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Energy transfer in peptides based on phthalimide derivatives of aliphatic aminoacids[*]

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Model peptides containing phthalimide derivatives of aliphatic aminoacids with various number of methylene groups in side chains have been synthesized and investigated spectroscopically. The study aimed at the creation of polymers with the intramolecular triplet–triplet excitation energy transfer. In all compounds investigated, efficient triplet–triplet energy transfer is observed, resulting in the phosphorescence only from phtalimide π-electronic system in frozen solutions at 77 K.

Key words*: peptides; electronic excitation; energy transfer; conformational analysis*

1. Introduction

The critical distance of a triplet exciton jump is known to be 1.8–2.0 nm [1–3]. This distance was calculated as an average value for copolymers of vinyl carbazole with octyl methacrylate with various contents of the first co-monomer units. Using a certain content of quenching admixtures, identical in all samples, the decrease of intensity of phosphorescence in comparison with the appropriate low molecular weight analogue was measured, as well as changes of delayed fluorescence intensity. In order to check the reliability of this value, from our point of view, it is convenient to use low molecular weight models. These models must have two π-electronic systems at a defined distance from one to another. Their lowest excited energy levels must ensure a triplet–triplet excitation energy transfer. The spectral investigations of such model compounds in low-concentration solutions guarantee the absence of intermolecular excitation energy transfer, whereas their conformational analysis enables one to estimate distances for energy transfer.

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As appropriate model compounds we chose compounds with non-conjugated benzyl and phthalimide groups. In our previous work [4], it was shown that their unselective photoexcitation caused an efficient intramolecular excitation energy transfer from benzyl to phthalimide π-system that results (frozen solutions at 77 K) in phosphorescence of the latter group only.

We have synthesized model compounds (Fig. 1b) containing the above-mentioned π-electronic systems at various distances from one another. The aim of this work is the evaluation of a critical distance between the π-systems, above which the excitation energy transfer will be not complete, that will be evident in an occurrence of a phosphorescence of the benzyl π-electronic system. The arrangement of the first excited singlet and triplet electronic energy levels of phthalimide and benzyl π-electronic systems are shown in Fig. 1.

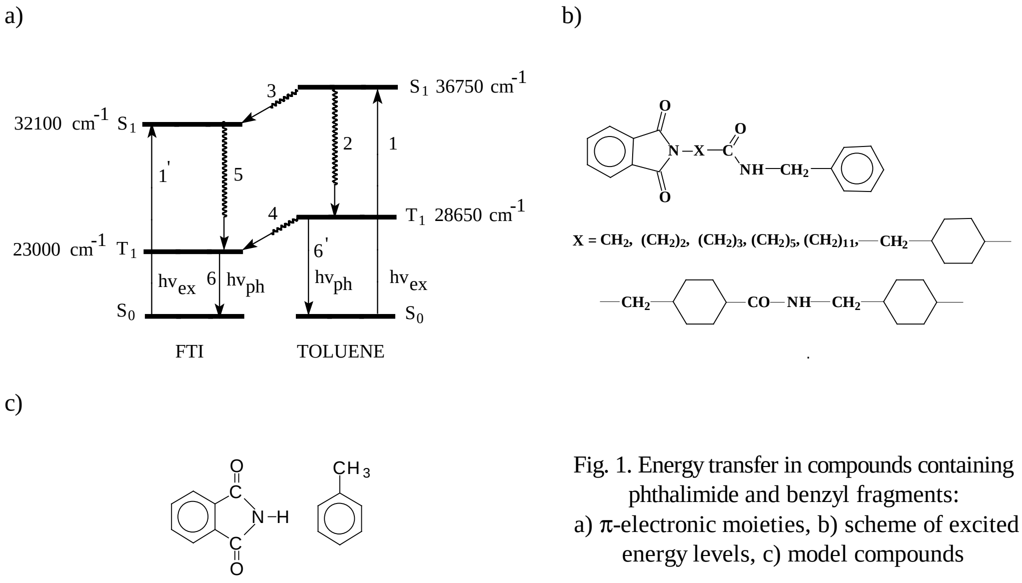
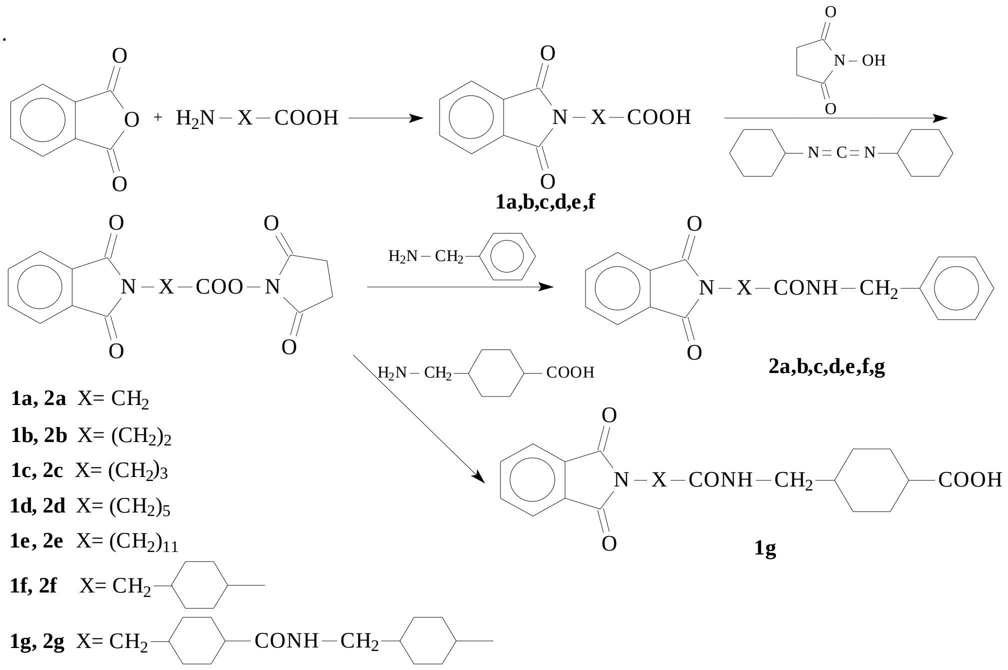


