon was observed for the first time by Martin et al. [48] in C_{60} thin films and by us in C_{60} clathrates with various solvents [49]. The analysis of the silent modes wavenumbers shows that the complex formation of fullerene C_{60} with donors leads to very small $(1-2 \text{ cm}^{-1})$ shifts of the band frequencies.

The spectra of $(EDT-TTF)_2C_{60}CS_2$, TPDP $(C_{60})_2(CS_2)_4$ and $(TMDTDMTTF)_2C_{60}(CS_2)_3$ are shown in Figs. 2–4, respectively. The spectra are limited by 1600 cm⁻¹ because all normal modes



Fig. 2. FT-IR spectra of the single crystal of $(EDT-TTF)_2 C_{60} CS_2$ (a) and EDT-TTF in a KBr pellet (b) in the range of normal vibrations of fullerene.



Fig. 3. FT-IR spectra of the TPDP $(C_{60})_2 (CS_2)_4$ complex (a) and the donor (b) in a KBr pellet in the range of normal vibrations of the fullerene.

of C_{60} are located at lower frequencies; at frequencies higher than 1600 cm⁻¹ only the higher-order combination vibrations are observed [50].

As was discussed above, charge transfer from the donors to C_{60} most strongly affects the frequency of the $F_{1u}(4)$ mode of fullerene. This mode is located at 1429 cm⁻¹ in a neutral C_{60} but is usually slightly downshifted in the CT complexes under study. Table 3 shows the frequency of the $F_{1u}(4)$ modes and their shifts with respect to 1429 cm⁻¹, for the CT complexes. The last column contains the estimated values of the CT degree yielded from Eq. (3). The frequency shifts are approximately 1 cm⁻¹, e.g. the parameter δ is below 0.03. One can notice that only for two complexes with the EDT-TTF donor does the CT degree approximate to 0.05. Thus, the CT rate is practically independent of the ionization potential of the donor.



Fig. 4. FT-IR spectra of the (TMDTDM-TTF)₂ C₆₀(CS₂)₃ complex (a) and the donor (b) in a KBr pellet in the range of normal vibrations of the fullerene.

We compared our data for the CT rate in the C_{60} complexes (Table 3), with those published in Refs [26,27,31,51–53] for TCNQ complexes with different planar donors. These data (Fig. 5) show the dependence of the CT rate versus the $(I_p - E_a)$ difference for C₆₀ complexes and TCNQ complexes. The dependence, which is similar to that for TCNQ, is characteristic of other π -acceptors and reflects the common tendency of the CT rate changes depending on the $(I_p - E_a)$ difference for a variety of π -acceptors. The deviations from this dependence are due to the differences in the overlapping integral for some complexes. For TCNQ complexes, the noticeable CT rate $(\delta > 0.1)$ was observed even at the $(I_p - E_a) \sim 5.2 -$ 4.6 eV. A strong increase of the CT rate ($\delta > 0.5$) starts from 4.0 eV and is characteristic of organic metals of the TTFs-TCNQ family [53]. Ion radical salts ($\delta \sim 1$) dominate if the $(I_p - E_a)$ value is less than 3.3 eV.

 C_{60} complexes with planar donors do not follow the common dependence characteristic of π -acceptors and the CT rate is close to 0 in all cases. This is unusual especially for such strong donors as DTDAF and TPDP. This can be understood from the consideration of crystal structures of the C_{60} complexes and is discussed for separate examples; for other samples the effects are similar.

C₆₀ molecules are coordinated with the donor TPDP by phenyl groups in the TPDP(C_{60})₂(CS_2)₄ complex. This is possible because the phenyl groups are deflected by 32.9° from the plane of the dipyranylidene framework. This deflection is much greater than those in the neutral donor which are 10.2° and 7.6° (for various phenyl groups), and are comparable with those for cation radical of TPDP sulphur analogue (26.5°) [55]. Such a great deflection of phenyl groups indicates that their conjugation with the dipyranylidene skeleton is broken. The central C=C bond remains unchanged in the complex (1.385 Å) as compared to that in the neutral donor (1.384 Å) [56]. In this case, electron density can be transferred only from the phenyl groups of TPDP to the C₆₀ molecule but not from the dipyranylidene skeleton. This is confirmed by spectral studies.

