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Spectral study of the structure and properties of complexes of unsubstituted indoline spiropyran with aluminum ions

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The methods of absorption electronic and NMR spectroscopy were used to study the processes of complexation during the interaction of molecules of unsubstituted indoline spiropyran with aluminum salts. The mechanism of formation and structure of complexes of two types has been established. Negative photochromism of the complex of the merocyanine form of spiropyran with aluminum ions was found. The stability of metal complexes to the action of various agents has been investigated.

Keywords: photochromism, spiropyrans, metal complexes, aluminum salts, electron spectroscopy, NMR spectroscopy.

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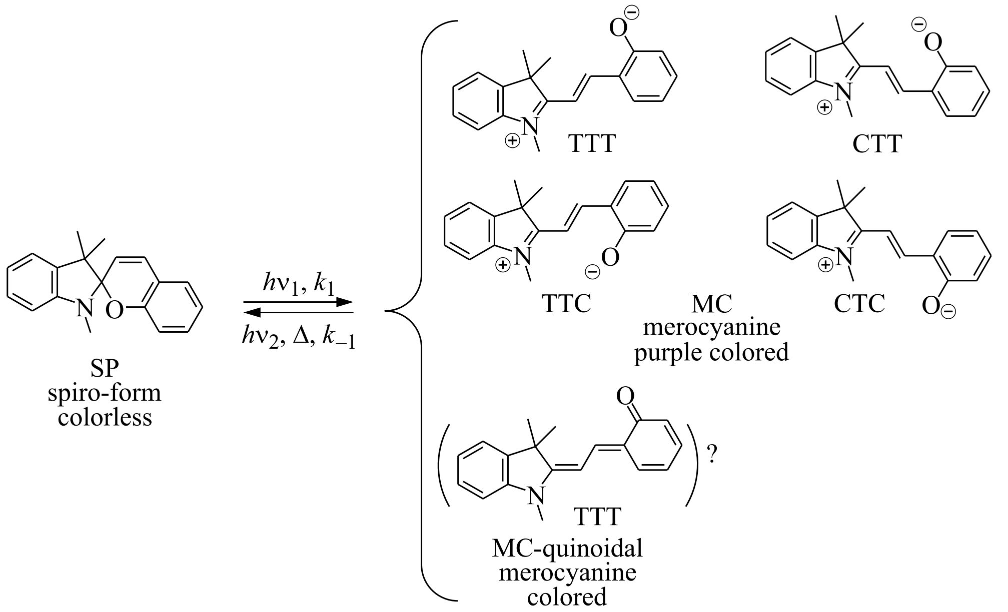
Introduction

Photocontrolled photochromic ionophores and artificial receptors, which make it possible to control the process of complex formation with various ligands and the properties of the resulting products, attract the interest of researchers in various fields [1–8]. It was previously shown that substituted derivatives of spiropyran — 1′, 3′, 3′-trimethylspiro[2*H*-1-benzopyran-2, 2′-indoline] (BIPS, SP1) undergoing photochromic transformations (Scheme 1) quite easily form complexes when interacting with salts of some *d*- and *f*-elements [3–12], as well as salts with inorganic acids [13,14].

In the process of photochromic transformations, the colorless cyclic (spiro) form of spiropyrans undergoes dissociation of the C–O bond in the pyran fragment under the action of UV light and subsequent dark *cis*→*trans*-isomerization with the formation of a colored merocyanine form (MC). It returns to its original state either spontaneously or upon irradiation with visible light absorbed by the MC form. The rate of the dark discoloration reaction increases as the photochromic system is heated. As intermediate products, the existence of a set of isomeric MC forms with the phenolate anion (TTT, TTS, STT, STS, etc.) is assumed, and the formation of isomeric quinoid structures is also possible.

Composition and stability of the resulting complexes of spiropyran molecules with metal ions depend both on the structure of the photochromic ligand and the properties of the solvent, and on the nature and valence of metal cations. Most often, the formation of $SP{-}M^{n+}$ complexes of the composition 2 : 1 or 1 : 1 is observed. There are known a number of such photocontrolled ion-complexing systems based on spiropyrans containing a nitro group in position 6 of the pyran fragment, as well as carboxy-, methoxy- or mercapto groups, or residues of crown ethers, podands, iminodiacetate, N-heterocycles, bipyridyls, and dendrimers used as ionophore or chelator components in various positions of the photochrome molecule [3–8].

In the study of the properties of spiropyrans and their photointermediates, in addition to spectral-kinetic methods (stationary and pulsed absorption spectroscopy and laser flash photolysis in the UV and visible spectral regions) [15–18], NMR spectroscopy has also been successfully used lately [9–11,19–23]. However, the wide application of the latter method in the study of the properties of photochromic compounds is limited due to the short lifetime of photointermediates of the MC form of spiropyrans. The solution to this problem is possible with the help of new equipment for NMR spectrometry, in which NMR spectra are recorded in the process of irradiating a sample with light of given wavelength [10]. An alternative solution to the problem is development of new methods for stabilizing the photoinduced MC form by using more viscous or polar solvents [9,11,19–23], as well as introducing additional functional substituents [11,12,19,21,23] or fragments



Scheme 1. Photochromic transformations of spiropyran.

of heterocycles into the pyran part of the photochrome molecule [9,10].

In the course of studying the mechanisms of complexation of spiropyran derivatives with salts of various metals and determining the presence, location, and nature of substituents in the photochromic molecule, in this article, we studied for the first time the process of interaction of the simplest precursor — unsubstituted indoline spiropyran (SP1) — with salts of aluminum. In this article, we used unsubstituted indoline spiropyran SP1, whose photochromic transformations were previously studied by pulsed spectroscopy and laser photolysis [15–18], since the photointermediate lifetime ranges from a fraction of a second to several seconds, which makes it technically impossible to study composition and structure of its photostationary mixture by NMR spectroscopy.

