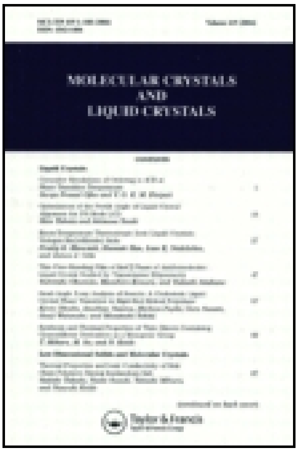

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The Search and Investigation of the Novel Photo-Thermochromic and Luminescent Flexible Structures with Intramolecular Proton Transfer

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THE SEARCH AND INVESTIGATION OF THE NOVEL PHOTO-THERMOCHROMIC AND LUMINESCENT FLEXIBLE STRUCTURES WITH INTRAMOLECULAR PROTON TRANSFER.

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Abstract Comparative findings of the experimental and quantum-chemical studies of the structures including Intramolecular H-Bond (OH··N or NH··N) with the endocyclic (A) and exocyclic (B) nitrogen atom have been obtained. The photochromic properties are shown only in the structures of B-type favorable for the diabatic formation of the metastable photocolored structure. The molecules of the A-type reveal the thermochromism and/or fluorescence with the Anomalous Stokes Shift.

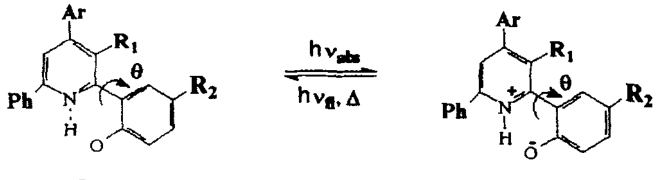
INTRODUCTION

The Ground and/or Excited State Intramolecular Proton Transfer (GSIPT or ESIPT respectively) plays principal role as a primer step followed by the adiabatic (adp) or diabatic (DBT) conformational processes forming the spectral, luminescent and photochemical properties of the molecular structures including Intramolecular H-Bond (IHB).[1-4] In the present work the investigations have been carried out to reveal the regularities determing the selection of the most perspective compounds with IHB for the novel organic photo-thermochromes and luminophores with Anomalous Stokes Shift (ASS) of the fluorescence band.

RESULTS AND DISCUSSION

The two different structure types including IHB O(N)··N with the endocyclic (A) and exocyclic (B) atom N have been studied by the UV, IR absorption, luminescent, PMR, spectroscopic methods with use of the semiempiric quantum-chemical (CNDO/S, AM1 and PM-3) calculations and the structure modeling method.

Type A. The derivatives of 2-(2-Hydroxyaryl)pyridines (I).[5]