Fig. 1. Energy transfer in compounds containing phthalimide and benzyl fragments:
a) π-electronic moieties, b) scheme of excited energy levels, c) model compounds

According to the scheme shown in Fig. 1, a partial S–T conversion (way 2) takes place under an unselective excitation of the model compounds (path 1 and 1′) except S–S crossing (path 3). After the complete triplet–triplet conversion of excitation energy (way 4), in the spectrum of their phosphorescence in diluted solutions only the phosphorescence of phthalimidic π-electronic system is observed (way 6). At an incomplete T–T conversion, the phosphorescence of benzyl fragment should be observed at shorter wavelengths (path 6′).

2. Experimental

Chemicals. The starting phthalimides of amino acids 1a–f were obtained by the condensation of equimolar amounts of phthalic anhydride and corresponding amino acids. The peptides 2a–f and 1g were synthesized using a standard technique [5] (Scheme. 1):



Scheme 1. Synthesis of starting phthalimides of amino acids: N1-benzyl-2-(1,3-dioxo-2,3-dihydro -1H-2-isoindolyl)acetamide – **2a** (m.p. = 225 °C, yield 70%), N1-benzyl-3-(1,3-dioxo-2,3-dihydro -1H-2-isoindolyl)propanamide **2b** (m.p. = 207–209 °C, yield 75%), N1-benzyl-4-(1,3-dioxo-2,3-dihydro-1H-2-isoindolyl)butanamide **2c** (m.p. = 157 °C, yield 80%), N1-benzyl-6-(1,3-dioxo-2,3-dihydro -1H-2-isoindolyl)hexanamide **2d** (m.p. = 133 °C, yield 87%), N1-benzyl-12-(1,3-dioxo-2,3-dihydro -1H-2-isoindolyl)dodecanamide **2e** (m.p. = 125 °C, yield 72%), N1-benzyl-4-(1,3-dioxo-2,3-dihydro -1H-2-isoindolylmethyl)-1-cyclohexanecarboxamide **2f** (m.p. = 190 °C, yield 70%), N1-benzyl -4-[4-(1,3-dioxo-2,3-dihydro-1H-2-isoindolylmethyl)cyclohexyl-carboxamidomethyl] -1-cyclohexanecarboxamide **2g** (m.p. = 269-271°C, yield 61%) were synthesized

The purity of the compounds synthesized was checked by thin-layer chromatography (TLC). Ethanol and methanol (Fluka AG), both of spectral grade, were used as solvents.

Spectral measurements. The structures of new compounds were characterized by NMR-spectroscopy. All measurements were carried out with a Bruker-100 NMR spectrometer. Acetone-d_6 was used as a solvent, and tetramethylsilane – as an internal standard. IR spectra were recorded with an UR-10 spectrometer in KBr pellets. The UV absorption spectra were measured with a SPECORD UV VIS spectrophotometer in ethanol solutions ($C = 10^{-5}$ mol/dm^3).

