

Experimental and theoretical insight into the complexation behavior of spironaphthopyrans bearing *o*-positioning benzazole moiety



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ABSTRACT

Metal coordination by spironaphthopyran derived merocyanines bearing benzazol substituents has been studied by means of experimental and theoretical methods. The formation of N-O coordinated chelate complexes have been observed by means of X-ray diffraction. Merocyanine scaffolds of these complexes possess *trans-trans-cis* conformation independently of both substituents in positions 1 and 5 of indoline moiety and benzazole heteroatom. Stability of merocyanine-metal complexes significantly depends on two factors: relative thermodynamic stability of spirocyclic and open isomers and complexation energy. Variation of the ligand structure involving chelating group significantly changes stability of complexes while replacement of the substituents in the indoline ring peripheral to the chelating parts of the molecules and biasing the spiropyran – merocyanine equilibrium provide the fine tuning of complexation selectivity. Complexes of diamagnetic ions (Mg^{2+} , Zn^{2+} , Cd^{2+}) undergo photodissociation. The complexes of benzoxazole containing ligands demonstrate higher quantum yields comparing to their benzothiazole analogue.

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1. Introduction

Spiropyrans, that under the action of UV light undergo heterolytic cleavage of the $C_{\text{spiro}}-O$ bond of the ground state colorless form **A** to convert to the deeply colored merocyanine form **B**, represent one of the most versatile type of photochromic compounds [1,2] which are widely employed for the design of optical light filters, photoswitches, optical memory elements and other applications [3–5]. The spiropyran merocyanine isomeric form containing a negatively charged phenolate oxygen atom readily behaves as a monodentate ligand in complexation reaction with metal ions [6,7]. Combination of photochromic and complexation properties opens vast perspectives for application of spiropyrans in the design of photodynamic sensors [8–10]. Stability of the complexes formed by metal ions and the ring-opened merocyanine forms of spiropyrans can be significantly enhanced by an appropriate functionalization of their molecules, particularly by

introduction of additional donor centers [11]. An efficient way to the proper functionalization of a spiropyran is associated with introduction of a heterocyclic substituent into an *ortho*-position 8 of the 2*H*-chromene ring vicinal to the oxygen, which provides for chelating the target metal ion and increased stability of the formed complex. Thus, morpholine- [12], pyridine- [13], quinoline-containing [14] spiropyrans demonstrate efficient complexation with several transition metal ions. Moreover, 8-benzothiazole-substituted spiropyrans exhibit high affinity to Co^{2+} and Ni^{2+} ions in acetonitrile solution [15]. In acetone solution, 5'-(4,5-diphenyl-1,3-oxazol-2-yl) substituted spiro(indoline-naphthopyrans) form intensely colored complexes with divalent transition metal ions [16]. Modification of the ligand structures is an effective tool to vary the stability of their complexes and as a consequence to increase response selectivity towards certain metal ion. Increasing of number of such spiropyran functionalization methods brings into the foreground revealing of the structure depended factors that control complexation selectivity towards target metal ions. As applied to spiropyran complexation, the features of spiropyran structure imply not only donor atoms nature of chelating site and possible steric effects but also the influence of spirocyclic form-merocyanine

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tautomeric equilibrium [17] on the resulting complex stability. This is related to the fact that the active merocyanine isomer is involved in two competitive processes: merocyanine-spiropyran equilibrium and complexation equilibrium. Roxburgh et al. [18,19] reported that in the case of metal ion chelation of crowned spirobenzopyran derivatives the introduction of an electron-withdrawing group at the indoline's 5-position is biasing the tautomeric equilibrium towards the spirocyclic isomer and destabilizes the merocyanine metal ion complex. Further, this aspect has been considered quantitatively. In the case of quinoline spiroopyran series the analysis of the dependence of 1:1 complex effective stability constants on the tautomeric equilibrium constant has been undertaken. The results provide a possibility to control complexation selectivity by adjusting spiroopyran-merocyanine equilibrium [20]. The same effect has been demonstrated by Yagi et al. [21] on the oligoether-linked bis(spiropyran) podands. It has been found that an increase of the electron-donating ability of the substituent in 5-position of the indoline moiety leads to an increase of the complex stability constants.

The present work is aimed at gaining insight into the effects exerted on composition and stability of metal complexes of merocyanine isomers of 5'-benzazole-substituted spiro(indoline-naphthopyrans) (SNP) by heteroatoms in the benzazole moiety as well as the substituents in the indoline ring peripheral to the active parts of their molecules involved into the pericyclic rearrangement and formation of the coordination site. For this purpose the complexation of 5'-(1,3-benzoxazol-2-yl) substituted spiro[indoline-naphthopyrans] (SNP **1**, **2**) with metal ions has been investigated. The results have been compared with the complexation data obtained for the previously studied 5'-benzazole substituted SNP's **3** [22] and **4** [23] under the analogous experimental conditions.

2. Results and discussion

2.1. Spectral characterization of isomeric form of SNP

Synthesis of the investigated spironaphthopyrans have been described earlier [23,24]. In acetone solution, SNP's **1–4** appear as an equilibrium mixture of their predominant ring-closed spirocyclic **A** and ring-opened merocyanine **B** isomeric forms. Spirocyclic forms **A** are characterized by two absorption bands – the long wavelengths absorption at 360–420 nm and the more intense band in the region of 330–350 nm.

