

Nature of the Electron Excited States and Energy Transfer in Bichromophore Coumarin Molecules

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Received November 3, 1997; accepted October 22, 1998

Results of experimental and theoretical research for three bichromophore molecules, *trans*-stilbene-CH₂-coumarin 120 (I), 4-methylumbelliferone-CH₂-UC 17, and 4-(3-fluoro)-methylumbelliferone-CH₂-UC 17 (II, III), are presented. Schemes of photophysical processes in the bichromophore molecules based on quantum chemical calculations by the INDO method and theory of radiationless transitions in polyatomic organic molecules are suggested. After optical excitation to the strong donor absorption band, the fast internal conversion processes develop there. As a result, the molecule is found in the S₁^{*}-state localized on the acceptor moiety. It is shown that a mechanism of intramolecular energy transfer in bichromophores different from that proposed by Förster may be realized. Excitation energy, initially located on D, will be transferred from the donor moiety to the acceptor chromophore in convenience of the internal conversion process. The intramolecular electronic energy transfer from energy donor to energy acceptor may be interpreted as the internal conversion process. The rate constants of internal conversion are calculated.

KEY WORDS: Bichromophore; intramolecular electronic energy transfer; photophysical processes; internal conversion process; process of singlet-triplet conversion.

INTRODUCTION

Photophysical processes such as electronic energy transfer (EET) play a key role in chemistry, biology, and physics. The theory of a nonradiative energy transfer between molecules in solutions was developed in 1947 by Förster [1]. The Förster theory was a basis for further investigations of nonradiative energy transfer [2–4]. Förster's equations for a constant of rate of energy transfer are based on inductive resonance or Coulombic mechanism of dipole-dipole interaction. The Förster mechanism is not overlap dependent, it tends to prevail for singlet-singlet energy transfer between chromophores that are separated by distances in excess of sum of their

van der Waals radii [1–4]. The Förster theory was advanced by Dexter to a case of other types of interactions: dipole-quadruple, quadruple-quadruple, etc. [5]. At short chromophore-chromophore distances and for energy transfer between states that are not coupled by significant radiative transition probability, the overlap-dependent Dexter exchange mechanism prevails [2–4].

Intra-EET can occur whenever two separated chromophores are incorporated in a single molecule [2,3, 6–18]. A bichromophoric molecule may be defined as a molecule is built from two distinguishable molecular units connected by a molecular bridge [6]. The properties of the bridge determine the flexibility of the whole bichromophoric structure. Bichromophoric molecules are ideal for investigating intra-EET processes. Specially designed rigid bichromophoric molecules allow us to pursue systematic studies of the mechanism of intra-EET and to detect the strong dependence of singlet energy transfer dynamics on the bridge configuration [7–10]. One of the

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most remarkable features of their results is the observation that a saturated hydrocarbon bridge can be highly effective in mediating electron transport [7]. Paddon-Row and co-workers [4,7–10] have been presented additional experimental evidence in support of their belief that a Dexter-type mechanism governs intramolecular singlet energy transfer in the series of molecules where a dimethoxynaphthalene chromophore and a carbonyl chromophore are separated by the hydrocarbon bridge. The bridge serves as a molecular spacer unit which does not influence the basic electronic structure of the two chromophores while preventing intrachromophore interaction in their ground state. However, electronic excitation of either chromophore may lead to intramolecular electronic interactions and to the observation of phenomena such as intramolecular complex formation [24–30] or intramolecular electronic energy transfer [31–38]. The main problem is to differentiate all these processes which may act simultaneously and competitively.

By using the powerful tools of synthetic organic and polymer chemistry, molecular systems can be engineered for a specific intra-EET study. Systematic studies of the mechanism of intra-EET were discussed by Speiser [6]. In this review the progress made in understanding of the photophysics and the mechanism of intra-EET within the general framework of radiative and nonradiative processes in molecules is discussed. It was noted that complete quenching of donor fluorescence was observed with concomitant emission solely from the acceptor; EET processes involve nonradiative transfer of electronic excitation from an excited donor molecule D^* to an acceptor molecule A ; both absorption and emission spectra should reveal two bands, attributed to D or A chromophores; the general features of the absorption spectra should be similar to a superposition of the separate spectra of the chromophores.

Study of intra-EET in bichromophoric molecules is interesting as a source of information on the relative importance of these competing processes in the photophysics of such molecular systems. In an ideal case one should be able to study the dependence of the transfer efficiency on the particular vibronic excitation of the donor moiety in the bichromophoric molecules and to determine the transfer mechanism [7].