Fluorescence was measured with a Perkin-Elmer LS-50 spectrofluorimeter. The excitation and emission spectra were both recorded at the 2.5 nm bandwidth in ethanol solution. The emission spectra were measured by adjusting excitation wavelengths to the maxima in the absorption and fluorescence excitation spectra. Fluorescence excitation spectra were recorded at the wavelengths corresponding to the maxima in the emission spectra or sometimes at selected wavelengths at the edges of the emission bands. Phosphorescence measurements were carried out using equipment based on ISP-28 quartz spectrograph in alcohol solutions at 77 K.

Calculations. The conformational analysis for compounds **2a–g** and the distribution of distances between π-electronic systems of benzyl and phthalimide was carried out by computer simulation (MM$^+$) with the subsequent geometry optimization (in each local minimum) in the semi-empirical AM1 approximation. The simulation was carried out for the ambient temperature. Only conformers with the heat of formation not exceeding 4 kcal/mol from optimal till energy of conformer were selected. As the duplicates similar structures with a difference of energy of 0.3 kcal/mol were considered.

3. Results and discussion

The structures of all compounds obtained were examined by spectral methods. We calculated the average distances between π-electronic systems for model compounds **2a–g**. The results of calculations are given in Fig. 2. It can be seen that while for compound **2a**, the average distance between systems is 0.35 nm, the elongation of the chain by one methylene group (**2b**) leads to 20% of molecules with the minimal distance between systems of about 0.7 nm. A further increase of the number of methylene groups between the π-systems (from 3 up to 11, **2c–2e**) results in the decrease of a portion of extended conformers (1–2%, **2d**), due to the increase of chain flexibility.

The use of "hard" cyclohexane rings as spacers allows one to achieve a considerable amount of extended conformers (Fig. 1) **2f–2g**. For compound **2f**, the distance between phthalimide and benzyl systems is 0.6–0.95 nm, and shorter conformers are absent. The addition of a second cyclohexane ring in the basic chain (**2g)** allows us to obtain more than a half of molecules with the distance between rings amounting to 1.0–1.3 nm and about 10% of molecules with the minimal distance equal to 1.5–1.6 nm.

So in Figure 3, the model of conformer **2g** with maximal length and minimal distance between phthalimide and benzyl π-electronic systems of 1.63 nm is represented.

In Figure 4, the phosphorescence spectra of compounds **2a–g** are shown. For comparison, the phosphorescence spectra of toluene and phthalimide are given. It is evident that only the emission from the phthalimide π-electronic system (with the maximum at about 460 nm) is observed in the samples pointing to a complete intramolecular triplet–triplet energy transfer from toluene to phthalimide π-electronic system.

