Research Article

Theoretical and Experimental Study of New Photochromic Bis-Spiropyrans with Hydroxyethyl and Carboxyethyl Substituents

E. L. Mukhanov, 1 I. V. Dorogan, 1 A. V. Chernyshev, 1 S. O. Bezuglyi, 2 I. V. Ozhogin, 1 M. B. Lukyanova, 1 and B. S. Lukyanov 1

1 Research Scientific Institute of Physical & Organic Chemistry, Southern Federal University, Stachky Avenue 194/2, Rostov-on-Don 344090, Russia
2 Southern Science Center, Russian Academy of Sciences, Chekhova Street 41, Rostov-on-Don 344006, Russia

Correspondence should be addressed to E. L. Mukhanov; jmukhanov@gmail.com

Received 31 May 2013; Accepted 25 July 2013

1. Introduction

Spiropyrans are one of the most studied and perspective photochromic organic compounds [1, 2]. Their photochromic properties are based on the photo-initiated scission of carbon-oxygen bond and consecutive isomerization yielding the open (or “merocyanine”) form (Figure 1) characterized by significant bathochromic shift of the longwave maximum in electronic absorption spectra.

Compounds of this type are usable for obtaining of new smart materials with controlled characteristics that are perspective for application in many areas [3–6]. Bis-spiropyrans contain two photochromic spiropyran units in the molecule and achievable opening of two pyran cycles allow one to suggest such compounds as prototypes for the multistate light-driven molecular switches [7] that can be controllably and reversibly switched between three or more well-distinguished states.

It should be pointed out that studies in this area of research are aimed mostly on the 1,3,3-trimethylindoline-based structures [2, 8] due to well-known synthetic and purification techniques for such compounds. One can obviously understand that such approach significantly narrows the range of possibly achievable characteristics of spiro-compounds. For instance, there were not any examples of observed and well-proved scission of two carbon-oxygen bond in a single bis-spiropyran molecule until quite recently, when we had shown that nonsymmetric bis-spiropyran Figure 2 (1) containing not only indoline but also benzoxazine moiety could undergo opening of two pyran cycles [9].

Open merocyanine isomers are usually characterized by low thermodynamic stability and consecutive low lifetimes due to possibility to undergo the ring closure back-reaction without additional photo activation [2, 8]. This phenomenon is a well-known disadvantage of spiropyran-like compounds, and various approaches are discussed to stabilize an open chain-like isomers and to reduce influence of reverse bleaching-cyclization reaction.

New bis-photochromic structures with two nonequivalent spirocyclic centers and theoretically grounded improved stability of the merocyanine isomers have been studied in our research group and the results are presented in this paper.
2. Materials and Methods

2.1. Methods of Photochemical Investigations. Electronic absorption spectra and kinetic curves of the investigated compounds were recorded on an “Agilent 8453” spectrophotometer equipped with the thermostatic cell. The irradiation of solutions with filtered light of a high pressure Hg lamp was performed on “Newport 66902” equipment. To isolate monochromatic irradiation, interferential light filters (λ = 365, 546, 578 nm) were used. The photon flux power was measured on “Newport Power Meter 2903-C.”

2.2. Computational Methods. Molecular structures were optimized within the framework of density functional theory [10–12] using PBE0 [13, 14] hybrid functional and 6-31G** basis set. Solvent effects have been taken into account by conductor-like polarizable continuum model (CPCM) [15]. Frequency analyses were carried out to confirm the nature of the stationary points (minima).

The vertical excitation energies have been calculated with the TDDFT [16] methodology at the same level of approximation. Systematic overestimations of the excitation energies of merocyanine isomers were corrected by the application of a linear scaling approach [17] as follows: \( E_{\text{corr}} = -0.0963 + 0.9321E_{\text{exc}} \). All the calculations were performed with use of GAUSSIAN 03 program package [18].

2.3. Methods of Synthesis. 3-Methyl-4-oxo-3,4-dihydro-2H-1,3-benzoxazine-2-spiro-2′H,8′H-pyrano-[2,3-f] chromene-8′-spiro-2′''-1''''-(3′′,3′′'-dimethylindoline (2a), 3-methyl-4-oxo-3,4-dihydro-2H-1,3-benzoxazine-2-spiro-2′H, 8′H-pyrano-[2,3-f]chromene-8′'-spiro-2′''-1''''-(2-carboxy-ethyl)-3′′,3′′'-dimethylindoline (2b) and 3-methyl-4-oxo-3,4- dihydro-2H-1,3-benzoxazine-2-spiro-2′H,8′H-pyrano-[2,3-f] chromene-8′'-spiro-2''''-1'''''''-3'''''''-3'''''''-trimethylindoline (2c) have been synthesized.