The related process of intra-EET in isolated, solvent-free, bichromophoric molecules may be investigated theoretically for better understanding of these phenomena. The theoretical and experimental study of dynamics of photophysical processes and spectral and lasing properties in polyatomic organic molecules is the principal direction of our investigations [11–23]. Using quantum chemical calculations by the INDO method and the theory

of radiationless transitions in polyatomic organic molecules, a new model for a description of intra-EET in the bichromophoric molecules has been suggested [11, 14–21]. The investigations have shown that bichromophores are more complicated molecular systems than a mere sum of two nonconjugated chromophores. A bichromophore is a united system—“supermolecule”—with a unified system of molecular orbitals belonging largely to separated chromophores, but on the other hand, there are mixed molecular orbitals attributed to D and A simultaneously. The calculations allowed us to identify the nature of both localized states on either chromophore and mixed molecular orbitals. It was obtained that after optical excitation, energy absorbed by the donor moiety is transferred in part to the acceptor moiety as a result of fast internal conversion process and mixed states play a key role in this photophysical process [19,20]. Thus, intra-EET from energy donor to energy acceptor that may be described in the terms internal conversion process [21].

In this paper we consider results of experimental and theoretical research on three bichromophore molecules: *trans*-stilbene- CH_2 -coumarin 120 (**I**), 4-methylumbelliferone- CH_2 -UC 17, and 4-(3-fluoro)-methylumbelliferone- CH_2 -(**II**, **III**) in detail (Fig. 1). Bichromophoric molecules presented consist of two distinguishable molecular units connected by a CH_2 - bridge. *trans*-Stilbene (TS), 4-methylumbelliferone (4-MU), and 4-(3-fluoro)-methylumbelliferone (4-FMU) were used as energy

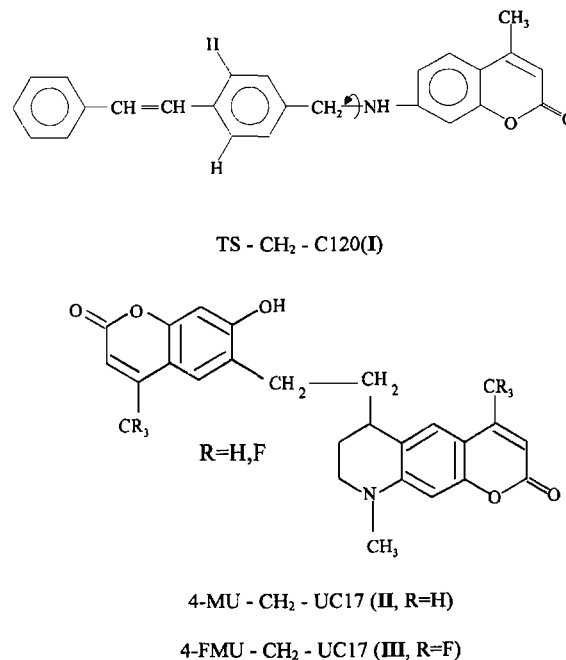


Fig. 1. Structure formulae of the tested bichromophores.

donors, and aminocoumarins of different structures were used as energy acceptors. In our investigation the approach developed in Refs. 11, 14–16, and 18–21 was used. The synthesis of the bichromophores studied was reported earlier [39,40].

QUANTUM CHEMICAL METHODS

The concepts and methods of quantum chemistry and the theory of nonradiative transitions in polyatomic organic molecules are the basis for our theoretical approach. The quantum chemical algorithms and programs are based on a semiempirical method of intermediate neglect of differential overlapping (INDO) involving particular spectroscopic parametrization [41]. This approach allows the spectra of energy states to be calculated accurately to 5–10% and provides the basis for the dynamics of ultrafast processes occurring in the kind of organic compounds studied.

The calculations were performed to determine the form of molecular orbitals (MOs), the electron density distribution in the ground and excited states, and the nature of the electronic excited states of the bichromophore molecules compared to the individual molecules. The nature of the electronic excited states was analyzed on the basis of the calculated expansion coefficients of MOs in terms of the atomic 2s, 2p_x, 2p_y, and 2p_z orbitals and wave functions of electronic-excited states to fit the Slater configurations [19, 20]. Wave functions of the excited electron states are represented in the form of a linear expansion in terms of one-electron excited configurations $|i \rightarrow k\rangle$:

$$\Psi_p = \sum_{ik} A_{ik}^p |i \rightarrow k\rangle \quad (1)$$

$$|i\rangle = \sum_{\mu} c_{i\mu} |\chi_{\mu}\rangle \quad (2)$$

where $|i\rangle$ is molecular orbital (MO) and $|\chi_{\mu}\rangle$ is atomic orbital (AO).

The analysis of the total wave function of a bichromophore in every case shows corresponding contributions from the donor and acceptor moieties of individual atoms and groups of atoms, and their roles in the formation of spectral and luminescent characteristics of bichromophore molecules as well.