As a result, the composition and detailed structure of photointermediates of spiropyran SP1 under irradiation with light of 320−350 nm have not yet been fully determined, since the exact configurations of possible intermediates of the MC-form of spiropyran SP1 and the presence of quinoid structures have not been established. In this connection, in this article, we used the method of stabilizing the short-lived MC form of unsubstituted indoline spiropyran by forming stable complexes between the molecules of this compound and aluminum salts.

In order to develop previously performed studies [13,24] the aim of this article was to study the structure of complexes of photochromic spiropyran SP1 during the interaction of its molecules with aluminum salt using the electronic, ^{1}H, ^{13}C and 2D MR spectroscopy.

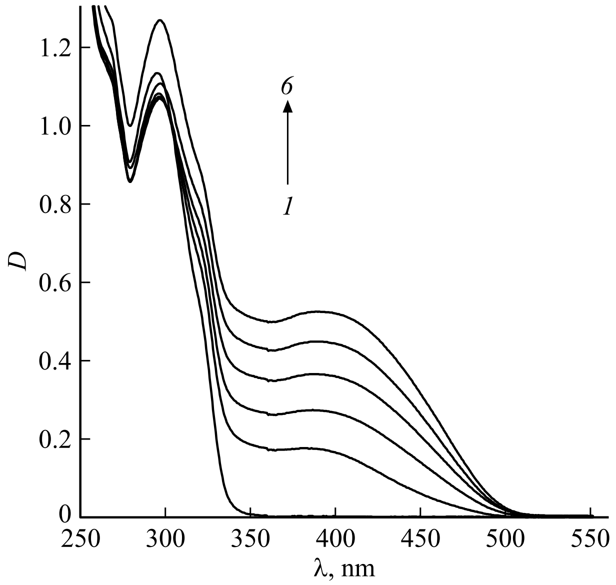


Figure 1. Changes in the absorption spectra of spiropyran SP1 in ethanol in the presence of $Al(NO_3)_3$ after addition of aluminum nitrate nonahydrate in the dark at different ratios of reagents: $2 \cdot 10^{-4}$ M SP1 (*1*); $2 \cdot 10^{-4}$ M SP1 + $5 \cdot 10^{-4}$ M $Al(NO_3)_3$ (*2*); $2 \cdot 10^{-4}$ M SP1 + $1 \cdot 10^{-3}$ M $Al(NO_3)_3$ (*3*); $2 \cdot 10^{-4}$ M SP1 + $2 \cdot 10^{-3}$ M $Al(NO_3)_3$ (*4*); $2 \cdot 10^{-4}$ M SP1 + $4 \cdot 10^{-3}$ M $Al(NO_3)_3$ (*5*); $2 \cdot 10^{-4}$ M SP1 + $8 \cdot 10^{-3}$ M $Al(NO_3)_3$ (*6*).

Experimental part

Spiropyran SP1 was obtained with yield of 96% by heating at boiling of solution of freshly distilled Fischer's base with salicylaldehyde in anhydrous ethanol in an argon atmosphere according to the known method [12,13]. The

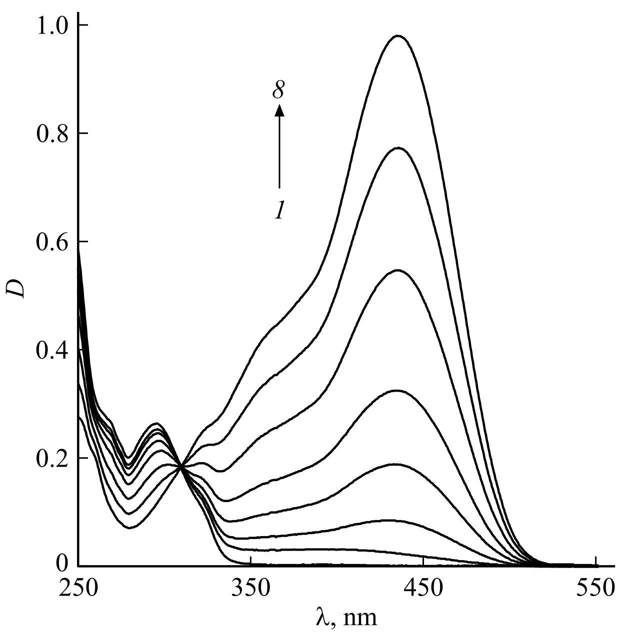


Figure 2. Change in the absorption spectra of spiropyran SP1 in ethanol ($C = 3.2 \cdot 10^{-5}$ M) in the presence of 10 eq. excess of $Al(NO_3)_3 \cdot 9H_2O$: before (*1*), immediately after introduction to solution $Al(NO_3)_3{\cdot}H_2O$ ($3.5 \cdot 10^{-4}$ M) (*2*), after storing the solution in the dark for 10 (*3*), 30 (*4*), 60 (*5*), 120 (*6*), 21 (*7*), 360 min (*8*).

structure of the target compound SP1 was proved by a set of modern physicochemical methods of analysis (UV, ^{1}H and ^{13}C NMR spectroscopy and mass spectra). LC-MS spectrum (m/z): 278 $[M+H]^+$, $C_{19}H_{19}NO$.

Measurements of the spectral and photochemical characteristics of compound solutions were carried out in quartz cells 10 mm thick on Shimadzu UV-2140PC spectrophotometer (Japan) and on a special bench based on a set of modular fiber optic spectrophotometric equipment from Ocean Optics (USA). Solutions of photochromic spiropyran were prepared using „ultra high purity“solvents, stirring them under thermostatically controlled conditions at temperature of 25°C.

The photoinduced MC form of spiropyran SP1 was obtained by UV irradiation of solutions with light of LightningCure LC8 lamp source (Hamamatsu, Japan, intensity 180 mW/cm^2) through UFS-2 light filter ($270 \le \lambda \le 370$ nm) with continuous stirring. Solutions were irradiated with visible light ($\lambda \ge 400$ nm) using ThorLabs OSL1-EC halogen lamp (USA, 25 W) in combination with light filter ZhS-10.