The nature of the observed absorption spectra of SNP isomers was elucidated by TD DFT calculations. The long wavelength absorption bands of the spirocyclic isomers **A 1–4** correspond to the S_1 and S_2 electronic excited states mainly contributed by HOMO - LUMO and HOMO-1 - LUMO transitions respectively. The first band (with low oscillator strength) is attributed to the charge-transfer (CT) from the indoline moiety to the spiroconjugated chromene fragment. The second one (with high oscillator strength) may be characterized as $\pi-\pi^*$ transitions within the chromene part of the molecule accompanied by the charge-transfer to the benzoxazolyl (benzothiazolyl) substituent. The more intense spectral absorption bands at 330–350 nm of the isomers **A 1–3** are attributed to $\pi-\pi^*$ transitions (HOMO-2 - LUMO) that involve orbitals localized on the chromene moiety including substituted fragments and correspond to S_0-S_3 (**A 1**, **A 2**) and S_0-S_4 (**A 3**) electronic transitions. For 5'-benzothiazol substituted isomer **A 4** this spectral region originate from S_0-S_4 and S_0-S_5 transitions both having a significant contributions from two excitations (HOMO-2 - LUMO and HOMO-1 - LUMO+1). The long wavelengths absorption bands of the merocyanines **B 1–4** appear in the region 550–650 nm and originate from the $\pi-\pi^*$ transitions S_0-S_1 (HOMO - LUMO), while the

observed absorption at 375–420 nm may be contributed by S_0-S_3 and S_0-S_4 transition of this isomers of the mixed (CT and $\pi-\pi^*$) nature. The variation of the substituents of both the indoline and the chromene parts of the molecules does not change significantly the position of the absorption bands maxima for both isomers of SNP **1–4**.

The relative amount of the merocyanine isomer of the compounds can be estimated by the intensity of absorption in the visible spectral region (Fig. 1).

As it is seen from the spectra shown in Fig. 1, the equilibrium content of the merocyanine isomer **2** is substantially lower than that observed for SNP **1**. The latter is caused by a decrease in relative stability of the merocyanine form **2** (on 1.2 kcal/mol according to the DFT calculation) upon introduction of an electron withdrawing chlor substituent in the position 5 of the indoline fragment. On the contrary, the introduction of an electron releasing methoxy group at the same position leads to increase of the equilibrium content of the merocyanine isomer **3** comparing to that observed for **1**. Enhancement of electron withdrawing properties of the substituents in 2*H*-chromene moieties of spiroopyrans is known to increase relative stability of their merocyanine form [1,25]. Theoretically predicted stabilisation effect has been calculated to be 0.8 kcal/mol. A qualitatively similar but more pronounced result has been observed upon the replacement of a benzoxazolyl group by a benzothiazolyl one. In this case a notable intensification of the longest wavelength absorption band of **B 4** as compared to the benzoxazolyl analogues **1–3** (Fig. 1) can be caused by several factors. One of them is attributed to the increase of the equilibrium amount of the colored ring-opened form (on 0.6 kcal/mol according to the calculation) due to increasing of electron withdrawing properties of the substituent group [26]. The other can be related to the enhancement of molar absorptivity of the merocyanine **B 4**.

2.2. Metal ion complexation

Addition of equivalent amounts of transition metal cation (Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+}) salts to a colorless solution of SNP **1**, **2** is accompanied by the intense coloration of the solution induced by the formation of the complexation reaction products. Among alkaline earth metals solely an addition of Mg^{2+} ions leads to the notable coloration of SNP **1**, **2** solutions. Positions of long wavelength absorption band maxima of thus formed solutions depend on the metal ion nature and they are hypsochromically

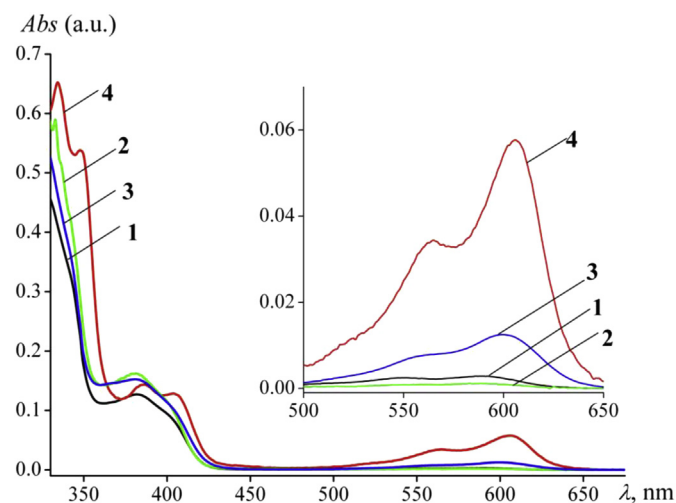


Fig. 1. Absorption spectra of SNP **1–4** in acetone, $C = 3 \cdot 10^{-5}$ M, $T = 293$ K.

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