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# Charge Transfer Complexes of Fullerene $C_{60}$ with *N,N*-Dimethylaniline Derivatives

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**Abstract—**Charge transfer complexes of a series of *p*-substituted dimethylanilines with $C_{60}$ fullerenes were studied by electron absorption spectroscopy. Energies of charge transfer bonds depend on three effects of substituents in the donor molecule (the inductive, resonance, and polarization effects) with domineering of the resonance effect. The energies are linearly proportional to the potentials of electrochemical oxidation of aniline derivatives.

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Nowadays it is proved that the use of fullerene derivatives in the devices transforming energy of the visible and near IR radiation to the electric current is promising, and the production of such devices is developing [1]. This application is based on the ability of fullerenes to form excitones at the excitation with light of its complexes with donor ligands. For the improvement of such devices it is necessary, in particular, to continue studies of physicochemical properties of charge transfer complexes with the participation of fullerenes. The formation and properties of charge transfer complexes giving tight ion-radical pair at the absorption of quantum of light may be studied by electron absorption spectroscopy [2]. Charge transfer complexes of aromatic compounds formed by aniline derivatives as donors and the fullerenes as acceptors are described [3–6]. It is shown that constants of complex formation of aromatic amines with $C_{60}$ are low (0.2–0.5 L/mol) which suggests the contact type of complexes [5]. Unlike that the complexes with participation of nitrogen macrocycles are characterized by constants which are three orders of magnitude larger ($10^3$–$10^4$ L/mol). Note that these constants were measured by another method [7]. The obtained data indicate the significant effect of intramolecular factors on the process of complex formation of $C_{60}$ with nitrogen bases. At the same time the systematic effect of substituents on the properties of the charge transfer complexes of fullerenes with amines is studied insufficiently.

The aim of this work is establishing the dependence between the energies of charge transfer bands in the electron absorption spectra of charge transfer complexes of aniline derivatives 1,4-X-$C_6H_4N(CH_3)_2$ with fullerene $C_{60}$ and electron-donor or electron-acceptor properties of substituents X.

Spectra of two charge transfer complexes of compounds **I** and **V** are presented in the Figs. 1 and 2. From the spectra it is clearly seen that the charge transfer bands are well resolved and the values of their energies $h\nu_{ct}$ depend on the type of substituent X in 1,4-X-$C_6H_4N(CH_3)_2$. It is significant that on the spectrum of the charge transfer complex of 1,4-$(CH_3)_2NC_6H_4N(CH_3)_2$ with $C_{60}$ in dichlorobenzene along with the charge transfer band the absorption band belonging to $C_{60}$ radical anion at 1020–1076 nm is also present. It shows the existence of an irreversible reaction of electron transfer with the formation of reaction products whereas the reversible excited state of charge transfer complex is the tight ion-radical pair. The separated ion pair may be evidently regarded as the transition state of addition of amines to fullerene [3]. This process depends on the nature of the solvent. In going from non-polar toluene to polar dichlorobenzene the extent of the irreversible reaction increases (Fig. 2), while the band at 1076 nm suffers a blue shift to 1020 nm. It proceeds probably due to relatively high electron-donor ability of compound **V**

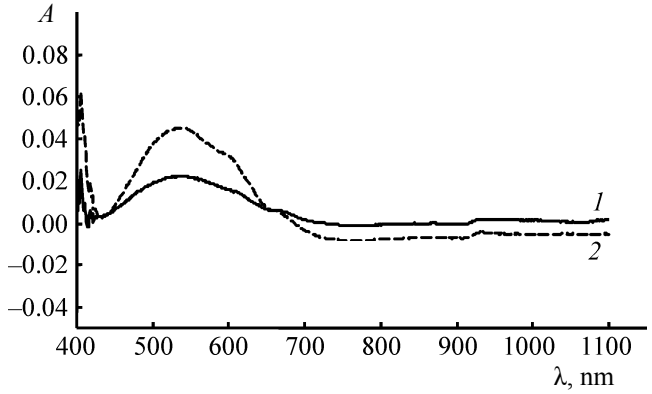


**Fig. 1.** Absorption spectrum of charge transfer complex of dimethylaniline with $C_{60}$ in toluene at DMA : $C_{60}$ molar ratio (*1*) 10 : 1 and (*2*) 20 : 1 with the compensation of absorption of solvent, of donor, and of acceptor.

