DESIGN, SYNTHESIS AND COMPLEXATION ABILITY OF SUBSTITUTED SPIRONAPHTHOXAZINES

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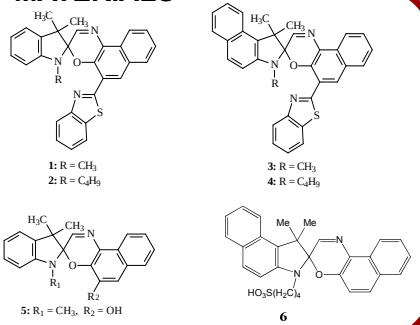
INTRODUCTION

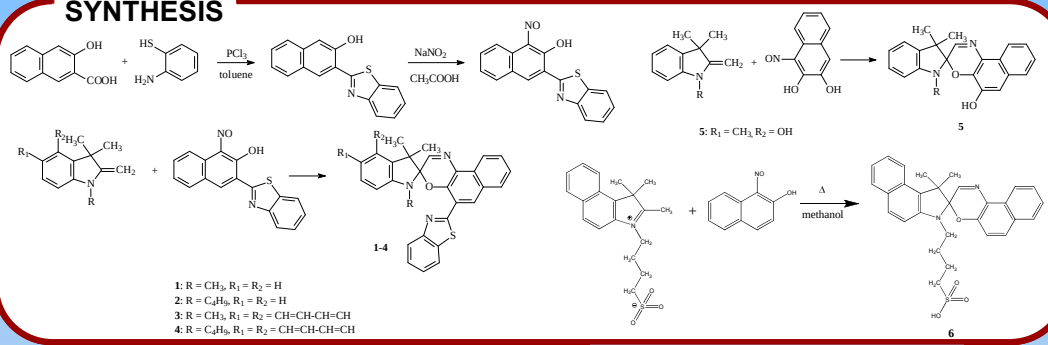
Chemical and photochemical processes based on intramolecular transformations are of significant importance to the development of technologies and medicine, prominent among which are the photochemical transformations. Their unique practical application refers to the photochromic transformations including optical recording and information storage, as well as optical switches, dynamic biosensors capable of storing solar energy, catalysis, optical electronics and bioelectronics in both photovoltaic and nonlinear optics. All these contemporary topics necessitated the synthesis and investigation of novel photochromic compounds. Currently, the major types of photochromic materials are classified, including both of their benefits and drawbacks with respect to their photophysical properties. Recent practical purposes have imposed strict requirements with respect to the optical characteristics, temperature regimes, as well as the operation stability of photochromic materials. The above listed criteria lead to the increase of the needs in developing both novel chemical structures and strategies in order to meet the requirements related to their application.

We have reported on the design, synthesis and complex ability of a series of spironaphthoxazine bearing different substituents on the basic skeleton [1-3]. Under steady UV irradiation, spironaphthoxazines containing hydroxyl substituent at the 5′ position in the naphthoxazine moiety, form complexes in polar solvents with Al(III), Cu(II) and Fe(II), those containing benzothiazolyl substituent with Co(II), Ni(II), Zn(II), and with sulfobutyl substituent on the indoline part of the molecule with Mg(II), Ca(II), Cd(II), Zn(II), и Pb(II) Continuing our investigations on this series of compounds, here we describe our spectroscopic studies to determine the effect of solvent and structure on the equilibrium between SO and MC.