The analysis of normal mode frequencies shows the frequency shifts (up to 8 cm^{-1}) and the intensity changes for TPDP in the C₆₀ complex relative to the individual donor. The strongest bands of the donor are

Complex	$\nu_{\rm N}~({\rm cm}^{-1})$	$\Delta \nu \ (\mathrm{cm}^{-1})$	CT rate (δ)	
$DTDAF(C_{60})_2CS_2$	1428	1	< 0.03	
$TPDP(C_{60})_2(CS_2)_4$	1428	1	< 0.03	
$(PhMeTTF)_2C_{60}C_6H_6$	1429	0	0	
(TMDTDM-TTF) ₂ C ₆₀ (CS ₂) ₃	1429 ^a	0	0	
$(PhTTF)_2C_{60}C_6H_6$	1428	1	< 0.03	
EDY-BEDT-DT C ₆₀ C ₆ H ₆	1428	1	< 0.03	
(BEDO-TTF) ₂ C ₆₀	1430	0	0	
BEDO-TTFC ₆₀ C ₆ H ₆	1430	0	0	
$(EDT-TTF)_2C_{60}CS_2$	1427	2	0.05	
EDT-TTF C ₆₀ C ₆ H ₆	1427	2	0.05	
DBTTFC ₆₀ C ₆ H ₆	1430 ^a	0	0	
$TBT-TTF(C_{60})_2$	1429	0	0	
BNDY C ₆₀	1428	1	< 0.03	
	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c } \hline Complex & ν_N (cm^{-1})$ \\ \hline DTDAF(C_{60})_2CS_2 & 1428 \\ TPDP(C_{60})_2(CS_2)_4 & 1428 \\ (PhMeTTF)_2C_{60}C_6H_6 & 1429 \\ (TMDTDM-TTF)_2C_{60}(CS_2)_3 & 1429^a \\ (PhTTF)_2C_{60}C_6H_6 & 1428 \\ EDY-BEDT-DT C_{60}C_6H_6 & 1428 \\ (BEDO-TTF)_2C_{60} & 1430 \\ BEDO-TTFC_{60}C_6H_6 & 1430 \\ (EDT-TTF)_2C_{60}CS_2 & 1427 \\ EDT-TTF C_{60}C_6H_6 & 1427 \\ DBTTFC_{60}C_6H_6 & 1430^a \\ TBT-TTF(C_{60})_2 & 1429 \\ BNDY C_{60} & 1428 \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c c c } \hline Complex & $\nu_{\rm N}$ (cm^{-1})$ & $\Delta\nu$ (cm^{-1})$ \\ \hline DTDAF(C_{60})_2CS_2 & 1428 & 1 \\ TPDP(C_{60})_2(CS_2)_4 & 1428 & 1 \\ (PhMeTTF)_2C_{60}C_6H_6 & 1429 & 0 \\ (TMDTDM-TTF)_2C_{60}(CS_2)_3 & 1429^{a} & 0 \\ (PhTTF)_2C_{60}C_6H_6 & 1428 & 1 \\ EDY-BEDT-DT C_{60}C_6H_6 & 1428 & 1 \\ (BEDO-TTF)_2C_{60} & 1430 & 0 \\ BEDO-TTFC_{60}C_6H_6 & 1430 & 0 \\ (EDT-TTF)_2C_{60}CS_2 & 1427 & 2 \\ EDT-TTF C_{60}C_6H_6 & 1427 & 2 \\ EDT-TTF C_{60}C_6H_6 & 1430^{a} & 0 \\ TBT-TTF(C_{60})_2 & 1429 & 0 \\ BNDY C_{60} & 1428 & 1 \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c c c } \hline Complex & ν_N (cm^{-1})$ & $\Delta\nu$ (cm^{-1})$ & CT rate (δ) \\ \hline DTDAF(C_{60})_2CS_2 & 1428 & 1 & <0.03 \\ TPDP(C_{60})_2(CS_2)_4 & 1428 & 1 & <0.03 \\ (PhMeTTF)_2C_{60}C_6H_6 & 1429 & 0 & 0 \\ (TMDTDM-TTF)_2C_{60}(CS_2)_3 & 1429^a & 0 & 0 \\ (PhTTF)_2C_{60}C_6H_6 & 1428 & 1 & <0.03 \\ EDY-BEDT-DT C_{60}C_6H_6 & 1428 & 1 & <0.03 \\ (BEDO-TTF)_2C_{60} & 1430 & 0 & 0 \\ BEDO-TTFC_{60}C_6H_6 & 1430 & 0 & 0 \\ (EDT-TTF)_2C_{60}CS_2 & 1427 & 2 & 0.05 \\ EDT-TTF C_{60}C_6H_6 & 1427 & 2 & 0.05 \\ EDT-TTF C_{60}C_6H_6 & 1429 & 0 & 0 \\ TBT-TTF(c_{60})_2 & 1429 & 0 & 0 \\ BNDY C_{60} & 1428 & 1 & <0.03 \\ \hline \end{tabular}$