Original 8′-formyl-7′-hydroxy-3-methylspiro(2,3-dihydrobenzo[1,3]oxazine-4-oxo-2,2'-[2H]chromene) was prepared by a previously reported method [19] from N-methyl-salicylamide and 2,4-dihydroxyisophthalic aldehyde.

Piperidine (0.1 mL, 1.1 mmol) was added dropwise with heating to a solution of the 8′-formyl-7′-hydroxy-3-methylspiro(2,3-dihydrobenzo[1,3]oxazine-4-oxo-2,2'-[2H]chromene) (1 mmol) and corresponding 2,3,3-trimethyl-1-R-indolenilium perchlorate (1 mmol) in 2-propanol (5 mL). The reaction mixture was refluxed for 10 min and cooled. The precipitate was filtered off and recrystallized from hexane with obtaining of corresponding (2a), (2b), or (2c) compounds.

3. Results and Discussion

3.1. Theoretical Modelling. Open chain-like isomers of spiro-pyrans could be stabilized, and influence of reverse bleaching-cyclization reaction could be reduced by the effect of competitive parallel processes that block either the former spiro carbon atom or the phenoxide oxygen atom and hinder cyclization into original spiro form. To realize this approach, we have investigated bis-spiropyrans (2a, b) with hydroxyethyl and carboxyethyl substituents in the indoline fragment of the molecule as shown in Figure 3.

Presence of the hydroxyethyl substituent could improve stability of open merocyanine isomer by obtaining of the cyclic oxazolidine isomers [20, 21]. Carboxyethyl substituent in the hetarene part could enable chelation by metal ions and preferentially stabilize the merocyanine form [22, 23] from thermal decay.
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Figure 3

(a) R1 = -CH2-CH2-OH
(b) R1 = -CH2-CH2-COOH

On the first stage thermodynamic properties of isomers with one opened ring (hereafter ≪1-OR-isomers≫) and two opened rings (hereafter ≪2-OR-isomers≫) have been investigated by quantum-chemistry methods. It is considered that most thermodynamically stable merocyanine form for a wide variety of spiropyran is the TTC (trans-trans-cis) isomer [24, 25]. So the open forms of bis-spiropyran (2) as shown in Figure 4 were studied: TTC-TTC (with two opened pyran cycles) and TTC-SP (with the open and closed pyran cycles at the indole and oxazine moieties, resp.).

Optimized molecular structures are presented in Figures 4–6, while their energetic characteristics are summarized in Tables 1 and 2.

Formation of oxazolidine cycle leads to stabilization of (2a)TTC-SP isomer by 3.4 kcal/mol, but by the meantime for 2-OR-isomer (2a)TTC-TTC, it could result in destabilization of 7.3 kcal/mol. This observations could be explained by decreasing of electron density delocalization in the course of oxazolidine cycle formation for (2a)TTC-TTC-ox. On the other hand, stabilization of (2a)TTC-SP-ox could take place due to weakening of steric hindrance between two methyl groups of indoline fragment and spiro-conjugative benzoazainone part.

Stabilization of merocyanine forms also could be achieved by formation of merocyanine-metal complexes. For this purpose structures of the closed and open isomers of (2b) have been calculated (Table 2, Figure 5).

According to the computational data merocyanine isomers of (2b) are able to form complexes with cation Zn$^{2+}$ coordinated by oxygen atom of carboxyl group, phenoexine oxygen of benzopyran moiety, and by the carbon atom of the methine bridge (Figure 6). Theoretical modeling has shown that complex (2b)TTC-TTC-Zn$^{2+}$ is energetically more favorable than (2b)TTC-SP-Zn$^{2+}$ by 7.8 kcal/mol.

On the basis of theoretical computations one can make a conclusion that both complex formation and intramolecular oxazolidine cycle formation are perspective ways for the stabilization of open merocyanine isomers.

3.2. Synthesis of the Compounds (2a–c). On the second stage bis-spiropyran (2a, b) and model compound (2c) have been synthesized as shown in Figure 7.

### Table 1: Full energies including zero point energy correction $E_{\text{tot}}$ + ZPE (a.u.) and relative energies $\Delta E$ (kcal/mol) of isomers (2a) and their oxazolidine forms calculated at the CPCM/PBE0/6-31G** level of theory (toluene solutions).

<table>
<thead>
<tr>
<th>Structure</th>
<th>$E_{\text{tot}}$ + ZPE, (a.u.)</th>
<th>$\Delta E$, (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2a)TTC-SP</td>
<td>-1681.720661</td>
<td>0</td>
</tr>
<tr>
<td>(2a)TTC-SP-ox</td>
<td>-1681.712120</td>
<td>5.4</td>
</tr>
<tr>
<td>(2a)TTC-TTC</td>
<td>-1681.723617</td>
<td>1.9</td>
</tr>
<tr>
<td>(2a)TTC-TTC-ox</td>
<td>-1681.726102</td>
<td>3.4</td>
</tr>
</tbody>
</table>

### Table 2: Full energies including zero point energy correction $E_{\text{tot}}$ + ZPE (a.u.) and relative energies $\Delta E$ (kcal/mol) of bis-spiropyran (2b) and its open isomers calculated at the CPCM/PBE0/6-31G** level of theory (acetonitrile solutions).