(I) (II)* or (II)$_c$

I
a: Ar = C_6H_5
b: Ar = $C_6H_4N(CH_3)_2$
R_1 = H, CH_3; R_2 = H, Cl

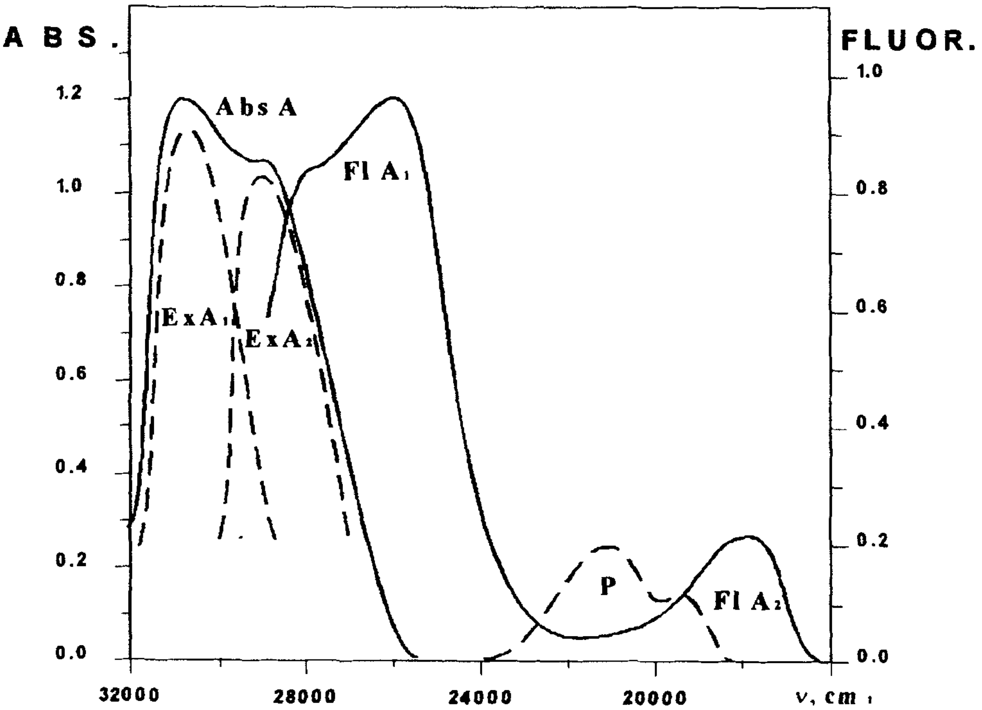


FIGURE 1. Absorption, luminescent emission and excitation spectra of Ia (ethanol, T=77 K)

In I_a (fig. 1) the ground state equilibrium between the acoplanar (θ>60°) and flattened (θ=0°) enol conformes (i) (λ_{max} : 345 - 350 nm) occurs. In the former the fluorescence A_1 (λ_{max} - 360 nm) and the phosphorescence P (λ_{max} =470 nm) of the structure (i) are observed by excitation in A (A_1 + A_2) absorption band. The flattened conformer undergoes the adiabatic ESIPT issuing in ASS fluorescence A_2 (λ_{max} = 535 nm, $\Delta\nu_{stokes}$ = 10000 cm^{-1}) from excited structure (ii*), θ = 0°) followed by the adiabatic ring twist ((ii)*, θ>45°) leading to the fluorescence quenching in liquid solutions.

Inclusion of the strong donor substituent (Ib) leads to the Ground State equilibrium displacement to the keto-structure (ii)$_c$ (λ_{max} = 390 nm) due to GSIPT ussuing in the thermochromism especially at the temperature increase.

So we found of the type I compounds to be luminescent and/or thermochromic.

Type B. The imines of O-hydroxyaldehydes (II).[4]

