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New spiropyrans based on 1,3-benzoxazine-2-one: acid catalyzed synthesis and theoretical insight into the photochromic activity

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ABSTRACT

A new series of spiropyrans based on 1,3-benzoxazine-2-one were synthesized using acid catalysis. Contrary to expectations, 6′-bromo-6-chloro-3-methyl-8′-nitro-spiro[1,3-benzoxazine-4,2′-chromene]-2-one and 6,6′-dichloro-3-methyl-8′-nitro-spiro[1,3-benzoxazine-4,2′-chromene]-2-one did not exhibit photochromic behavior, which was explained by TD DFT calculations to be a consequence of the existence of an effective non-radiative decay pathway allowing the structural relaxation of the spiropyrans in the first singlet excited state.

Introduction

Spiropyrans (**1**) represent one of the most intensively studied classes of organic photochromic compounds.[1–4] At ambient conditions these compounds are usually more stable in the non-colored ring-closed form **1a**, but under the action of external stimuli (light, heat, mechanical stress, pH) they can undergo transformation into the deeply colored open merocyanine form (**1b**, Scheme 1).

As easy tunable molecular switches, spiropyrans have found diverse applications in the areas of chemosensors,[5–8] molecular electronics,[9–13] non-linear optics,[14–16] bio-imaging,[17–19] control of cellular processes,[20–22] photocontrolled drug delivery,[23–25] and the development of dynamic smart materials.[26]

Most of the current research of spiropyrans is focused on indoline derivatives (**2**, Scheme 2) due to the ready availability of starting reagents and fairly simple and well developed methods of synthesis.[27,28] Much less studied are spiropyrans with other heteroarene fragments, even though the local atomic environment of the spirocyclic carbon has a direct impact on the photochemical parameters of photochromic compounds, such as the quantum yield of photoisomerization, position of the absorption maxima, lifetime of the open form and resistance to photodegradation.[2–4] Therefore, the search for new spiropyrans with different heteroarene parts presents a promising direction of research in the chemistry of organic photochromes.

This work is aimed at the synthesis and investigation of spiropyrans of the 1,3-benzoxazine-2-one series **3**, which differ from the previously studied spirocompounds of the 1,3-benzoxazine-4-one series **4**[29] by the relative position of the carbonyl group and the spirocyclic carbon atom. We envisaged that comprehensive study of the effect of structural modifications on the photochemical activity of spiropyrans would facilitate a deeper insight into their photochromic properties and guide the rational design of compounds with predetermined properties.

Results and discussion

To obtain the required 4-methylene-1,3-benzoxazin-2-one, a two-step procedure of a previously reported one-pot synthesis was chosen involving the condensation of an *o*-hydroxyacetophenone with alkylamines and cyclization of the resulting Schiff base using triphosgene.[30,31] The method was modified by the utilization of chloroform as a solvent and bubbling methylamine through the warm solution of 5-chloro-2-hydroxyacetophenone **5**. This allowed use of the intermediate Schiff base **6** without isolation and purification. The new methylene base, 6-chloro-3-methyl-4-methylene-1,3-benzoxazine-2-one **7**, was synthesized in 84% yield and the structure proven by NMR, IR, and mass spectroscopy (ESI).

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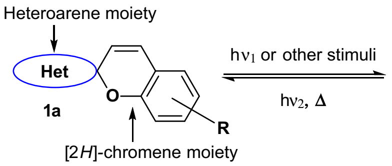


Scheme 1. Reversible isomerization of spiropyrans.

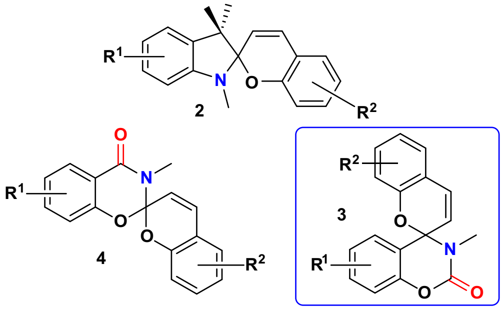
The basic procedure for the synthesis of spiropyrans consisting of heating the methylene base with the corresponding aldehyde in polar protic or aprotic solvents (MeOH, EtOH, *i*-PrOH, $CHCl_3$, MeCN, THF) was unsuccessful because of the poor solubility of the base or its low reactivity in these solvents. A positive result was reached by carrying out the reactions under acid catalysis. Heating methylene base **7** and salicylaldehydes **8** in glacial acetic acid at reflux in the presence of catalytic acid (Scheme 3) allowed us to obtain spiropyrans of a new series **3a,b** with medium yields and short reaction times. The catalyst in this case was *in situ* generated protonated acetic acid $[MeC(OH)_2]^+ClO_4^-$.[32,33]