Table 3 Frequencies of the $F_{1u}(4)$ modes and the evaluated degrees of charge transfer for the investigated complexes

^aThe frequency coincides with the donor vibration.

observed at 530, 582, 630, 651, 687, 757, 764, 817, 840, 918, 996, 1012, 1029, 1077, 1181, 1227, 1265, 1308, 1327, 1341, 1445, 1493, 1576, 1586, 1598 and 1660 cm⁻¹ [Fig. 3(b)]. The spectra of the TPDP(C_{60})₂(CS₂)₄ complex exhibit the strongest bands of the donor at 665, 687, 758, 823, 916, 995, 1027, 1070, 1267, 1313, 1337, 1447, 1491, 1576, 1597 and 1662 cm⁻¹ [Fig. 3(a)]. Some typical vibrations of the phenyl groups near 800 cm⁻¹, and between 1010 and 1265 cm⁻¹ are shifted by ~6–8 cm⁻¹. The bands corresponding to C-H vibrations of TPDP phenyl groups and C-H stretching vibrations in the dipyranylidene skeleton of the neutral donor and the donor in its CT complex are presented in Fig. 6. It is seen that all C-H vibrations have approximately equal intensities in the individual donor [Fig. 6(b)],while the intensity of C-H vibrations of phenyl groups (3098, 3081, 3055, 3034 cm⁻¹) is significantly enhanced relative to C-H stretching vibrations in the dipyranylidene skeleton (2920, 2909 cm⁻¹) in the complex [Fig. 6(a)].



Fig. 5. The CT rate versus the $(I_p - E_a)$ differences for C₆₀ complexes (squares) and TCNQ complexes (circles). For C₆₀ complexes, the numbers are according to Table 3, and for TCNQ complexes, the numbers are: (1) toluene [31], (2) o-xylene [31], (3) anisole [31], (4) naphthalene [26], (5) p-terphenyl [27], (6) hexamethylbenzene [27], (7) acenaphthene [27], (8) carbazole [27], (9) anthracene [27], (10) phenothiazine [27], (11) perylene [51], (12) dimethylhydrophenazine [29], (13) N-methylphenazine [52], (14) tetraselenofulvalene [53], (15) TTF [52], (16) N,N,N',N'-methyl-p-phenyl-lenediamine [26], (17) hexamethylenetetraselenafulvalene [53]. The values of the adiabatic I_p of the donors are taken from Refs [26,39,41,54]. The adiabatic E_a of TCNQ is 2.82 eV [4].