<table>
<thead>
<tr>
<th>Structure</th>
<th>$E_{\text{tot}}$, (a.u.)</th>
<th>$\Delta E$, (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2b)TTC-SP</td>
<td>-1794.994270</td>
<td>0</td>
</tr>
<tr>
<td>(2b)TTC-SP-ox</td>
<td>-1794.985809</td>
<td>5.3</td>
</tr>
<tr>
<td>(2b)TTC-TTC</td>
<td>-1794.988572</td>
<td>3.6</td>
</tr>
</tbody>
</table>

3.3. Investigation of Photochromic Behavior. Photochemical investigations of compounds (2a–c) have been carried out (Table 3).

Solutions of compounds (2a–c) are colorless that confirms presence of only spirocyclic isomer under basic conditions. Bis-spiropyran (2a–c) are characterized by shortwave absorption maxima at 250 nm and 340 nm, while longwave absorption is not observed in the basic conditions.

Monochromatic irradiation with $\lambda = 365, 546$, or 578 nm did not lead to any significant change in the absorbance spectrum. Three maxima were observed in the long-wavelength region of the absorption spectra of (2a) at 415, 507, and 603 nm while irradiating with unfiltered light (Figure 8).

The thermal bleaching reaction of the photoinduced forms (2a) (Figure 9) leads to the disappearance of two absorption bands from the spectrum, at $\lambda_{\text{max}} = 415$ and 603 nm, while the 507 nm peak is retained. However, irradiation with light at a wavelength of $\lambda_{\text{max}} = 436$ nm resulted in the disappearance of the absorption band at 507 nm.

Such photochromic behavior fully coincides with previous results obtained for iso-structural bis-spiropyran (I) [9]; hence one can expect analogous nature of the absorption bands. This assumption was proved by the quantum-chemical calculations of vertical excitation energies for 2-OR and 1-OR-isomers of (2a).

According to the theoretical modeling results (Table 4) the observed absorption at 507 nm (2.446 eV) most likely corresponds to the $S_0\rightarrow S_1$ and $S_0\rightarrow S_2$ transitions for the fully open 2-OR-isomer (TTC-TTC) (2.539 eV, 2.578 eV). Meanwhile, $S_0\rightarrow S_2$ transition for 1-OR-isomer (TTC-SP) revealed in the same spectral area is characterized by far too low oscillator strength. On the other hand, absorbance maxima at 603 nm (2.056 eV) and 415 nm (2.988 eV) must correspond...
to $S_0-S_1$ and $S_0-S_3$ transitions (2.077 eV, 2.871 eV) in 1-OR-isomers (TTC-SP), while 2-OR-isomer (TTC-TTC) has not any absorbance at the discussed areas.

Analysis of the experimental data (Table 3) allowed one to underline that 2-hydroxyethyl substituent in the hetarene part of the bis-spiropyran structure makes photoinduced 1-OR isomers 4 times more stable, although it does not verify the obtaining of cyclic oxazolidine form.

Irradiation of colorless acetonitrile solution of spiropyran (2b) with $\lambda_{\text{max}} = 365$ nm induces photochemical isomerization (Figure 10). Diffusive absorbance maximum is located at 596 nm, while additional increasing in absorbance is observed in the area of 400 nm.

Kinetic curve of the thermal bleaching reaction registered at 588 nm corresponds to the biexponential equation (Figure 11).

This could be evidence of two parallel processes—the fast one with characteristic time 46 s and the slow one with characteristic time 349 s. It is proposed that these processes correspond to the recycilation of two different merocyanine isomers into the spirocyclic form.

Investigations of interaction with metal ions have been carried out. Addition of quantitative amounts of metal ions Cu$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, and Co$^{2+}$ to the colorless solution of bis-spiropyran (2b) leads to accumulation of the colored products (Figure 12) that most likely are complexes of bis-spiropyran-metal type.

It was observed that most intensive absorption band was located at 413 nm, while less intensive absorption band is located in the area of 500–600 nm depending on the cation type. UV-light irradiation of the bis-spiropyran solution in the presence of metal ions regardless of irradiation wavelength leads to the decreasing of intensity of the longwave absorption band due to the photo dissociation of complex bis-spiropyran metal.

4. Conclusions

It has been shown that introduction of hydroxyethyl as well as carboxyethyl substituents in the hetarene part of the bis-spiropyrans is perspective to fulfill necessary requirements of a molecular switch on the basis of a bis-spiropyran, that
Figure 5: Structural properties of (2b) and its merocyanine isomers (2b)TTC-SP and (2b)TTC-TTC calculated at the CPCM/PBE0/6-311G** level of theory (acetonitrile solutions).