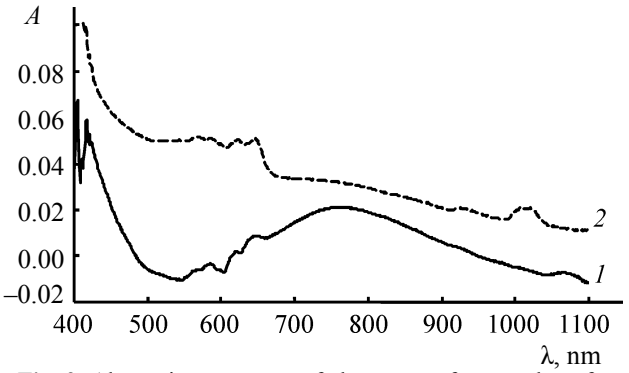


**Fig. 2.** Absorption spectrum of charge transfer complex of *N,N,N,N*-phenyltetramethylenediamine with $C_{60}$ in (*1*) toluene and (*2*) dichlorobenzene with the compensation of absorption of components of complex.

and a possible formation of excited triplet state $C_{60}$. The obtained data agree with the results of studies of Zn-porphyrine–$C_{60}$ diades where it has been shown that polar solvents decrease the energy level of the state with separated charge deeper, than the excited singlet state of $C_{60}$ (1.65 eV). It results in the formation of the triplet excited state of $C_{60}$ (with the energy 1.5 eV) [10]. This state is reactive and leads to the formation of the reaction products. Our measurements of complex formation constants by Benes–Hildebrandt method [2] show that in the majority of cases they have negative or close to zero values. Low values of constants for dimethylaninile derivatives [5] indicate the contact type of complex formation in this series of compounds.

The dependence of $h\nu_{ct}$ on the ionization potentials of a series of donors is typical for the complex formation under study. The correlation equation for a series of complexes of substituted aromatic amines of the type $R_2NC_6H_5$ where R = H, $CH_3$, $C_2H_5$, and also $CH_3C_6H_4NH_2$ and 2.6-$(CH_3)_2C_6H_3NH_2$ with $C_{60}$ was obtained in [5].

$$h\nu_{ct} = (0.84 \pm 0.07)I_p - (3.85 \pm 0.57)\ (\text{eV}), \qquad (1)$$

$$R = 0.98,\ SY = 0.05,\ N = 6.$$

We have obtained analogous equation for electrochemical oxidation potentials of the series of compounds under study.

$$h\nu_{ct} = (0.85 \pm 0.06)E_{1/2}^{ox} - (1.72 \pm 0.05)\ (\text{eV}), \qquad (2)$$

$$R = 0.97,\ SD = 0.05,\ N = 7.$$

Note the coincidence of the slope in the Eqs. (1) and (2). It indicates the analogous character of dependences of energy characteristics of charge transfer complexes on the characteristics of donors in photochemical and electrochemical processes. The obtained values of charge transfer frequencies ($\nu_{ct}$) and also electrochemical oxidation potentials are presented in Table 1.

It is seen from the table that the values of charge transfer frequencies vary in wide range depending on the donor and acceptor properties of substituents. The characteristics of such properties are their correlation constants. In Table 2 the values of inductive ($\sigma_I$), resonance ($\sigma_R$), and polarization ($\sigma_\alpha$) constants of substituents are presented, as well as the Hammet constants ($\sigma_p$) for a series of compounds under study.