The rate constant of internal conversion involving the electron states g and f is estimated by the formula [21,42]:

$$k_{gf} = \Omega_{gf} k_{gf}^{(0)} \quad (3)$$

where $k_{gf}^{(0)}$ is the rate of the $g \rightarrow f$ internal conversion in

the one configuration approximation and Ω_{gf} is the factor describing overlapping of wave functions of the electronic states g and f [21,42]:

$$\Omega_{gf} = N_{CH} \sum_{\alpha=1}^{N_{CH}} \left| \sum_{ik,jl} A_{ik}^g A_{jl}^f \langle i \rightarrow k | \mathbf{V} | j \rightarrow l \rangle \right|_{\alpha}^2$$

where \mathbf{V} is the nonadiabaticity operator and N_{CH} is the number of C–H bonds.

A computer program is developed for calculating the matrix elements of the spin-orbital interaction operator, which makes it possible to estimate the rate of singlet–triplet conversion K_{ST} [42].

EXPERIMENTAL

UV and visible absorption spectra were recorded using a Specord M 40 spectrophotometer. The spectra of luminescence from ethanol solutions were carried with an Hitachi-850 spectrofluorimeter. Concentrations of the dye solutions measured were of the order of 10^{-6} M. Fluorescence quantum yields were determined with a standard error of about $\pm 5\%$. Coumarin 1 in ethanol was used as a standard, whose quantum yield is $\phi = 0.5$ [43].

From Fig. 2 it can be seen that, for the given bichromophoric molecules, the electronic absorption spectra cannot be described by a simple superposition of the absorption spectra of the parent chromophores. The absorption spectra of TS, C120, and bichromophore **I** in ethanol are shown in Fig. 2a. The absorbance of C 120 and TS moieties increases by 10 and 12%, respectively, as compared to the absorbance of the corresponding parent molecules. The TS extinction coefficient (ϵ) is of the order of $30 \times 10^3 M \times \text{cm}^{-1}$. Furthermore, the absorption maxima of stilbene and coumarin moieties of **I** occur at longer wavelengths ($\lambda = 320$ nm and 345 nm) in comparison with the corresponding maxima of the separated chromophore molecules ($\lambda = 312$ and 340 nm). Figures 2b and c show also that the absorption spectra of bichromophores **II** and **III** as a whole are not an additive sum of the spectra of their constituent fragments.

The fluorescence yield of TS is very low ($\phi = 0.02$) [44] by virtue of high trans–cis photoisomerization rate. The quantum yield for trans–cis photoisomerization in the absence of bimolecular quenching of TS* is 0.5 [45]. The bichromophoric fluorescence is assigned to C120 emission ($\lambda = 440$ nm; Fig. 3a).

Bichromophores **II** and **III** are built from two distinguishable coumarin dyes. Coumarin dyes are widely used in dye lasers to achieve tunable blue–green light and are also employed in other important applications of indus-

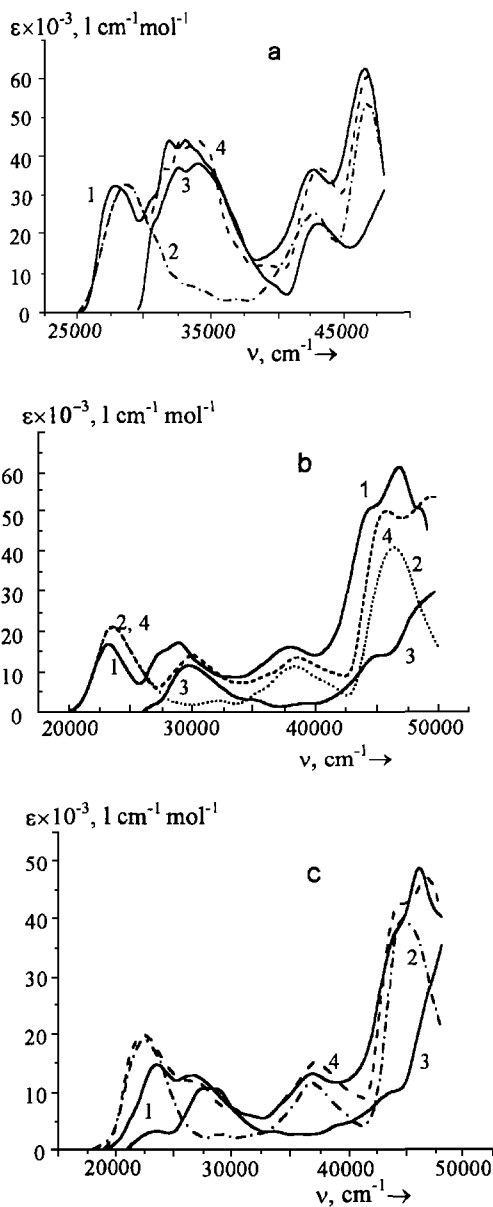


Fig. 2. Absorption spectra of tested bichromophores: a, I; b, II; c, III. 1, spectrum of bichromophore; 2, acceptor; 3, donor; 4, equimolar mixture. Solvent:ethanol concentration: $2 \times 10^{-5} M$.