Figure 6: Structural properties of complex compounds (2b)TTC-SP-Zn²⁺ and (2b)TTC-TTC-Zn²⁺ calculated at the CPCM/PBE0/6-311G** level of theory (acetonitrile solutions).
is, to achieve number of thermodynamically stable states or multistability, with facile interconversion between the states.

Compound (2a) with hydroxyethyl substituent is characterized by 4 times larger value of the lifetime for photoinduced 10R-isomers in comparison with model bis-spiropyran (2c).

Photochemical research of complex formation had revealed the possibility of fully reversible stabilization of merocyanine form for the compound (2b).

Thus theoretical and experimental study of the nonsymmetrical bis-spiropyrans exposes effective routes for improving spectral and photodynamic parameters of spiropyans by modifying its structures.

**Conflict of Interests**
Authors have not any possible conflict of interests with any trademark mentioned in this paper. Authors or the author’s institutions have not any financial or personal relationships that inappropriately influence the research.
Table 3: Spectral and kinetic properties of the bis-spiropyans (2a–c) ($\lambda_{\text{max}}^A$, $\varepsilon(\lambda_{\text{max}}^A)$ are parameters of the absorption spectra before irradiation (i.e., characteristics of the spirocyclic isomers); $\lambda_{\text{max}}^B$ is positions of the longwave maxima generated under irradiation; $\tau_{20}^B$ is lifetime of the photoinduced forms).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}^A$, nm</th>
<th>$\varepsilon(\lambda_{\text{max}}^A)$, M$^{-1}$ cm$^{-1}$</th>
<th>$\lambda_{\text{max}}^B$, nm</th>
<th>$\tau_{20}^B$, s</th>
<th>$\lambda_{\text{max}}^R$, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2a)</td>
<td>248</td>
<td>33180</td>
<td>Sh 274</td>
<td>23180</td>
<td>603</td>
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<tr>
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<td>Sh 290</td>
<td>18970</td>
<td>Sh 325</td>
<td>2840</td>
<td>Sh 340</td>
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<tr>
<td>(2b)</td>
<td>331</td>
<td>3370</td>
<td>596</td>
<td>349</td>
<td></td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>2920</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2c)</td>
<td>Sh 326</td>
<td>3270</td>
<td>Sh 3270</td>
<td>613</td>
<td>412</td>
</tr>
<tr>
<td></td>
<td>Sh 341</td>
<td>2310</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 10: UV absorption spectrum of a bis-spiropyran (2b) in acetonitrile solution before and after continuous irradiation with $\lambda_{\text{max}} = 365$ nm ($[c] = 1.86 \cdot 10^{-4}$ M; $T = 293$ K; curves are recorded with 15 s interval).

Figure 11: Kinetic curve ($\lambda_{\text{abs}} = 588$ nm) of the thermal bleaching reaction for (2b) ($[c] = 1.86 \cdot 10^{-4}$ M; $T = 293$ K) in toluene solution.

Acknowledgments

The work was carried out with financial support from Grant of the President of the Russian Federation MK-1629.2012.3 as well as from Russian Foundation for Basic Research (RFBR) Grant 12-03-31455mol_a. Calculated geometries of the compounds (2a, b), NMR $^1$H, and IR-spectroscopic data for
Table 4: Excitation energy $E_{\text{ex}}$ (eV), corrected [17] excitation energy $E_{\text{corr}}$ (eV) and oscillator strength $f$ of the first three singlet transitions of the merocyanine (2a)TTC-SP and (2a)TTC-TTC according to the TD DFT CPCM/PBE0/6-31G** calculation in toluene solution.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Transition</th>
<th>$E_{\text{ex}}$ (eV)</th>
<th>$E_{\text{corr}}$ (eV)</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2a)TTC-SP</td>
<td>$S_0$-$S_1$</td>
<td>2.332</td>
<td>2.077</td>
<td>0.5305</td>
</tr>
<tr>
<td></td>
<td>$S_0$-$S_2$</td>
<td>2.821</td>
<td>2.533</td>
<td>0.0021</td>
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<tr>
<td></td>
<td>$S_0$-$S_3$</td>
<td>3.184</td>
<td>2.871</td>
<td>0.6352</td>
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<tr>
<td>(2a)TTC-TTC</td>
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<td>2.828</td>
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<tr>
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<td>2.869</td>
<td>2.578</td>
<td>1.1975</td>
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<td></td>
<td>$S_0$-$S_3$</td>
<td>2.990</td>
<td>2.691</td>
<td>0.1199</td>
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compounds (2a–c) are presented in Supplementary Material available online at http://dx.doi.org/10.1155/2013/752949.

References


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