II

a: R=Ph

b: R=$(CH_2)_{11}CH_3$

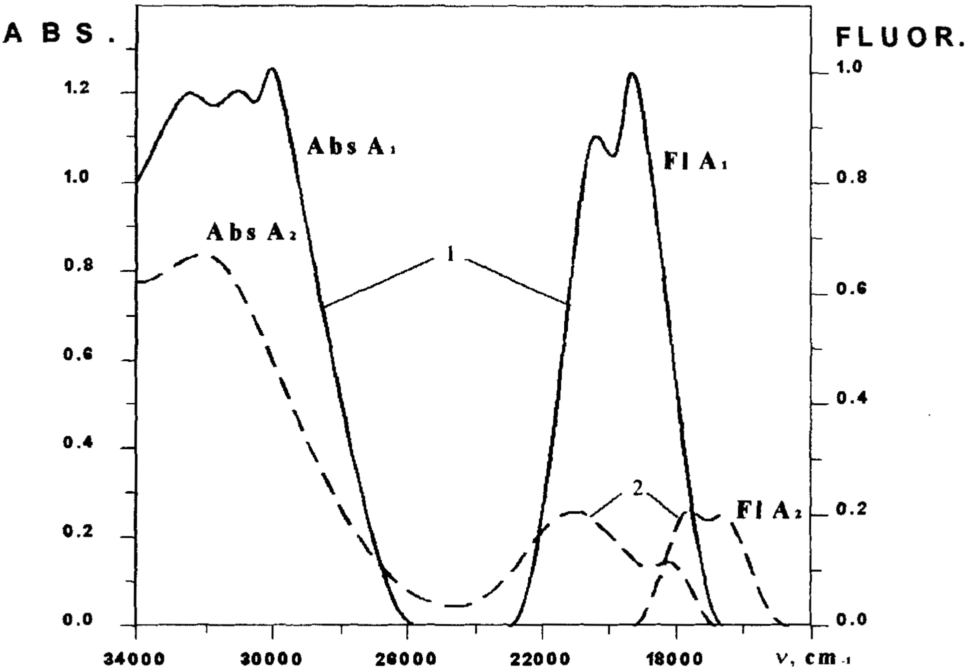
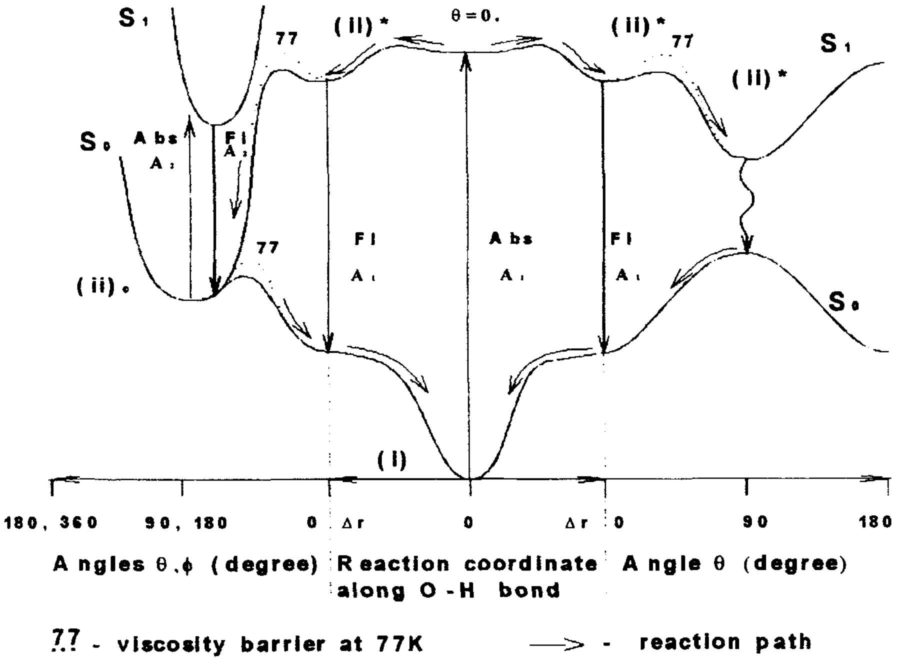


FIGURE 2. Absorption and fluorescence spectra of IIa before (1) and after (2) irradiation (15 min, ethanol, T=77 K)

The compound II (fig.2 and Scheme 1) in the ground state is only in the enol form (i) with the strong IHB. The ESIPT issues in the formation of the flattened structure (ii)* (θ = 0° ; ϕ = 0°) responsible for ASS-fluorescence. It is followed by the two competing processes of the formation of the quenching TICT-structure (ii*) (θ =

90° ; ϕ = 0°) (adiabatic) and the twisted metastable colored product (ii)$_c$ (θ = 60° - 70° ; $\phi > 120°$) (diabatic) stabilized by the rigid medium. In the compound IIb the structure (ii) may be formed both in the ground (ii)$_c$ and excited (ii)* states (thermo and photochromism respectively).



SCHEME 1.

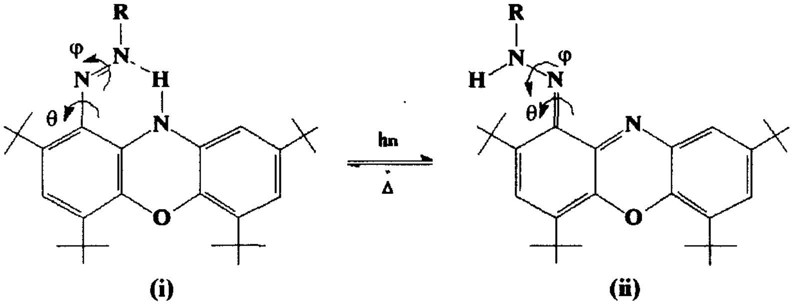
The principal structural differences between A and B type molecules are represented in the Table 1.