trial and biological interest [46]. Acceptor chromophores have high fluorescence quantum yields and are used by us as active laser dyes (Table 1 [47–49]). It is worthwhile to note that in electronically excited state the molecules 4-MU and 4-FMU may lead to the following four possible fluorescent species depending on solvent and pH: neutral (N^*), protonated or cationic (C^*), anionic (A^*), and long-wavelength emitting tautomeric form (T^*) [50–52]. The fluorescence spectrum of 4-MU in ethanol shows, besides a band centered around 384 nm and ascribed to the N^*

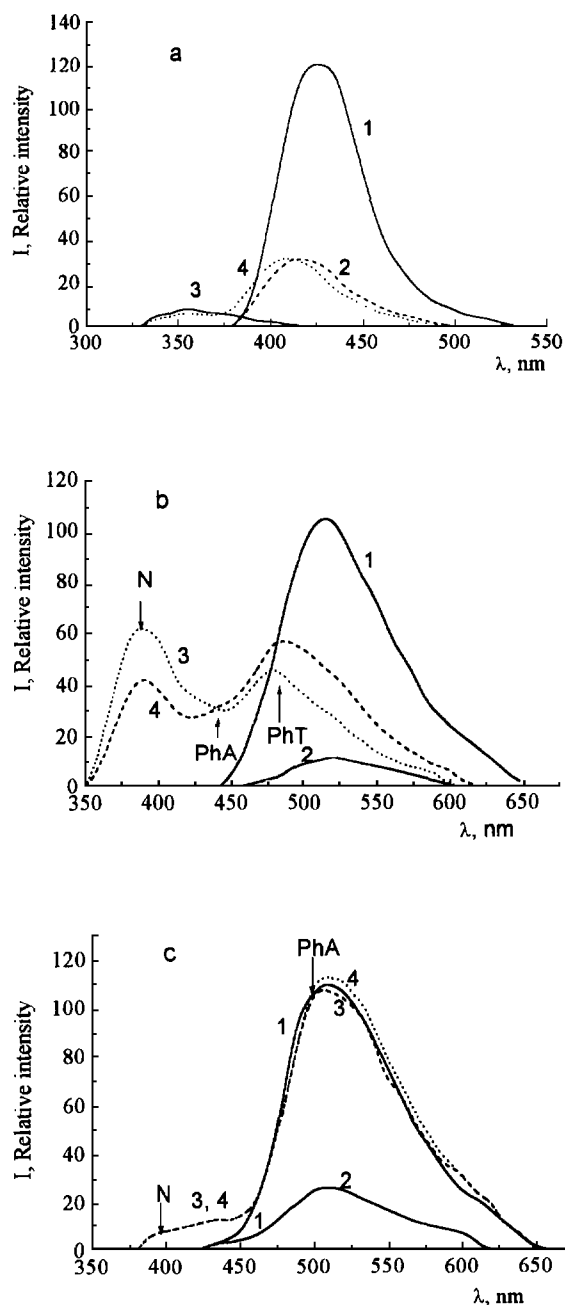


Fig. 3. Fluorescence spectra: a, TS-CH₂-C120 (I); b, 4MU-CH₂-UC17 (II); c, 4FMU-CH₂-UC17 (III). 1, bichromophore; 2, acceptor; 3, donor; 4, equimolar mixture. Solvent:ethanol concentration; $2 \times 10^{-6} M$. Excitation wavelength: 314 nm (a); 330 nm (b); 340 nm (c).

form, a band around 485 nm, due to T^* emission (Fig. 3b). The latter band is attributed to a tautomer formation via specific dye–ethanol complex interactions leading to ultrafast excited-state intramolecular proton transfer [51–53]. The phototautomerization of 4-MU is most likely to be a biprotonic transfer in which the first step

Table I. Spectral Properties of the Tested Bichromophores (φ , Fluorescence Quantum Yield)

Molecule	φ^{Aa}	φ_B^D/φ^{Ab}	φ_B^D/φ^{Ac}
TS-CH ₂ -C120 (I)	0.82	1.0	1.0
4-MU-CH ₂ -UC 17 (II)	0.50	1.0	0.8
4-FMU-CH ₂ -UC 17 (III)	0.50	0.8	0.6

^a Fluorescence quantum yield of energy acceptor.

^b Relation of fluorescence quantum yield of bichromophore to that of energy acceptor upon excitation of energy acceptor.

^c Relation of fluorescence quantum yield of bichromophore to that of acceptor upon excitation of energy donor.

is rate limited by the diffusion of one ethanol molecule toward the phenolic group, leading to deprotonation of the neutral form into the intermediate anionic A* form. Then rapid electronic reorganization of A* occurs, and a fast protonation of enolate limiting structure yields the neutral ketotautomer of the initially excited neutral form of the dye [51, 53]. Ethanol solution of 4-FMU may lead to two possible fluorescent species: neutral (N*) and photoanionic (A*) forms (Fig.3C[53]). It is noteworthy that the fluorescent intensity of the N* form is weak compared to the that of the A* form.