The NMR spectra of spiropyran SP1 and its complexes with aluminum ions were measured in deuterochloroform and deuteromethanol on Bruker Avance III-500 spectrometer (Germany) with operating frequency of 500 MHz for protons and 126 MHz for carbon nuclei. The complete assignment of the proton and carbon signals was done by a combination of 1D and 2D NMR pulse sequences $^1H-^1H$ COSY, $^1H-^{13}C$ HSQC and $^1H-^{13}C$ HMBC. The signals of tetramethylsilane nuclei for deuterochloroform or the signals of methyl groups δ 3.35 and 49.3 ppm for deuteromethanol were used as standards.

Results and discussion

According to previous studies [14–17,24], the main absorption band of the original cyclic form of spiropyran SP1 in ethanol has an absorption maximum at 295 nm ($\varepsilon_{295} = 6.0 \cdot 10^3\,M^{-1}cm^{-1}$). Under UV irradiation, formation of a photoinduced MC form was recorded, which manifests itself in appearance of an absorption band in the visible region of the spectrum ($\lambda_{max} = 550$ nm, $\varepsilon_{550} = 35.0 \cdot 10^3\,M^{-1}cm^{-1}$), which quickly spontaneously disappears after turning off the light ($k_{-1} = 0.48\,s^{-1}$) with regeneration of the original SP1 cyclic form. However, in the dark, an equilibrium occurs between two forms, and the solution acquires a faint violet color, since some of the MC form is present in it.

Immediately after introduction of sufficiently large amounts of Al^{3+} ions into EtOH or MeOH, a new broad absorption band is observed in the electronic absorption spectrum with a maximum at 380 nm (Fig. 1).

During long-term storage of solution of SP1 in ethanol in the presence of $Al(NO_3)_3$ in the dark, a new absorption

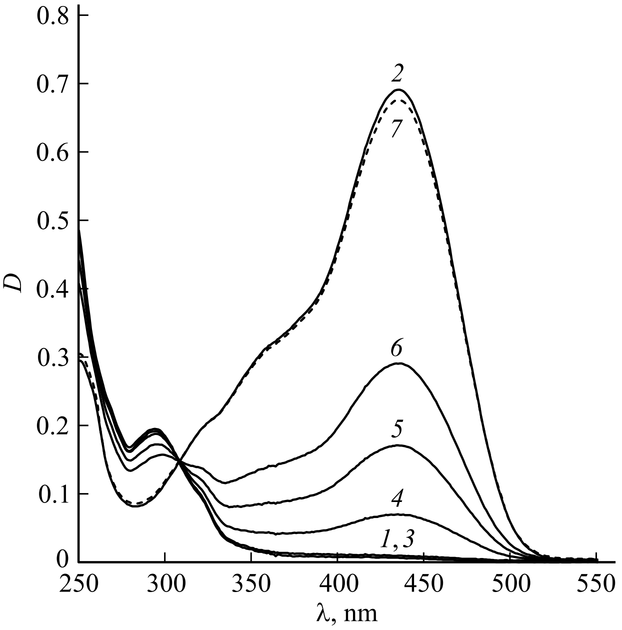
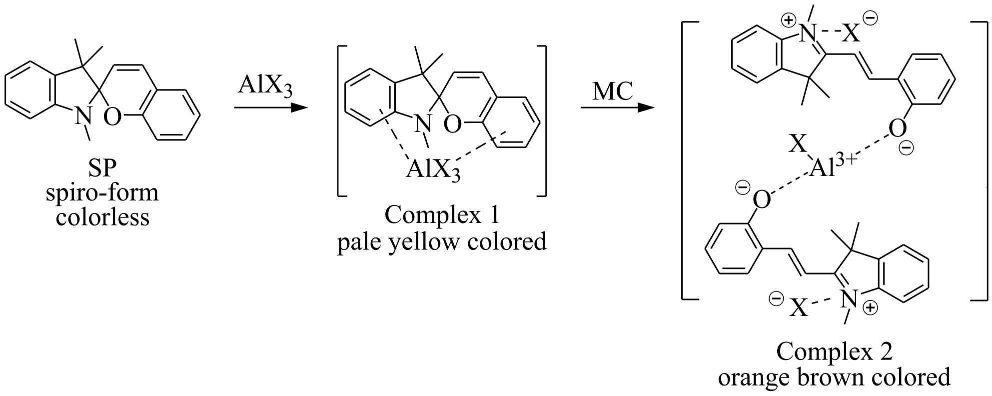
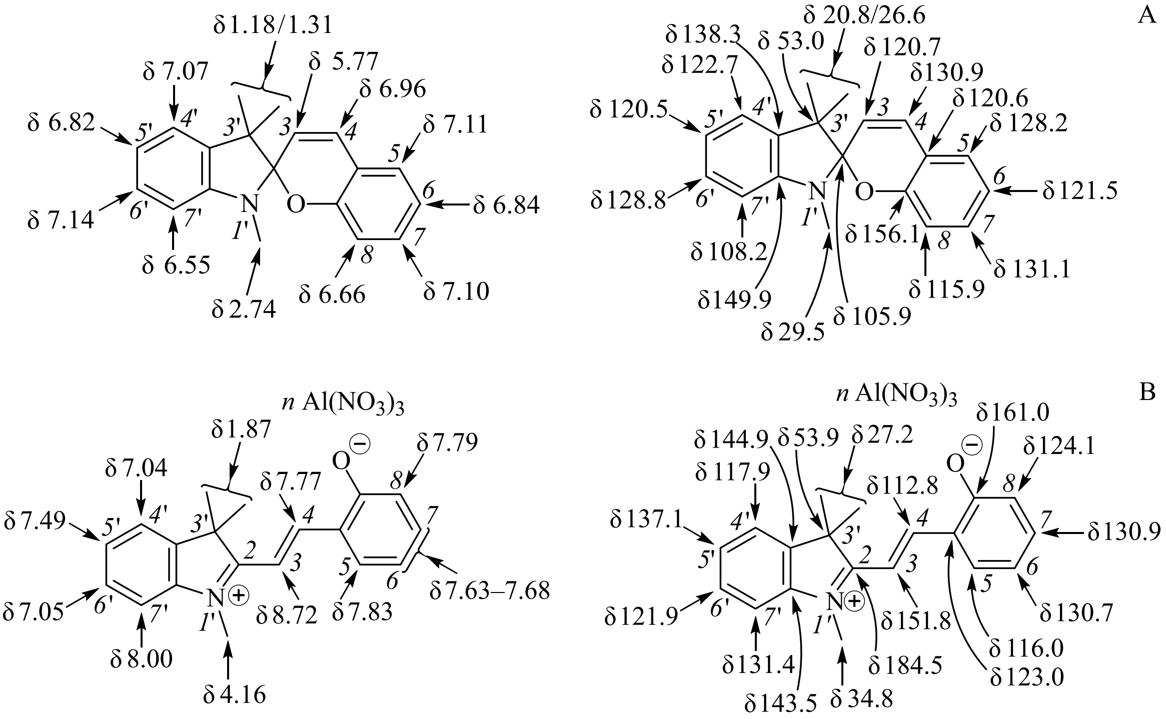