Fig. 6. FT-IR spectra of the single crystal of TPDP $(C_{60})_2$ (CS₂)₄ (a) and the donor (b) in a KBr pellet in the range of C–H vibrations (2900–3100 cm⁻¹).

The similar modification and enhancement of these vibrations were recently observed by Świetlik et al. [57] for numerous solvated crystals of the fullerene C₆₀. It was suggested that there is a significant interaction between the π clouds of C₆₀ and the solvent molecules. This effect has an influence on the position and shape of the IR bands assigned to the CH stretching vibrations of the guest molecule, as well as the slight frequency changes of the vibrational C₆₀ bands. It should be noted that the central C=C and C-H stretching vibrations of the dipyranylidene skeleton remain practically unchanged in the complex formation. The vibrations of the C=C central bond which is the most sensitive to the changes in electron density in the TPDP molecule is shifted only from 1660 cm^{-1} in the neutral donor to 1662 cm^{-1} in the CT complex [58].

Similarly to the CT complexes of C_{60} with TPDP, the changes in the geometry of the donor molecule were observed for C₆₀ complexes with the donors of the TTF family. The effect is especially pronounced in the CT complexes with TMDTDM-TTF donor: $(TMDTDM-TTF)_2 C_{60} (CS_2)_3$. The complex shows a sandwich-like molecular packing [7]: each C_{60} sphere is sandwiched between two donor molecules (Fig. 7). The efficient packing is provided by a 'concave' conformation of TMDTDM-TTF molecule. The dihedral angles between the central TTF core, and the outer tetramethylenedithio and dimethyl planes of the donor are 27.7° and 23.6° , respectively. Such a conformation allows a close packing of donor and C_{60} molecules. The C(C₆₀)-S (donor) shortest intermolecular contacts are between 3.4 and 3.5 Å, i.e.



Fig. 7. The packing of TMDTDM-TTF donors molecule around the C_{60} molecule in the structure of (TMDTDM-TTF)₂ $C_{60}(CS_2)_3$ (according to the data [7]).

they are close to the sum of van der Waals radii of sulphur and carbon atoms (3.57 Å) [7]. Therefore, this close coordination with C_{60} results in a strong deformation of the initially planar donor molecule.

The changes in the molecular conformation of TMDTDM-TTF result in numerous shifts and changes in bands intensities of normal vibrations of the donor in the complexes with C_{60} with respect to the spectrum of the neutral donor [Fig. 4(a),(b)]. The strongest IR absorption bands of the donor are observed at 407, 438, 555, 775 (vs), 805, 865, 890, 975, 1082, 1181, 1283, 1298, 1436(s), 1486 and 1537 cm⁻¹ [Fig. 6(b)], whereas those in the spectra of the complex are recorded at 454, 622, 722, 749, 776, 1297, 1429 (coincides with C_{60} vibration), 1460, 1508 cm⁻¹.

The analysis of the normal vibrations of BEDO-TTF and EDT-TTF donor molecules also shows the shifts and changes in the bands intensities of some normal vibrations which are obviously associated with the changes of a donor molecule geometry. The strongest IR absorption bands of BEDO-TTF are observed at 462, 587, 669, 767, 864, 962, 1015, 1082, 1157, 1168, 1199, 1240, 1269 and 1444 cm⁻¹ [Fig. 1(c)], whereas those for BEDO-TTF·C₆₀ C₆H₆ single crystals are at 668, 788, 849, 1042, 1212, 1361 and 1484 cm⁻¹ [Fig. 1(b)]. The strongest IR absorption bands of EDT-TTF are observed at 507, 652, 729, 776, 792, 898, 1091, 1128, 1254, 1288, 1423 and 1543 cm⁻¹ [Fig. 1(c)], whereas those for (EDT-TTF)₂C₆₀ CS₂ single crystals are at 729, 739, 780, 792, 898, 1091, 1128, 1254, 1284, 1404, 1558 cm⁻¹ [Fig. 2(a)]. The similar spectral changes are observed for other investigated complexes of C₆₀ with planar donors. The changes of the donor molecule conformation were observed earlier in other complexes of C₆₀ with TTF derivatives (BEDT-TTF)₂C₆₀ [12] and (BDMT-TTeF)C₆₀ CS₂ [13].