DISCUSSION

The efficiency of intra-EET can be estimated from the analysis of the donor fluorescence decay and enhancement of acceptor fluorescence [53]. In all these cases, a complete quenching of donor fluorescence was observed, with concomitant emission solely from the acceptor. From this point of view the energy transfer efficiency should be fairly high. Upon excitation of the energy donor the emission of energy acceptor was observed, thus indicating that the intra-EET rate was much higher than donor decay by fluorescence. Table I shows that the fluorescence resulting from bichromophores **II** and **III** is strongly dependent on the excitation wavelength. Upon excitation of energy donor emission the fluorescence quantum yield of these bichromophores is less than that upon excitation of the energy acceptor. On the contrary, the fluorescence quantum yield of **I** is the same that of C 120.

From the absorption spectra presented above it may be concluded that the CH₂ bridge does not prevent intrachromophore interaction in the ground state. In our opinion, this bridge is too short for this conformation of separated moieties [19]. As is evident from comparison of fluorescence spectra of **III**, the anionic form of 4-FMU emits in the same region as an ethanol solution of UC 17,

therefore it is difficult to attribute the fluorescence band of **III** to D or A chromophores correctly.

Quantum chemical calculations by the INDO method have been performed to determine the schemes of photophysical processes in bichromophore molecules. In this study we present the absorption spectra calculated for TS, C 120, 4-MU, 4-FMU, UC 17, and bichromophores created on their basis. Figures 4–6 give the calculated energies of the singlet and triplet levels, oscillator strengths of the lower singlet excited states (f), rate of internal conversion k_{ic} , and rate of singlet–triplet conversion of electron transitions k_{ST} . Analysis of the electronic excited states shows that the internal conversion process is a basic channel of the excitation energy activation ($k_{ic} = 10^{10} \div 10^{12} \text{ s}^{-1}$) for the molecules tested. Calculation of the geometry of bichromophores **II** and **III** has shown that, in these molecules, the planes of the two coumarins are perpendicular, and so are their corresponding transition dipole moments between the ground and the first excited singlet states. In the present work the data for **I** are given for this geometry, though in a precedent work [13] the other conformations were considered for this bichromophore [13]. The analysis of charge distribution showed that under excitation in electronically excited states S_1^* , S_2^* , and S_3^* in bichromophore **I**, the transfer of electronic density from the coumarin to the stilbene moiety and to the methylene group mainly ($\sim 0.1 \text{ e}$) occurs. Two types of states in the absorption spectra of the tested bichromophores have been detected: the excited states localized on the separated moieties (donor or acceptor) and the mixed states with a considerable charge transfer. Using quantum chemical calculations transitions due to localized states on either chromophore can be identified. Expansion of the wave functions of three lower electronic states in terms of one-electron configurations showed that for bichromophore **I**, all the states are mixed:

$$\Psi(S_1^*) \approx 0.91|C_1 \rightarrow C_2^*\rangle - 0.29|C_2 \rightarrow ST_1^*\rangle - 0.16|C_2 \rightarrow ST_4^*\rangle$$

$$\Psi(S_2^*) \approx 0.94|C_1 \rightarrow C_4^*\rangle + 0.15|C_1 \rightarrow C_2^*\rangle + 0.14|C_2 \rightarrow ST_1^*\rangle$$

$$\Psi(S_3^*) \approx -0.88|ST_2 \rightarrow ST_1^*\rangle + 0.17|ST_2 \rightarrow ST_3^*\rangle + 0.25|C_1 \rightarrow ST_1^*\rangle$$

This results in a redistribution of the intensities of the absorption spectrum of **I** in comparison with the intensities of absorption spectrum of the equimolecular mixture of TS and C 120.