Figure 3. Photoinduced spectral changes in complex 2, which arises in the interaction of SP1 spiropyran and $Al(NO_3)_3$ salt at 10 eq. excess of the latter: *1* — immediately after mixing solutions of SP1 ($C = 3 \cdot 10^{-5}$ M) and salt $Al(NO_3)_3 \cdot 9H_2O$ ($C = 3 \cdot 10^{-4}$ M); *2* — after storing for 48 h in the dark; *3* — after 20 s irradiation with ThorLabs OSL1-EC halogen lamp light through ZhS-10 light filter; *4, 5, 6* — after holding the sample for 10, 30, 60 min in the dark, respectively; *7* — after sample storage for 29 days in the dark at 25°C.



Scheme 2. Formation of metal complexes of spiropyran SP1 with aluminum ions.



Scheme 3. Chemical shifts of NMR spectra of cyclic form (A) and complex 2 (B) (SP1) in CD_3OD: ^{1}H-NMR (2 left figures) and ^{13}C-NMR (2 right figures), $n = 1/2$.

band appears in the absorption spectrum with a maximum in the spectral region $\lambda_{\max} = 430{-}434$ nm (Fig. 2).

These spectral changes can be explained by formation of metal complexes of two types (Scheme 2).

The process of SP1 complexation was studied in EtOH, MeOH and in a mixture of $MeOH + H_2O$ (up to 20% by volume). The dark-stable complex 2 is formed in two stages. First, a labile short-lived π-complex 1 of aromatic fragments of the cyclic form SP1 with aluminum ions with lifetime of less than a minute is formed, which then slowly transforms in the dark into a complex 2 consisting of two molecules of spiropyran SP1 and one aluminum cation. The rate constant of the complex formation reaction in ethanol in the dark with a tenfold excess of aluminum nitrate is $k = 8.56 \cdot 10^{-5}\,\mathrm{s}^{-1}$. Preliminary results concerning the kinetics of complex 2 formation and its stoichiometry were published by us in the article [13]. Complex 2 exhibits negative photochromism (Fig. 3).

It transforms into its original cyclic form upon irradiation with visible light ($\lambda > 400$ nm) (Fig. 3, curve *3*). When the solution is stored in the dark, the initial complex 2 is regenerated (Fig. 3, curves *4–6*). Complex 2 is thermodynamically stable for more than 4 weeks (Fig. 3, curve *7*), but is rapidly destroyed when HCl acid or EDTA complexone is added to the solution. Formation of complexes of two types is confirmed by NMR spectroscopy data.