While comparing the charge transfer energies with the above-mentioned constants we have calculated

**Table 1.** Values of electrochemical potentials of halfwave of oxidation $E_{1/2}^{ox}$ for compounds 1,4-$XC_6H_4N(CH_3)_2$ and energies of their charge transfer complexes ($h\nu_{ct}$) with $C_{60}$ fullerene

| Comp. no. | X | $\nu_{ct}$, $cm^{-1}$ | $E_{1/2}^{ox}$, eV [9] | $h\nu_{ct}$, eV |
|---|---|---|---|---|
| **I** | $CH_3$ | 18520 | –1.00 | 2.30 |
| **II** | CN | 21050 | –0.17 | 2.61 |
| **III** | CH(O) | 20200 | –0.41 | 2.50 |
| **IV** | $CH_3O$ | 17240 | –1.10 | 2.14 |
| **V** | $(CH_3)_2N$ | 14700 | –1.66 | 1.82 |
| **VI** | Br | 19700 | –0.60 | 2.44 |
| **VII** | H | 18870 | –0.83 | 2.34 |

**Table 2.** Values of correlation constants of substituents X in dimethylaniline derivatives [10]

| Comp. no. | X | $\sigma_I$ | $\sigma_R$ | $\sigma_\alpha$ | $\sigma_p$ |
|---|---|---|---|---|---|
| **I** | $CH_3$ | –0.05 | –0.12 | –0.35 | –0.17 |
| **II** | CN | 0.51 | 0.15 | –0.46 | 0.66 |
| **III** | CH(O) | 0.33 | 0.09 | –0.46 | 0.42 |
| **IV** | $CH_3O$ | 0.29 | –0.56 | –0.17 | –0.27 |
| **V** | $(CH_3)_2N$ | 0.15 | –0.98 | –0.44 | –0.83 |
| **VI** | Br | 0.45 | –0.22 | –0.59 | 0.23 |
| **VII** | H | 0 | 0 | 0 | 0 |

three-parameter correlation equations connecting charge transfer energy with the inductive, resonance, and polarization constants for all series of donors under study forming the charge transfer complexes in dichloromethane [Eq. (3)] as well as two-parameter equation without the consideration of polarization constants [Eq. (4)].

$$h\nu_{ct} = (2.34\pm0.03) + (0.33\pm0.09)\sigma_I + (0.58\pm0.04)\sigma_R - (0.07\pm0.09)\sigma_\alpha, \quad (3)$$

$$R = 0.99,\ SY = 0.04,\ N = 7.$$

$$h\nu_{ct} = (2.36\pm0.02) + (0.37\pm0.07)\sigma_I + (0.58\pm0.04)\sigma_R, \quad (4)$$

$$R = 0.99,\ SY = 0.04,\ N = 7.$$

The comparison of parameters of Eqs. (3) and (4) shows the absence of polarization contribution to the series of charge transfer complexes of dimethylaniline derivatives with $C_{60}$.

Analogous equation was obtained by us for C- and N-substituted dimethylaniline on the basis of the data from [5] [Eq. (5)].

$$h\nu_{ct} = (4.87+0.12) + (0.34\pm0.23)\sigma_I + (1.43\pm0.08)\sigma_R - (0.64\pm0.08)\sigma_\alpha, \quad (5)$$

$$R = 0.98,\ SY = 0.03,\ N = 6.$$

The comparison of parameters of Eqs. (3) and (5) shows that the main role is played by the resonance effects of substituents on nitrogen atom [Eq. (4)] as well as in benzene ring [Eq. (3)]. Meanwhile, the polarization effects playing insignificant role in the case of *p*-disubstituted dimethylaniline derivatives become very significant while varying substituents on nitrogen atom as well as in *o*-position of the benzene ring. It occurs probably because of the fact that nitrogen atom coordinated by fullerene becomes the reaction center, and *p*-position of the benzene ring becomes the most remote from it. Equations (3) and (4) were calculated for all the series of substituents X in this position. When only the compounds with donor substituents are taken into consideration, the equation acquires the form (6).

$$h\nu_{ct} = (2.35\pm0.02) + (0.40\pm0.05)\sigma_I + (0.64\pm0.03)\sigma_R - (0.10\pm0.05)\sigma_\alpha, \quad (6)$$

$$R = 0.99,\ SY = 0.02,\ N = 5.$$

The polarization effect in this case becomes significant, but the resonance one still plays the main role.

The effect of substituents in charge transfer complexes of amino derivatives with $C_{70}$ [6] completely differs from that observed for $C_{60}$ [Eq. (7)].

$$h\nu_{ct} = (0.55\pm0.22) + (1.25\pm0.51)\sigma_I - (1.04\pm0.18)\sigma_R + (0.82\pm0.29)\sigma_\alpha, \quad (7)$$

$$R = 0.97,\ SY = 0.05,\ N = 5.$$

Resonance and polarization effects are not only more significant in this case, but change their sign to the opposite one. The obtained data show higher reactivity of fullerene $C_{70}$ in the reaction with amines.