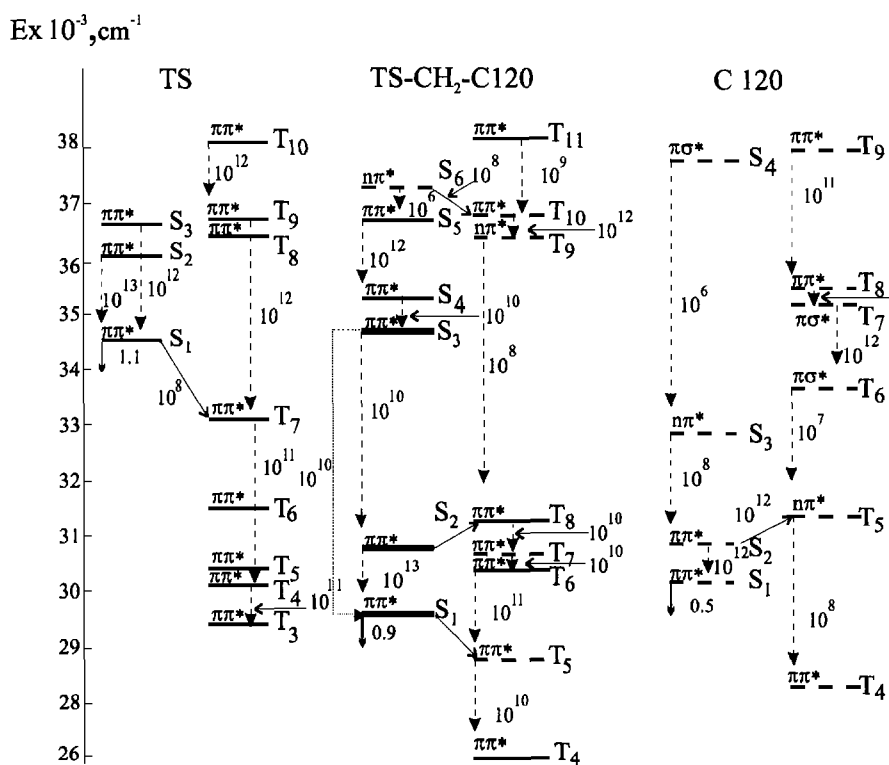


Fig. 4. Schemes of electronic excited states for TS-CH₂-C 120 and its separated molecules calculated by the INDO method: vertical dashed lines, k_{ic} ; slanted solid lines, k_{ST} . Bold lines show mixed states.

For bichromophores **II** and **III** the lowest electron state (S_1^*) is located only on the acceptor moiety, and all other π , π^* states are mixed. The electronic state (S_1^*) is formed by a combination of transitions from the i th occupied MO UC 17 to its j th vacant MO.

As a result of expansion of wave functions, electronic states for **II** have been obtained:

$$\begin{aligned}\Psi(S_1^*) &\approx 0.97|C_1 \rightarrow C_2^*\rangle \\ \Psi(S_2^*) &\approx 0.94|C_1 \rightarrow C_4^*\rangle + 0.15|C_1 \rightarrow C_3^*\rangle \\ &\quad + 0.14|C_2 \rightarrow U_2^*\rangle \\ \Psi(S_3^*) &\approx 0.75|U_2 \rightarrow U_2^*\rangle + 0.46|U_2 \rightarrow U_2^*\rangle \\ &\quad - 0.15|U_1 \rightarrow U_2^*\rangle \\ \Psi(S_4^*) &\approx 0.89|C_1 \rightarrow C_5^*\rangle + 0.18|C_1 \rightarrow C_7^*\rangle \\ &\quad + 0.19|C_1 \rightarrow C_8^*\rangle \\ \Psi(S_5^*) &\approx 0.56|U_2 \rightarrow U_2^*\rangle - 0.76|U_2 \rightarrow C_3^*\rangle \\ &\quad + 0.12|U_2 \rightarrow U_4^*\rangle\end{aligned}$$

where C's mean UC 17 and U's mean 4-MU.

Expansion of wave functions of electronic states for **III** can be written as follows:

$$\begin{aligned}\Psi(S_1^*) &\approx 0.97|C_1 \rightarrow C_2^*\rangle + 0.12|C_4 \rightarrow C_5^*\rangle \\ \Psi(S_2^*) &\approx 0.94|C_1 \rightarrow U_5^*\rangle + 0.12|C_4 \rightarrow C_8^*\rangle \\ &\quad + 0.14|U_2 \rightarrow U_1^*\rangle \\ \Psi(S_3^*) &\approx 0.14|C_1 \rightarrow U_5^*\rangle + 0.93|C_1 \rightarrow U_1^*\rangle \\ &\quad + 0.15|U_2 \rightarrow U_3^*\rangle + 0.13|C_6 \rightarrow U_1^*\rangle \\ \Psi(S_4^*) &\approx 0.93|C_1 \rightarrow C_6^*\rangle + 0.15|U_5 \rightarrow C_6^*\rangle \\ &\quad + 0.31|C_6 \rightarrow U_6^*\rangle + 0.12|U_9 \rightarrow U_1^*\rangle \\ \Psi(S_5^*) &\approx 0.86|U_2 \rightarrow U_3^*\rangle + 0.23|K_5 \rightarrow U_1^*\rangle \\ &\quad + 0.27|U_7 \rightarrow U_1^*\rangle + 0.13|U_7 \rightarrow U_3^*\rangle\end{aligned}$$

where C's mean UC 17 and U's mean 4-FMU.