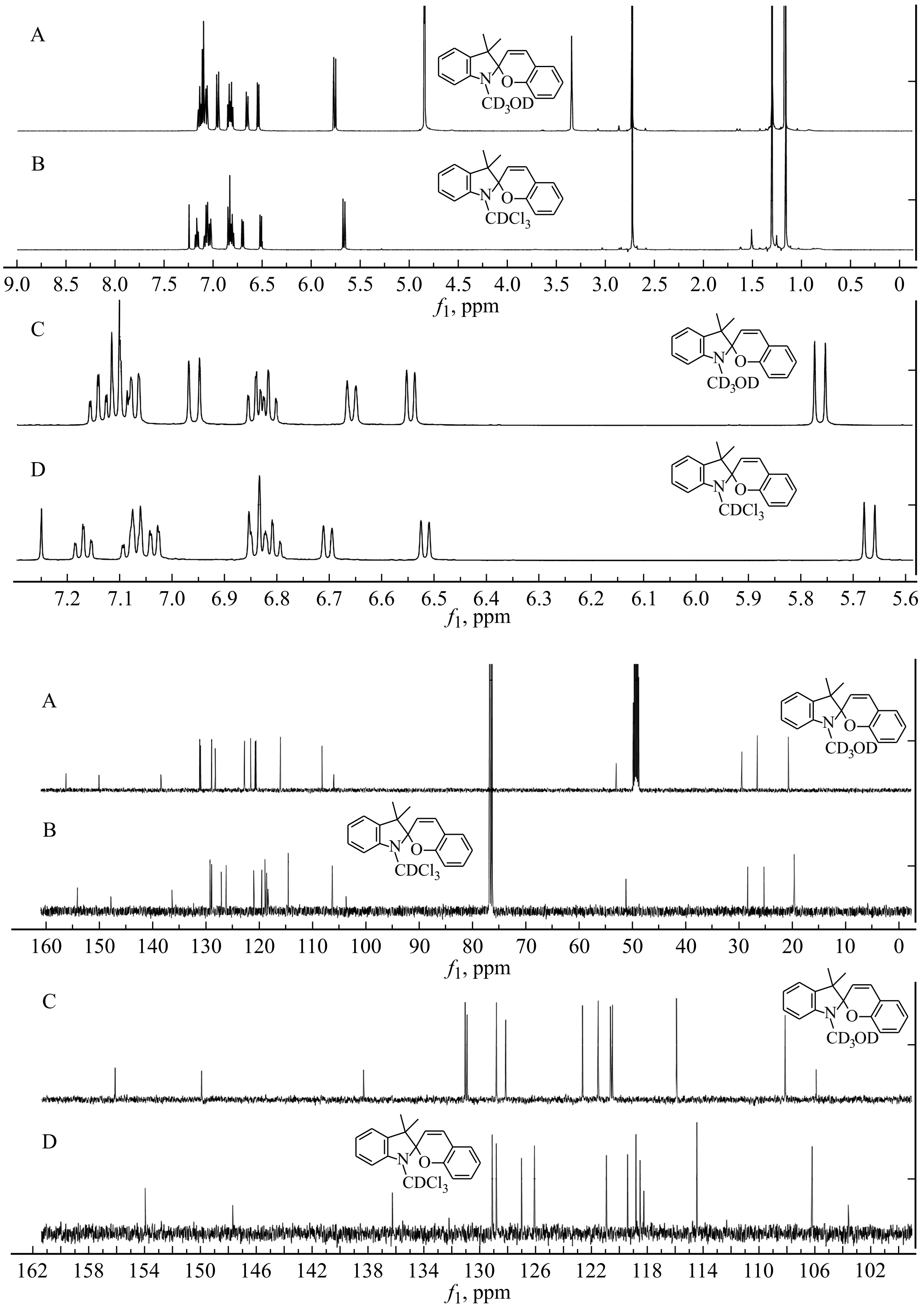


Figure 4. ^{1}H (upper panel) and ^{13}C (lower panel) NMR spectra of the spiro form in $CDCl_3$ (upper spectra) and in CD_3OD (lower spectra), where A, B — spectra of the full range of chemical shifts of signals, C, D — spectra fragments of signals from nuclei of aromatic rings (indoline and benzopyran).

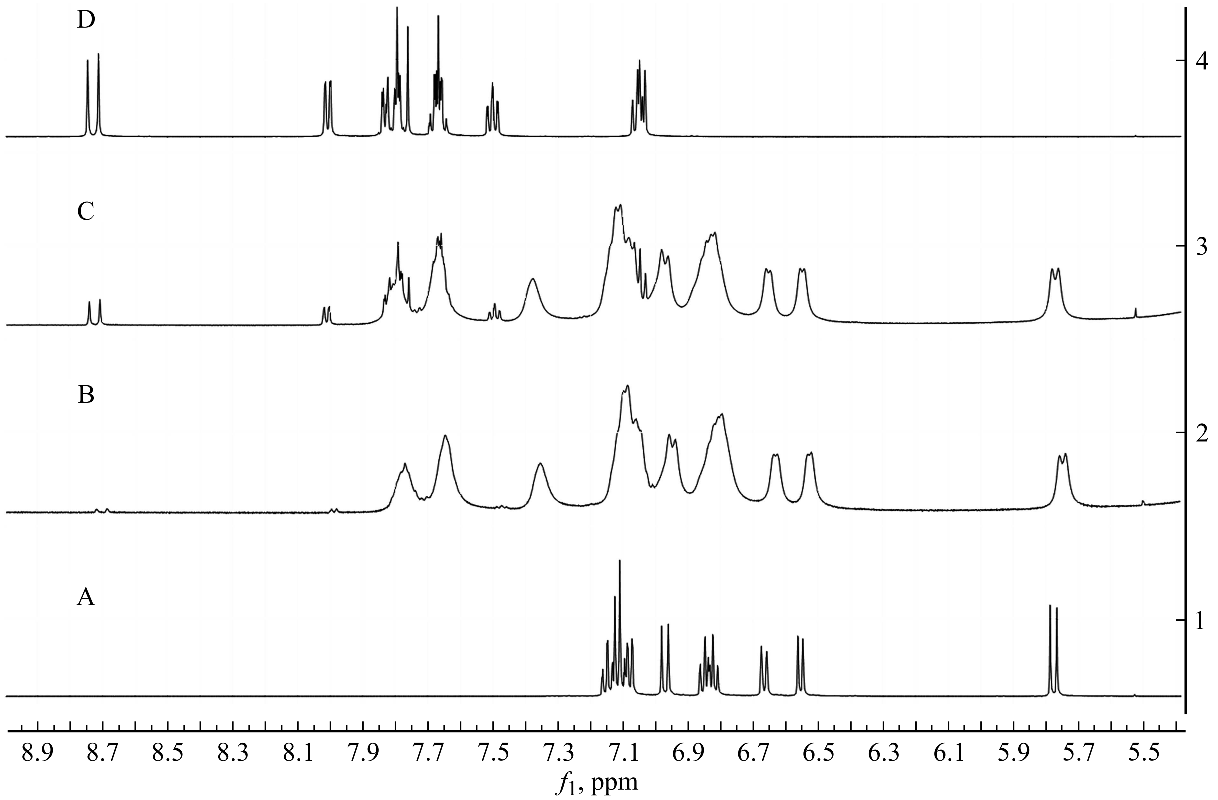


Figure 5. Fragments ^{1}H of NMR spectra of aromatic ring proton signals (SP1) SP — ($6.0 \cdot 10^{-2}$ M) in CD_3OD: A — without adding $Al(NO_3)_3 \cdot 9H_2O$ (0.2 M); B — for complex 1 immediately after adding $Al(NO_3)_3 \cdot 9H_2O$ (0.2); C — for a mixture of complex 1 (80%) and complex 2 (20%) after addition of $Al(NO_3)_3 \cdot 9H_2O$ (0.2 M) and holding for 0.5 h; D — for complex 2 after adding $Al(NO_3)_3 \cdot 9H_2O$ (0.2 M) and holding for 24 h.