Solvents also significantly influence the electronic effects of substituents in charge transfer complexes under study. We have calculated the dependences of charge transfer energies on Hammet constants in dichloromethane, toluene, and dichlorobenzene [Eqs. (8)–(10)].

$$h\nu_{ct} = (2.3\pm0.02) + (0.52\pm0.04)\sigma_p\ (\text{eV}), \quad (8)$$
$$R = 0.98,\ SY = 0.05,\ N = 7\ (CH_2Cl_2),$$

$$h\nu_{ct} = (2.3\pm0.03) + (0.71\pm0.07)\sigma_p\ (\text{eV}), \quad (9)$$
$$R = 0.98,\ SY = 0.08,\ N = 6\ (C_6H_5CH_3),$$

$$h\nu_{ct} = (2.3\pm0.05) + (0.65\pm0.10)\sigma_p\ (\text{eV}), \quad (10)$$
$$R = 0.96,\ SY = 0.11,\ N = 6\ (C_6H_4Cl_2).$$

The comparison of slope in the Eqs. (8)–(10) shows the highest sensitivity of charge transfer energies to the effects of substituents in toluene, while in dichloromethane this sensitivity is the lowest. The correlation in dichlorobenzene considering the experimental error has the slope close to that in toluene. On the basis of the data presented it may be concluded that the sensitivity to the effects of substituents in the charge transfer complexes studied in aromatic solvents is higher, but considering the experimental error this effect is of small significance.

Hence, dimethylaniline derivatives having substituents in *p*-position of benzene ring form charge transfer complexes with $C_{60}$ fullerene. Their energy of formation varies within the range 1.82–2.61 eV. The charge transfer energy in the charge transfer complexes linearly correlates with the electrochemical oxidation potentials of substituted dimethylanilines, and also with the sum of inductive, resonance, and polarization constants of substituents. In all complexes under study the contribution of the resonance effect of substituents is domineering. Therefore these effects play the decisive role in evaluation of complex formation energy. The contribution of polarization effect becomes significant at varying substituents on nitrogen.

## EXPERIMENTAL

Charge transfer complexes of fullerene $C_{60}$ with aniline derivatives of the general formula 1,4-$XC_6H_4N(CH_3)_2$ were studied by electron absorption spectroscopy on a Perkin-Elmer Lambda 25 UV-Vis spectrometer in the range 400–850 nm. The concentration of fullerene solution was $10^{-3}$ mol/L, of the amine derivatives, $10^{-2}$ mol/L. Thickness of the absorbing layer of the cell was 1 cm. Dichloromethane, toluene, and dichlorobenzene were used as solvents. In the comparison channel the fullerene solution was placed, and in the cell with the same solution samles of donors of the series under study were added in succession. For performing spectral correction of absorption of charge transfer complexes the absorption of donors in the same concentration in the spectral range under study was recorded in the computer memory, and then subtracted from the summary spectrum. In the spectra of charge transfer complexes the appearance of new bands absent in the spectra of starting substances was observed.

Fullerenes of 99.9% purity were obtained according to [11]. Aniline derivatives 1,4-$XC_6H_4N(CH_3)_2$ were additionally purifiedcation. *N,N,N'N'*-tetramethyl-*p*-phenylenediamine (Fluka) **V** and 4-cyano-*N,N*-dimethylaniline **II** were purified by double sublimation. 4-Methyl-*N,N*-dimethylaniline (Aldrich) **I**, and *N,N*-dimethylaniline (Aldrich) **VII** were distilled. 4-Formyl-*N,N*-dimethylaniline (Fluka) **III** and 4-bromo-*N,N*-dimethylaniline (Aldrich) **VI** were crystallized from hexane. 4-Methoxy-*N,N*-dimethylaniline **IV** was synthesized according to [12]. The calculation of three-parametric correlation equations was carried out with the "Statgraphics 2.1" complex of programs.

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