One of the important conclusions obtained from expansions of wave functions and calculations of matrix elements for the nonadiabaticity operator (V) of the internal conversion process between the electronic excited states localized on the different moieties occurs via con-

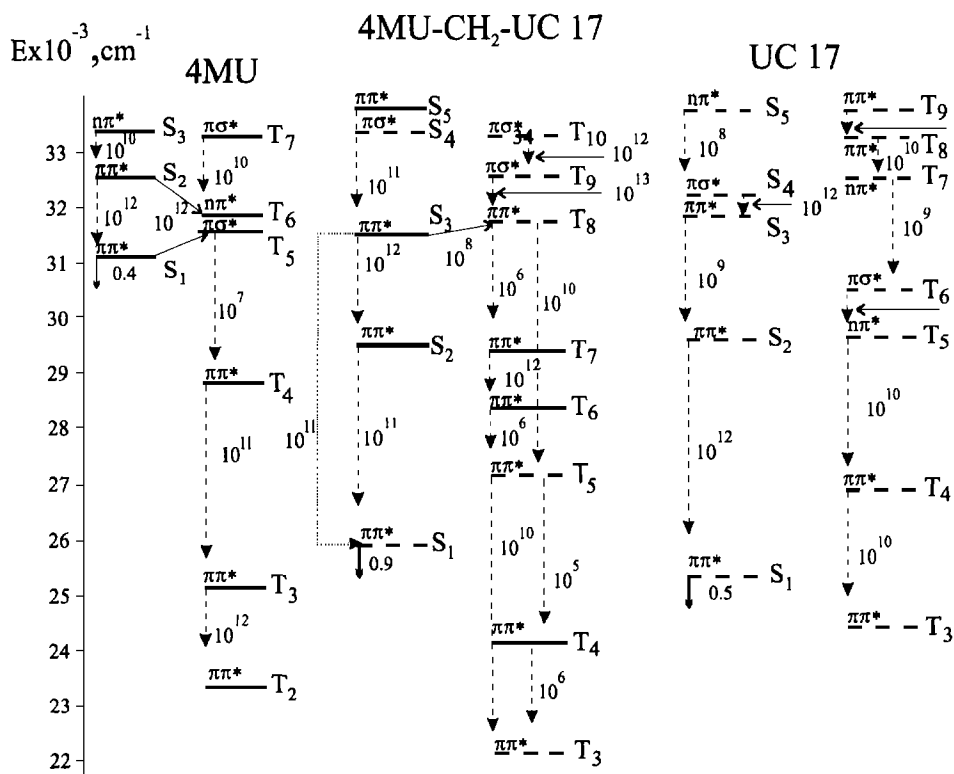


Fig. 5. Schemes of electronic excited states for 4-MU-CH₂-UC17 and its separated molecules calculated by the INDO method: vertical dashed lines, k_{ic} ; slanted solid lines, k_{st} . Bold lines show mixed states.

figuration mixing. The appearance of electronic excited mixed states results in the disappearance of the additivity of the absorption spectra. As shown in Ref. 19, with lengthening of the bridge (CH₂)_n (where $n = 1 \div 6$), mixed MOs and all MOs belonging to either chromophore disappear.

Both bichromophores have a high excited state within of 260–270 nm, formed by a significant charge transfer from energy acceptor to energy donor ($\sim 1 e$) (Figs. 4–6). Moreover, in bichromophore **III** a similar state is located below ~ 300 nm due to fluorination of the methyl group of the donor moiety. Fluorination decreases the energy of the mixed states, and consequently, these states may play a more important role in the photoprocesses proceeding in bichromophores. Recognizing the mixed character of the electronic states of the tested bichromophores and treating them as a unified molecular system, we have assumed the following scheme for photophysical processes in bichromophore molecules. After optical excitation into the strong donor absorption band, an excitation energy, initially located on D, is transferred from the donor moiety to the acceptor chromophore as a result of the internal conversion process. As a consequence, the molecule is found in the

S₁^{*} state localized on the acceptor moiety. Otherwise, a mechanism of intra-EET different from Förster's may be realized in the bichromophore. Electronic energy transfer processes involve nonradiative transfer of electronic excitation from an excited donor molecule to an acceptor molecule. Thus, the intra-EET from energy donor to energy acceptor may be interpreted as an internal conversion process. The rate constants of internal conversion (k_{ic}) are given in Figs. 4–6. These figures show that the rate constants k_{ic} increase by an order of magnitude due to the fluorination of the donor fragment. This fact is correlated with the change in the energy gap between the interacting states [13]. The analysis of constants of internal and singlet–triplet conversion in our calculations (see Figs. 4–6) shows that we may suggest the following schemes of photophysical processes in the test bichromophores, which are described in Fig. 7 (where τ_{rad} is the rate constant of radiative decay of the S₁^{*} state). Fig. 7 shows, for **I** and **II**, the radiative channel of the excited energy degradation to be predominant. It was observed that there are no changes in the fluorescence quantum yield of bichromophore **I** with respect to that of C 120. For bichromophore **III**, the singlet–triplet conversion between S₃^{*} and T₁^{*} states is possible. In our opinion, the