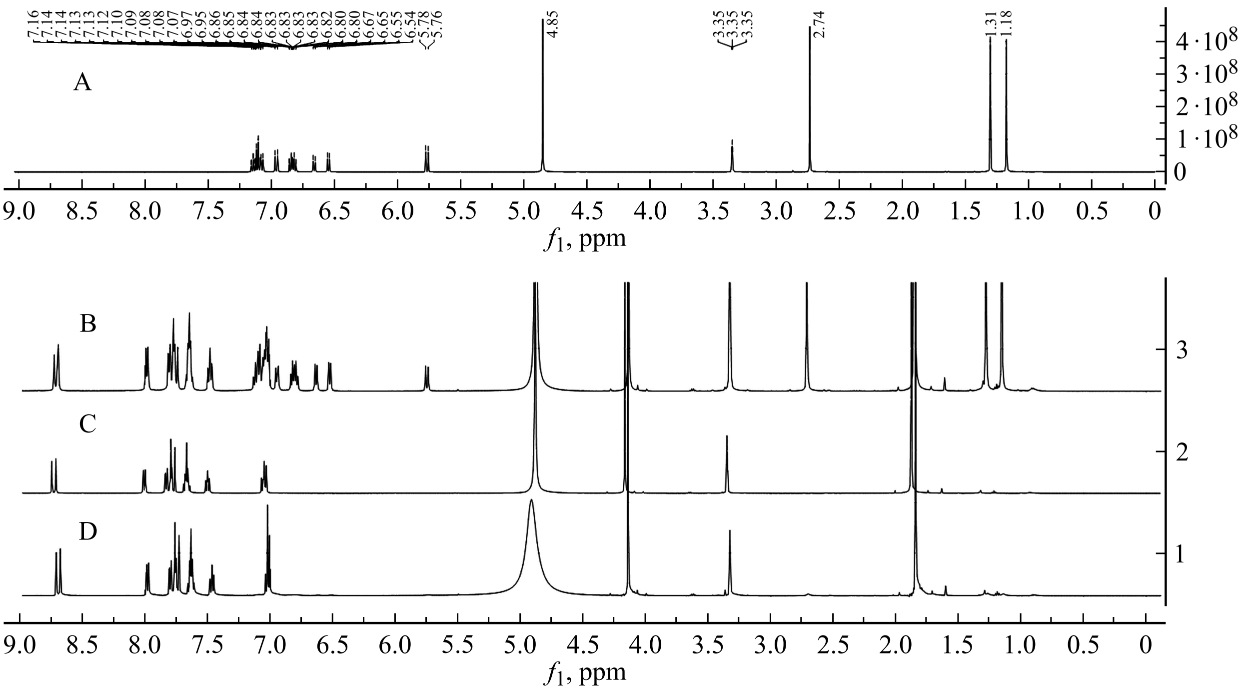


Figure 6. ^{1}H-NMR titration: ^{1}H NMR spectra (SP1) ($6.0 \cdot 10^{-2}$ M) in CD_3OD without addition (A) and after addition of $Al(NO_3)_3 \cdot 9H_2O$ solution in concentrations (M): (B) $1.5 \cdot 10^{-2}$; (C) $3.0 \cdot 10^{-2}$; (D) $6.0 \cdot 10^{-2}$ and holding samples in the dark for 24 h.

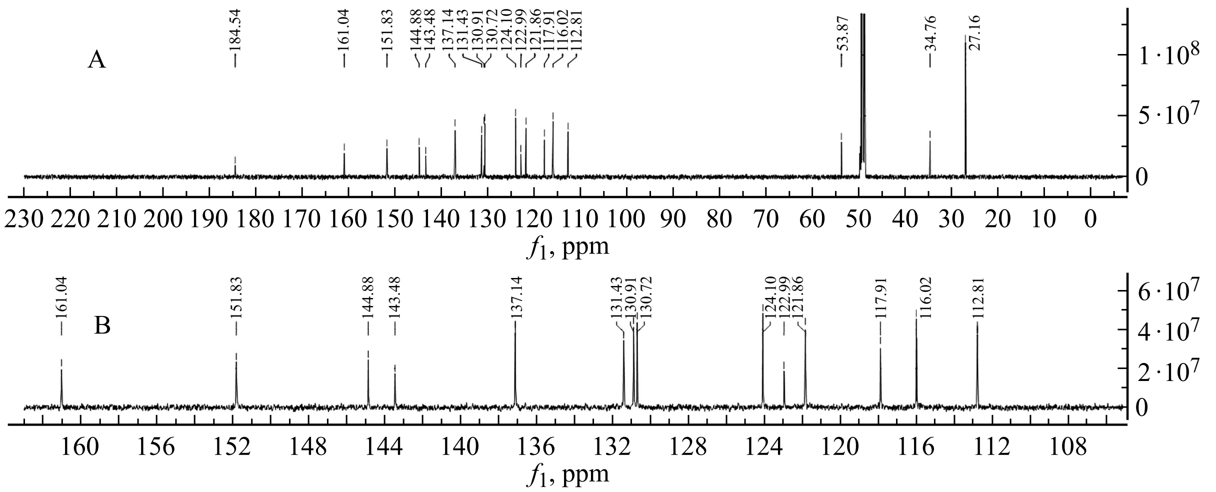


Figure 7. ^{13}C NMR spectrum of complex 2 (SP1), SP ($C = 6.0 \cdot 10^{-2}$ M) in CD_3OD: A — ^{13}C NMR-spectrum of the entire range of complex 2 after addition of $Al(NO_3)_3 \cdot 9H_2O$ (0.2 M) and holding of the sample solution in the dark for 24 h, B — fragment ^{13}C of the NMR spectrum, region of signals of carbon nuclei of aromatic rings (indoline and benzopyran).