UV-VIS-NIR optical absorption spectra of C_{60} complexes are investigated. The spectrum of EDT-TTF·C₆₀·C₆H₆ (a) in 220–2000 nm range and the spectra of (PhTTF)₂ C₆₀·C₆H₆ (b), (EDT-TTF)₂C₆₀·CS₂ (c), (PhMeTTF)₂C₆₀·C₆H₆ (d), EDY-BEDT-DT·C₆₀·C₆H₆ (e) and C₆₀ (g) in the CT range 600–1400 nm are presented in Fig. 8. The comparison of VIS-NIR spectra of these complexes with those of C₆₀ and the corresponding donors shows that the bands in the 800–1150 nm range are absent in the spectra of C₆₀ and donors, and are associated with CT. The intensities of the CT bands of the complexes



Fig. 8. Electron absorption spectrum of EDT-TTF·C₆₀·C₆H₆ (a) in 220–2000 nm and the spectra of (PhTTF)₂C₆₀·C₆H₆ (b), (EDT-TTF)₂C₆₀·CS₂ (c), (PhMeTTF)₂C₆₀·C₆H₆ (d), EDY-BEDT-DT·C₆₀ C₆H₆ (e) and C₆₀ (f) in the 600–1400 nm region in KBr pellets.

presented in Fig. 8 are quite close to each other and are the highest for the complexes investigated. The CT bands of lower intensities were also found for: $(TMDTDM-TTF)_2C_{60}(CS_2)_3$, $TPDP(C_{60})_2$ (CS₂) and DBTTFC₆₀ C₆H₆. All CT bands are very broad and have the positions of the maxima in the 850–950 nm range and about 1250 nm for TPDP(C_{60})₂(CS₂). For (BEDO-TTF)₂C₆₀, BEDO-TTFC₆₀C₆H₆, TBT- $TTF(C_{60})_2$ and BNDY C_{60} complexes, the CT bands were not found at all. It should be noted that the intensity of CT bands which are observed for the C₆₀ complexes with planar donors in the near IR range is low or CT bands are absent. This is obviously associated with a small overlapping of donor and fullerene (HOMO-LUMO) orbitals.

Most complexes investigated can be formally classified as CT complexes (due to the presence of the CT band), but the role of the CT interaction is not significant. The degree of charge transfer is very low and does not practically depend on ionization potentials of planar donors, and the CT absorption bands are rather weak or practically absent. There are some reasons for that. Large planar donor molecules cannot be arranged quite close, and parallel to hexagonal or pentagonal planes of the spherical C_{60} molecule. As a result, the arrangement of their HOMO-LUMO molecular π -orbitals quite close and parallel to each other for the effective overlapping is hindered even at the change of the conformation of donor molecules. For example, the angles between the corresponding planes of TPDP donor phenyl rings and hexagonal or pentagonal rings of C_{60} are ~ 25 and 19° for various phenyl groups in TPDP(C_{60})₂(CS₂) [56]. The C(TPDP phenyl rings)...C(C_{60}) distances are close to the van der Waals sum of carbon atoms (3.35 Å) between two carbon atoms of phenyl rings (3.33, 3.40 Å and 3.27, 3.43 Å), and pentagonal and hexagonal rings of C₆₀, respectively [56]. The TMDTDM-TTF molecule has a concave conformation [7], but only the central planar part of the molecule (S_4C_2) is arranged quite parallel to a hexagonal ring of C_{60} in the (TMDTDM-TTF)₂ C_{60} (CS₂)₃ complex (Fig. 7). The S(TMDTDM-TTF)...C(C_{60}) distances are close to the van der Waals sum of sulphur and carbon atoms (3.55 Å) for two sulphur atoms of S_4C_2 fragment (~3.5 Å) [7]. These data indicate low efficiency of the donor- C_{60} π -interaction and a small overlapping of their HOMO-LUMO