It is worth noting that spiropyrans **3** can only be obtained by the reaction shown in Scheme 3 using aldehydes **8** bearing at least two electron withdrawing substituents. Attempts to obtain the targeted products using salicylaldehydes either with one or without acceptor group failed. Therefore, both spiropyrans **3a,b** contain acceptor substituents in the 6′ and 8′ positions of the [2*H*]-chromene moiety. The structures of compounds **3a,b** were determined using NMR (^1H, ^{13}C, ^1H–^1H COSY, ^1H–^1H NOESY, HMQS ^1H–^{13}C), IR, MS, and elemental analysis.[34] The molecular structure of compound **3a** was additionally clarified by single crystal X-ray diffraction (Fig. 1).[35]

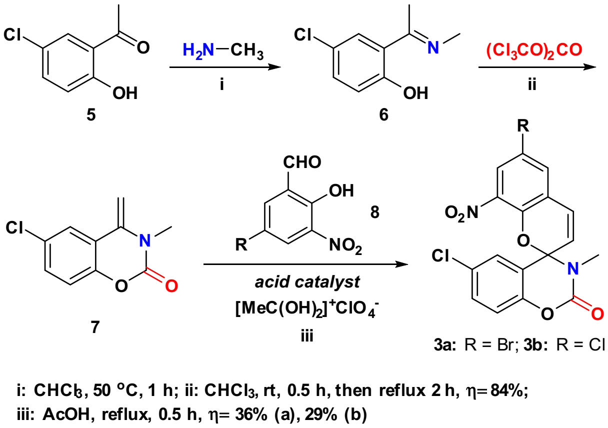
The study of the photochromic properties of spiropyrans **3a**,**b** was carried out by irradiation of their solutions in different solvents (toluene, acetonitrile, acetone) by UV light in the steady state mode and under nanosecond flash photolysis conditions. In all cases no changes in the absorption spectra of spiropyrans were initiated, thus indicating that irradiation of compounds **3** with UV light does not result in the formation of their colored merocyanine forms.

We were puzzled by the obtained results because many structurally related spiropyrans **4** based on 1,3-benzoxazine-4-one exhibit photochromic properties both in solutions and the solid state.[29,36,37]

The main reason for the lack of photochromic properties of compounds **3a,b** may be the existence of effective deactivation pathways of the excited states of spiropyrans at the initial stages of the photoinitiated ring opening reaction. To gain insight into the observed phenomenon we performed a comparative theoretical study of compounds **4** and **3a** by means of TD DFT methods.



Scheme 2. Representative classes of spiropyrans: known indoline **2**, 1,3-benzoxazin-4-one **4** and new 1,3-benzoxazin-2-one **3**.



Scheme 3. Acid catalyzed synthesis of novel spiropyrans based on 1,3-benzoxazin-2-one.

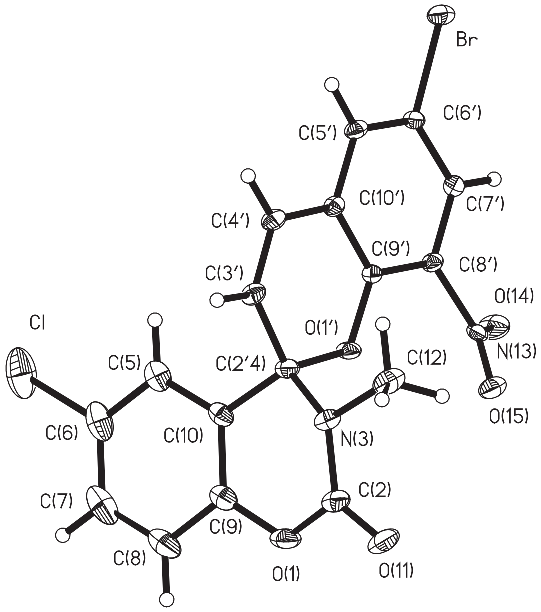


Figure 1. Molecular structure of spiropyran **3a** according to single crystal X-ray analysis data.

Table 1
Excitation energy E_{ext} (eV), oscillator strength *f* and main composition (H = HOMO, L = LUMO) of the first three singlet transitions of compounds **3a**, **4** according to the TD PCM-PBE0/6-311+G(d,p) calculation in toluene solution.

Compound	Transition	Main composition	E_{ext}	*f*
3a	S_0–S_1	H–L	3.4941	0.0844
	S_0–S_2	H–2–L H–5–L H–7–L	3.9212	0.0223
	S_0–S_3	H–1–L	3.9564	0.0004
4	S_0–S_1	H–3–L	3.6464	0.0012
	S_0–S_2	H–L	3.8626	0.1303
	S_0–S_3	H–1–L	4.3742	0.0218

According to the calculations (Table 1, Fig. 2) the longest wavelength absorption maximum of **3a** corresponds to the S_0-S_1 transition with main (HOMO – LUMO) contribution. It can be characterized as a predominately π–π* transition localized within the chromene moiety with a pronounced intramolecular charge transfer toward the nitro group in the 8′ position. Thus, upon