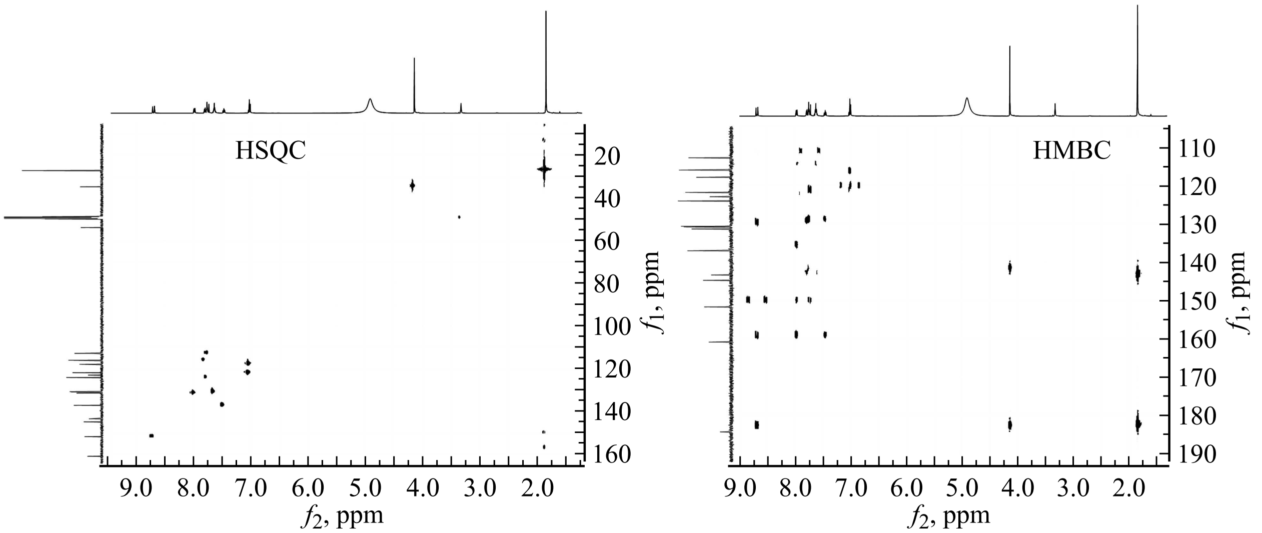


Figure 8. Fragments of 2D NMR spectra of complex 2 (SP1) in CD_3OD: (left panel) $^1H-^{13}C$-HSQC and (right panel) $^1H-^{13}C$-HMBC.

First, a detailed analysis and assignment of the signals of proton nuclei and carbon of the cyclic form molecule SP1 were carried out (Fig. 4, Scheme 3A). The presence of 2 fragments of 1,2-substituted benzene in the cyclic form of the SP1 molecule with similar magnetic properties of atoms made measurements very difficult even with a modern device with operating frequency of 500 MHz for protons, so the spectra were first measured in two different solvents ($CDCl_3$ and CD_3OD) and additionally 2D NMR spectroscopy was used with pulse sequences: $^1H-^1H$-Correlation Spectroscopy (COSY) and $^1H-^{13}C$-HSQC. The chemical shifts of the ^1H nuclei signals for the SP1 cyclic form were close to those obtained in deuteroacetone [23] and in deuterochloroform [12].

As a result, a complete assignment of signals for both protons and carbon nuclei of the SP1 cyclic form molecule and the complex 2 (SP1 with $Al(NO_3)_3$) was made using the set combinations of 1D and 2D NMR pulse sequences DEPT, $^1H-^1H$ COSY, $^1H-^{13}C$ HSQC and $^1H-^{13}C$ HMBC (Figs 4–8).

The NMR spectra of SP1 change significantly with addition (0.25–10 eq.) of $Al(NO_3)_3 \cdot 9H_2O$. In case of the SP1 cyclic form and complex 1, the upfield initial signals of protons and carbons of two nonequivalent 3,3-methyl groups in the form of 2 singlets at δ 1.18 ppm/1.31 ppm (20.8/26.6 ppm) become equivalent due to the quasiplanar structure of the merocyanine form of the complex 2 and transform with a downfield shift into a single singlet (6H) at δ 1.87 ppm/(27.2 ppm). Similarly, the signal $N-CH_3$ in the SP1 cyclic form, in complex 1 at δ 2.74 ppm/(29.5 ppm) and in the MC form of complex 2 has downfield shift at

δ 4.16 ppm/(34.8 ppm) due to the presence of a positively charged N-atom.

In the SP1 cyclic form and in the complex 1, the signals of the AB nuclei in the C3–C4 position of the pyran ring in the form of 2 doublets at δ 5.77 ppm/6.96 ppm with J 10.2 Hz are also shifted downfield in the spectrum of complex 2 (δ 8.72 ppm/7.77 ppm, J 16.4 Hz), which makes it possible to unambiguously attribute the C=C bond configuration to merocyanine form of complex 2 as the *trans*-isomer (TTT) (Schemes 1, 2, 3 B, Figs 5–8).

Value δ of signal at 184.5 ppm of complex 2 (signal of quaternary protonated $C_{(2)}{=}N^{+}$-) in the ^{13}C NMR spectrum clearly indicates the absence of quinoid structures in the complex 2. Comparison of the features of the spectra of the SP1 cyclic form and complex 1 shows the appearance of two new signals — broadened singlets with integrated intensity over 1H at δ 7.38 ppm and 6.83 ppm with significant broadening of the shape of all signals in the aromatic range (5.7–7.2 ppm and 7.3–7.9 ppm), a decrease in J value from 10.2 to 9.5 Hz, which indicates the presence of coordination interactions between AlX_3 and aromatic fragments of the SP1 cyclic form with formation of labile π-complex. ^{1}H-NMR titration (Figs 5, 6) tested the formation of complex 2 in the dark for 24 h and confirmed its final composition of two molecules of the MC form and one aluminum salt molecules. Similar data were obtained by the Job method using spectrophotometric titration [13].