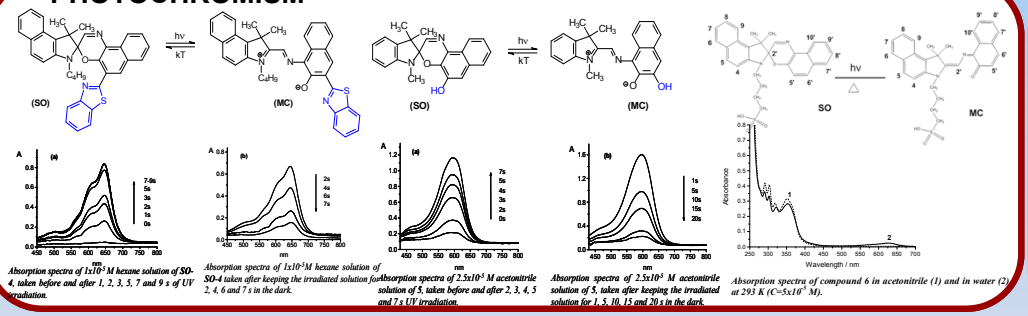
MATERIALS



SYNTHESIS



PHOTOCHROMISM



Absorption spectra of 1x10⁻⁵ M hexane solution of SO-4, taken before and after 1, 2, 3, 5, 7 and 9 s of UV irradiation.

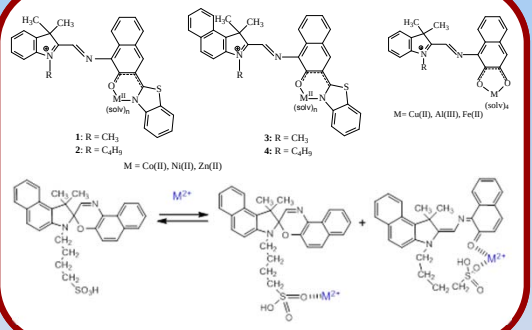
Absorption spectra of 1x10⁻⁵M hexane solution of SO-4 taken after keeping the irradiated solution for 2, 4, 6 and 7 s in the dark.

Absorption spectra of 2.5x10⁻⁵ M acetonitrile solution of 5, taken before and after 2, 3, 4, 5 and 7 s UV irradiation.

Absorption spectra of 2.5x10⁻⁵ M acetonitrile solution of 5, taken after keeping the irradiated solution for 1, 5, 10, 15 and 20 s in the dark.

Absorption spectra of compound 6 in acetonitrile (1) and in water (2) at 293 K (C=5x10⁻⁵ M).

COMPLEXATION ABILITY



The time dependence of absorbance changes at λ compl

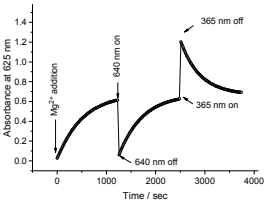


Fig. 1. Variation of absorbance at 625 nm of 5x10⁻⁵ M of 6 in acetonitrile on Mg(ClO₄)₂ addition in the dark, after red light (λ=640 nm) and UV (λ=365 nm) irradiation versus time. C_{SO}=$C_{Mg^{2+}}$ = 5x10⁻⁵ M, T = 298 K, MeCN.

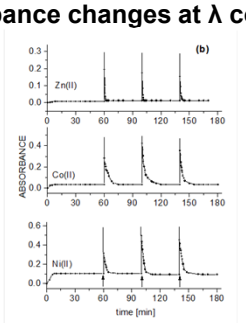


Fig. 2. Absorbance changes of hexane/acetone (1:1) solution of 4 in the presence of: 1 equiv. of Zn(II) at 605 nm; Co(II) at 615 nm and Ni(II) at 625 nm, following short UV illumination after the thermal equilibration in the dark. Upward arrows show 10 s UV irradiation; c_{SO}=1.25x10⁻⁵ M (a) and 1.0x10⁻⁵ M (b).

CONCLUSION

1. Some novel spironaphthoxazines, containing chelating functional groups are synthesized and their physical and spectroscopic characteristics are determined.
2. Complexation of metal ions with the merocyanines induces a slight hypsochromic shift of its visible absorption band and drastically slows down its thermal bleaching in the dark.
3. The study on the complex formation of the synthesized spiroindolinonaphthoxazines describes them from kinetic, thermodynamic and structural point of view.
4. The relaxation time at 20 ºC ranges from 2 to 42 min, the actual value depending on the ion and compound.
5. Thermal equilibrium between the ground state populations of the colourless and coloured forms is influenced by the solvent polarity as well as by the nature of the substituents.
6. The values of Ea for coloration process in the dark show no effect of the metal ion nature. Therefore the process of thermal ring opening of the spiro form is the rate limiting step of complex formation.

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