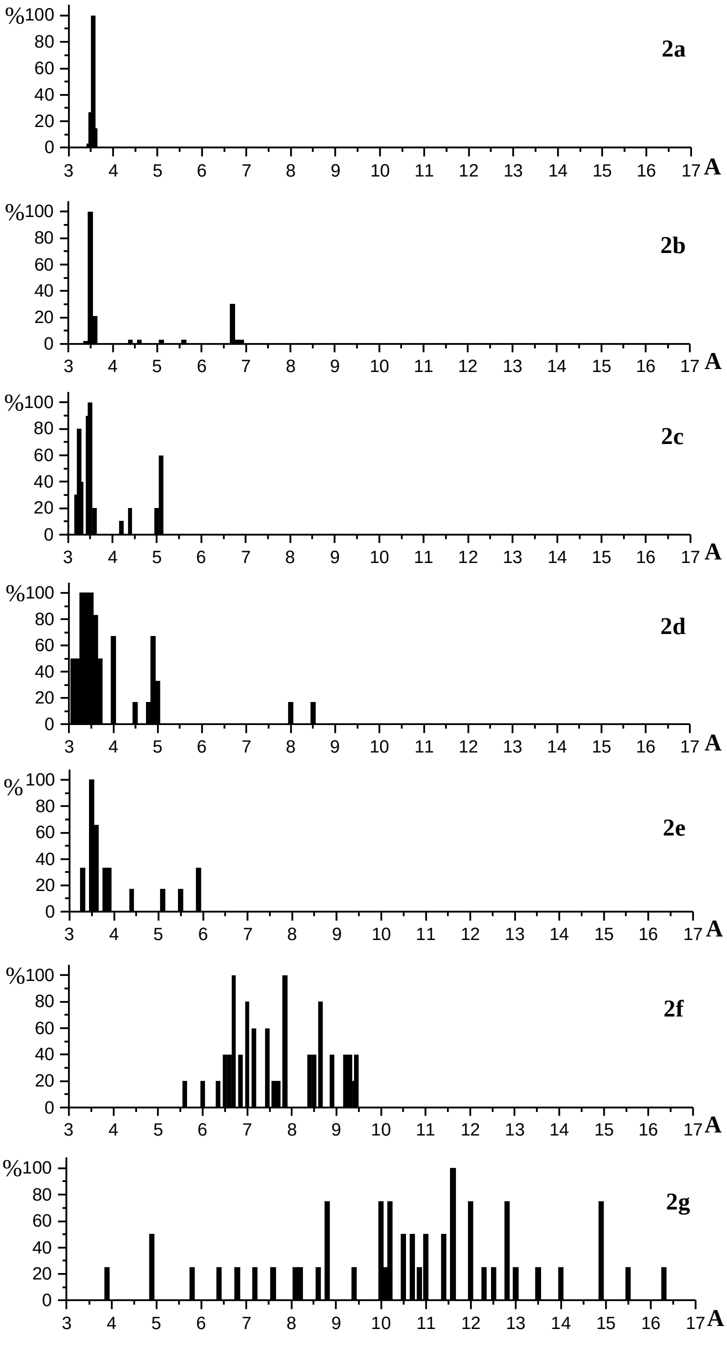


Fig. 2. Estimation of distances between phthalimide and benzyl π-electronic systems for the conformers **2a–g**. The relative contributions of various conformers were normalized to the most probable structure. The distances are expressed in Ångström units

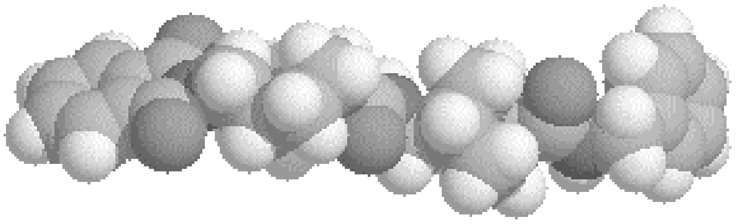


Fig. 3. Model of a compound **2g** molecule with a minimal distance between phthalimide and benzyl π-electronic systems of 1.63 nm

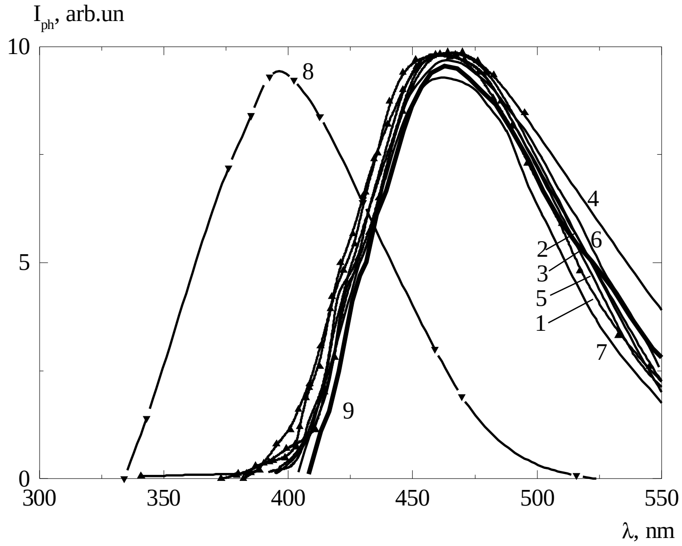


Fig. 4. Phosphorescence spectra of: 1 – 2a; 2 – 2b; 3 – 2c; 4 – 2d; 5 – 2e; 6 – 2f; 7 – 2g; 9 – phthalimide in ethanol at 77 K ($C = 10^{-5}$ mol/l, $\lambda_{ex} = 254$ nm), 8 – toluene ($C = 10^{-2}$ mol/l, $\lambda_{ex} = 254$ nm)

Conclusions

It was shown that the increase of a spacer length consisting of methylene groups does not result in the increase of the distance between π-electronic systems. Thus it is possible to obtain only 1–2% of conformers with the distances between π-electronic systems equal to about 0.8–0.85 nm. By using cyclohexane rings as spacers, the flexibility of chains is decreased, and for **2g** about 60% of molecules with a minimal distance between rings 1.0–1.3 nm and about 10% of molecules with 1.5–1.6 nm can be obtained. Availability of a complete intramolecular excitation energy transfer in the frozen solutions of all compounds investigated is proved by spectral methods. The longest distance between the donor and acceptor π-electron systems achieved in the systems under study do not allow for the inhibition of the triplet energy transfer. Our results thus indicate that the critical distance of a "simple" triplet exciton jump, at which the excess of the excitation energy transfer will be incomplete, exceeds 1.6 nm.

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