Conclusion

As a result of a systematic study of the complexation processes of 1',3',3'-trimethylspiro [*2H*-1-benzopyran-2,2′-indoline] molecules with aluminum cations by absorption, electron and NMR spectroscopy, the appearance of complexes of two types is found. One of them is an unstable intermediate π-complex of aluminum ions with cyclic form spiropyran molecules, and the second (thermodynamically stable) is the result of the interaction of two molecules of the merocyanine form of spiropyran with one aluminum cation. As a result of the study, the exact structure of the thermodynamically stable complex of photochromic spiropyran was established for the first time and the negative photochromism of this complex was discovered.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] *Organic Photochromic and Thermochromic Compounds* ed. by J.C. Crano, R.J. Gugliemetti, (Plenum Press, N.Y., London, 1999), vol. 1–2.

[2] *Photochromic Materials*, ed. by H. Tian, J. Zhang (Wiley-VCH Verlag, Weinheim, 2016).

[3] A.A. Ali, R. Kharbash, Y. Kim. Analytica Chimica Acta, **1110**, 199 (2020). DOI: 10.1016/j.aca.2020.01.057

[4] L. Kortekaas, W.R. Browne. Chem. Soc. Rev., **48** (12), 3406 (2019). DOI: 10.1039/c9cs00203k

[5] P.R. Sahoo, K. Prakash, S. Kumar. Coordination Chemistry Rev., **357** (1), 18 (2018). DOI: 10.1016/j.ccr.2017.11.010

[6] C. Coudret, A.V. Chernyshev, A.V. Metelitsa, J.C. Micheau. In: *Photon-Working Switches*, ed. by Y. Yokoyama, K. Nakatani (Springer, Japan, 2017), ch. 1, p. 3–36. DOI: 10.1007/978-4-431-56544-4

[7] K.V. Zvezdin, N.E. Belikov, A.V. Laptev, A.Yu. Lukin, O.V. Demina, P.P. Levin, S.B. Brichkin, M.G. Spirin, V.F. Razumov, V.I. Shvets, A.A. Khodonov. Rossiyskiye nanotekhnologii, **7** (5–6), 112 (2012) (in Russian). DOI: 10.1134/S1995078012030172

[8] V.A. Barachevsky. Review J. Chem., **3** (1), 52 (2013). DOI: 10.1134/S2079978012040012

[9] J. Ren, H. Tian. Sensors, **7** (12), 3166 (2007). DOI: 10.3390/s7123166

[10] T.J. Feuerstein, R. Muller, C. Barner-Kowollik, P.W. Roesky. Inorg. Chem., **58** (22), 15479 (2019). DOI: 10.1021/acs.inorgchem.9b02547

[11] V.K. Seiler, K. Robeyns, N. Tumanov, D. Cincic, J. Wouters, B. Champagne, T. Leyssens. CrystEngComm, **21**, 4925 (2019). DOI: 10.1039/c9ce00805e

[12] E.I. Balmond, B.K. Tautges, A.L. Faulkner, V.W. Or, B.M. Hodur, J.T. Shaw, A.Y. Louie. J. Org. Chem., **81** (19), 8744 (2016). DOI: 10.1021/acs.joc.6b01193

[13] P.P. Levin, N.E. Belikov, I.I. Levina, A.S. Tatikolov, A.A. Khodonov, I.V. Khudyakov. J. Phys. Org. Chem., **32**, e4012 (2019). DOI: 10.1002/poc.4012

[14] L. Kortekaas, J. Chen, D. Jacquemin, W.R. Browne. J. Phys. Chem. B., **122** (24), 6423 (2018). DOI: 10.1021/acs.jpcb.8b03528

[15] V.A. Murin, V.F. Mandzhikov, V.A. Barachevsky. Opt. i spektr., **40**, 1084 (1976) (in Russian).

[16] V.A. Murin, V.F. Mandzhikov, V.A. Barachevsky. Opt. i spektr., **42** (1), 89 (1977) (in Russian).

[17] A.K. Chibisov, H. Gorner. Phys. Chem. Chem. Phys., **3** (3), 424 (2001). DOI: 10.1039/b007713p

[18] H. Gorner. Phys. Chem. Chem. Phys., **3** (3), 416 (2001). DOI: 10.1039/b007708i

[19] S. Toppet, W. Quintens, G. Smets. Tetrahedron, **31** (16), 1957 (1975). DOI: 10.1016/0040-4020(75)87058-X

[20] J. Hobley, V. Malatesta, R. Millini, L. Montanari, W.O. Parker. Phys. Chem. Chem. Phys., **1** (14) 3259 (1999). DOI: 10.1039/A902379H

[21] J. Hobley, V. Malatesta. Phys. Chem. Chem. Phys., **2** (1), 57 (2000). DOI: 10.1039/A908360J

[22] C.L. Fleming, S. Li, M. Grotli, J. Andréasson. J. Am. Chem. Soc., **140** (43), 14069 (2018). DOI: 10.1021/jacs.8b09523

[23] S.-R. Keum, K.-B. Lee, P.M. Kazmaier, R.A. Manderville, E. Buncel. Magnetic Resonance in Chemistry, **30** (11), 1128 (1992). DOI: 10.1002/mrc.1260301119

[24] P.P. Levin, A.S. Tatikolov, A.V. Laptev, A.Y. Lukin, N.E. Belikov, O.V. Demina, A.A. Khodonov, V.I. Shvets, S.D. Varfolomeev. J. Photochem Photobiol. A, **231**, 41 (2012). DOI: 10.1016/j.jphotochem.2011.12.024