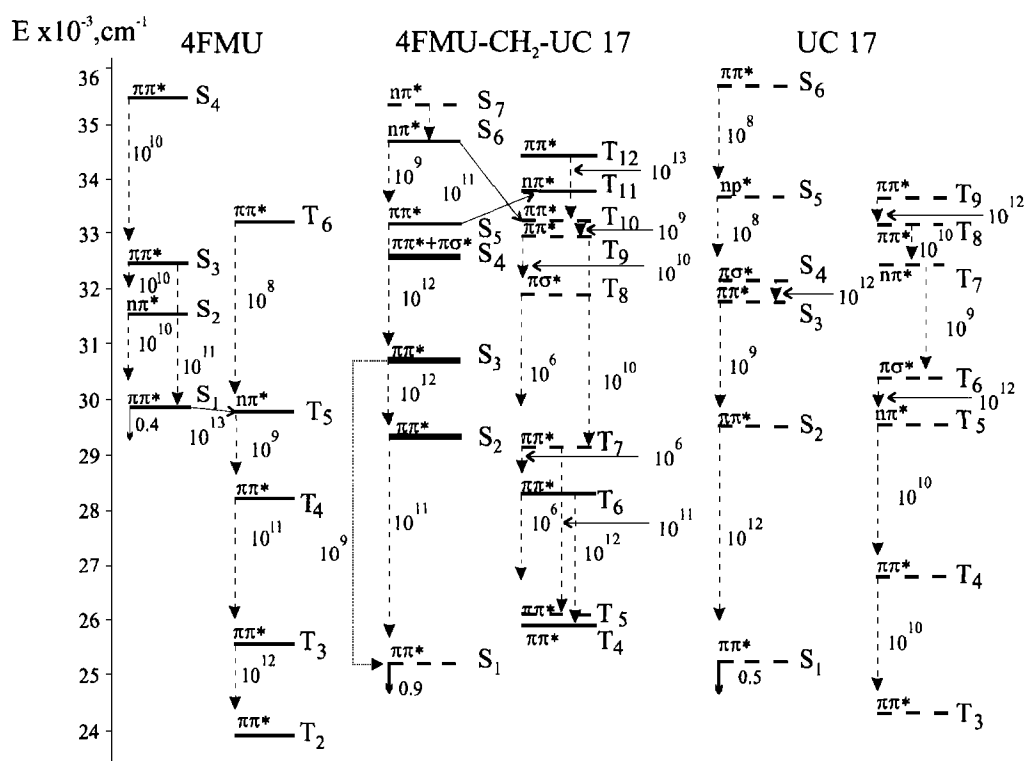


Fig. 6. Schemes of electronic excited states for 4-FMU-CH₂-UC17 and its separated molecules calculated by the INDO method: vertical dashed lines, k_{ic} ; slanted solid lines, k_{ST} . Bold lines show mixed states.

competition of the process of singlet–triplet conversion with the process of radiative energy degradation of a molecule may be a reason for the decreasing fluorescence efficiency of bichromophore **III** (see Table I).

CONCLUSION

It was shown that in the tested bichromophores fluorescence of the energy donor is absent and enhanced

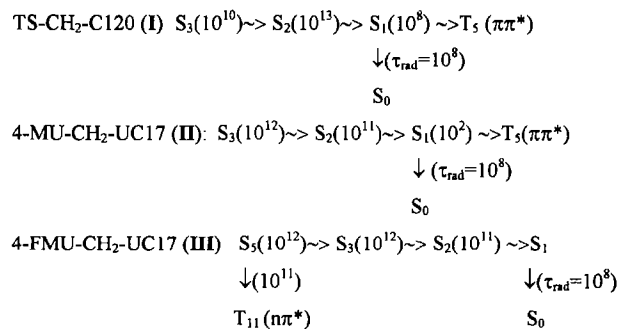


Fig. 7. Schemes of photophysical processes in the tested bichromophores.

emission of the energy acceptor is observed. As a result the effective intra-EET process take place in these molecules. The phenomena of intra-EET in biochromophores is considered on the basis of conception of internal conversion processes. It was shown that after optical excitation, energy absorbed by the donor moiety is transferred in part to the acceptor moiety due to internal conversion processes. Our calculations show that the mixed states play an important role in the efficiency of the intra-EET process. For bichromophore **I** the fluorescence quantum yield was found to be equal to that of C 120, within the experimental accuracy ($\pm 2\%$). Our analysis of constants of internal and singlet–triplet conversion for bichromophores **I** and **II** allows us to conclude that a radiative channel of excited energy degradation is predominant.

ACKNOWLEDGMENTS

The authors are grateful to Drs A. Kropachev and A. Il'chenko (Institute of Organic Chemistry, National Academy of Science, Kiev, Ukraine) for the presentation of bichromophore compounds. We are also grateful to a referee for constructive comments.

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