TABLE 1. The principal structural differences between A and B type molecules

NN	Kind of findings	i_a	ii_a
		A	B
1	^{1}H NMR (OH) (ppm)	15	17
	IR (OH) (cm^{-1})	3433	2730
2	Change of the electron dencity on $S_0 \rightarrow S_1$ excitation Δq (C=N)	0.002	0,140
3	Active angular coordinate	θ	θ, φ

It follows from the table that the Ground state IHB in the B-type compounds is more strong than in the A-type ones (the line 1), the basicity of C=N-group is stronger changed by S_o - S_1 excitation in the B-type molecules than in the A-type ones (line 2) and structures B-type are more flexible than A-type ones (line3).

The novel photochromic compounds (1-p-phenyl (tozyl)azo-2,4,6,8-tetraphenoxazines (III) were found among the structures of the B-type.



III

a: R=Ts

b: R=Ph

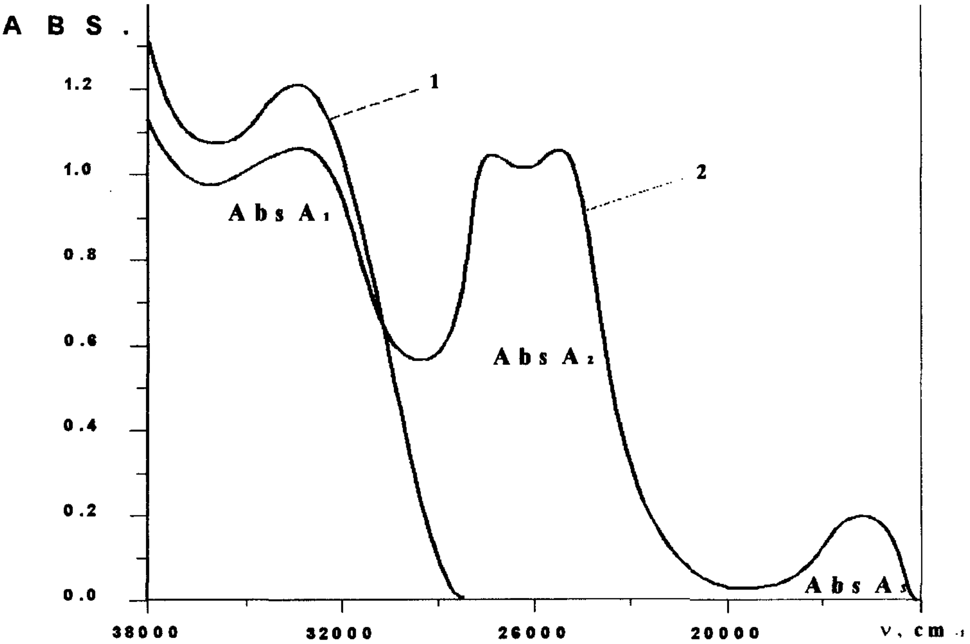


FIGURE 3. Absorption spectra of IIIa before (1) and after (2) irradiation (15 min, ethanol, T=77 K)

In these compounds (fig.3) metastable photocolored structure (ii) (λ_{max} = 617 nm) is formed as well as in the II by the ESIPT followed by diabatic isomerization about C=N and N-N-bonds. Unlike II the ASS-fluorescence is absent apparently due to presence of the nπ*-states.

CONCLUSIONS

The photochromic properties are displayed in the structures of the type B with exocyclic nytrogen atom. It followes from the results of the comparative investigations of the A and B type of structures that the favorable circumstances for the photochromism of the B structure type unlike A type arises from both stronger IHB and more structure flexiblility (the angels θ and ϕ) issuing in the opportunity of the diabatic formation of the highly energetic metastable photocolored structure.

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