molecular orbitals. This results in the decrease of the donor-acceptor overlapping integral and consequently the decrease of the CT rate in these complexes. The coordination of the donor with practically spherical C₆₀ molecules results in changes in initially planar molecules. Some substituents of the donors are strongly turned or form significant dihedral angles between the central part of the molecule and the outer planes. This results in the disruption of conjugation in the molecule and in a partial localization of electron density of HOMO orbital on the planar fragments of the donor that hinders charge transfer from such deformed donors to C₆₀ molecule.

CT without sterical hindrances is possible only for small donor molecules that approach quite close to the C_{60} molecule with the arrangement of their HOMO orbitals parallel to hexagonal or pentagonal rings of C_{60} . They are different metallocenes, substituted benzenes and some amines.

Considering a very small degree of charge transfer in the investigated complexes and a high polarizability of the C₆₀ molecule, one can assume that the polarization interaction is dominating in the stabilization of the complexes. This interaction is relatively strong only if the donor molecule can approach quite close to the spherical C₆₀ molecule. The formation of the CT complexes of fullerene with the planar donors results in the deformation of the initially planar shape. In this case, the donor- C_{60} interaction depends on the difference between the energy of the efficient polarization interaction between both components and the energy expended for the changes in the initial geometry of the donor molecules. It should be noted that such changes in the donor conformation are associated only with the polarization interaction, but not with CT, and are possible due to a high polarizability of the C₆₀ molecule. The polarization interaction is maximal for donors with high polarizability which are able to come close to the C₆₀ molecule with minimal changes in the molecule geometry. In this case, molecules with initially concave form, e.g. the 'butterfly' or 'double butterfly' shapes, e.g. 9,9'-bistrans-(telluraxanthenyl) [BTX] [11] are more suitable for complexation with C_{60} . The geometry of BTX molecules corresponds to C_{60} spherical surface [11]. Thus, the coordination with C₆₀ does not request the changes of the geometry of donor molecules. The complexes with such donors are obviously more stable. The precipitation of the crystals of the C_{60} complex with such donors was already observed in a solution, although the preparation of C_{60} complexes with planar donors usually requires molar excesses of the donor and proceeds only in the evaporation of the solvent [5–10].

5. Conclusion

Extensive infrared and VIS-NIR studies of the CT complexes of fullerene with planar donors, e.g. tetrathiafulvalenes, dithiadiazafulvalene and pyranylidene were performed. It is shown that C_{60} forms only weak CT complexes with planar donors even with such strong ones as DTDAF and TPDP. This is defined not only by weak acceptor properties of fullerene but by unfavourable steric factors for charge transfer. As a result, the degree of charge transfer is very low and does not depend on the ionization potentials of these π -donors; the CT absorption band is very weak too. The main contribution to the binding energy of the complex is made by van der Waals polarization interactions. Under these conditions, the formation and stability of the CT complexes are defined mainly by molecular polarizability of the donor molecule and the steric compatibility between the donor and spherical C_{60} molecule. The energetically favourable are the donors which do not require the deformation of the molecule in their coordination with C₆₀. Therefore, the donors which reveal a peculiar spatial structure, e.g. the donors with a 'butterfly' or 'double butterfly'-type form more stable complexes with C₆₀. CT is more effective for small donor molecules. In these cases, the degree of CT would be higher and dependent on the ionization potentials of the donors.

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