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X-ray, kinetics and DFT studies of photochromic substituted benzothiazolinic spiropyrans

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ABSTRACT

Photochromic molecules have the potential to find utility in a wide variety of applications including photoswitchable binding and optical memory. This work explores the relationship between photochromism and structural parameters such as particular bond lengths for this class of compounds for which very few crystal structures have been published. Photochemical kinetics. Density Functional Theory (DFT) and X-ray crystallography were used to study the benzothiazolinic spiropyran 3-methyl-6-nitro-3'-methylspiro-[2H-l-benzopyran-2,2'-benzothiazoline]. A second benzothiazolinic spiropyran 3methyl-8-methoxy-6-nitro-3'-methylspiro-[2H-l-benzopyran-2,2'-benzothiazoline] was synthesized and subjected to photochemical and computational studies. Selected structural and photochemical data for these, related benzothiazolinic spirooxazines and spiropyrans, and related thiazolidinic spiropyrans are compared. Both benzothiazolinic spiropyrans exhibit photochromic properties that are influenced by substituents, solvent, and temperature. The crystallographic C_{spiro}-O bond distance of 3-methyl-6nitro-3'-methylspiro-[2H-l-benzopyran-2,2'-benzothiazoline] that has been shown to correlate with photochromic properties is 1.458 Å. The crystallographic C_{spiro}–O bond distance matches that of the structure generated by DFT calculations exactly. The effect of substituents on calculated bond lengths and photochemical parameters was determined. For this class of compounds, both X-ray geometry and DFT optimized geometry may be used to predict photochromism, but not degree of photocolorability.

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1. Introduction

Photochromic spiropyrans have attracted considerable attention recently owing to their diverse applications, such as in optical memory devices, light filters, drug delivery systems, and biological calcium signal mimics [1-6]. These spiropyrans isomerize reversibly between two structures (closed, colorless and open, colored) in response to light as shown in Fig. 1 for 3-methyl-6-nitro-3'-methylspiro-[2H-l-benzopyran-2,2'-benzothiazoline] (1). In many cases, thermal (dark) processes compete with the photochemical conversion of the less stable to the more stable form. Photochromism of spiropyran compounds has been reviewed extensively by Bertelson [7,8]. The C_{spiro}-O bond length and substituents have been correlated with photochromic properties of spiropyrans and spirooxazines [9-13]. Specifically, for spiropyrans and spirooxazines, such as those shown in Fig. 2, the C_{spiro}-O bond lengths are elongated by 0.03–0.06 Å from the normal C_{sp3}–O bond length in 6-membered heterocycles of 1.41–1.43 Å. The corresponding C_{spiro}–N₁ bond lengths are found to be shorter than those found in 5-membered heterocycles of 1.47–1.48 Å. For spirooxazines, better photocolorability correlates with longer C_{spiro} –O bond lengths. These correlations are thought to reflect the degree of interaction between the lone pair on one heteroatom bound to the spiro carbon with the σ^* antibonding orbital of the polar C_{spiro} –O bond that breaks during photochemical ring opening [12].

Our interest in this subject derives from the fact that suitably functionalized spiropyran compounds have potential for application in mimicking calcium oscillations in biological systems [14,15]. While spirobisbenzopyran compounds do not have appropriate photophysical properties at room temperature, benzothiazolinic spiropyran compounds offer a significant improvement. In order to understand the photochromic properties of benzothiazolinic spiropyrans, we have studied some photochemical properties and determined the crystal structure of compound 1. The related compound 2 was also synthesized and characterized. The synthesis of **1** and **2** were first reported by Guglielmetti et al. [16,17]. However, no crystal structure was reported. In fact, no crystal structure for a closed form of a benzothiazolinic spiropyran has been reported in the literature. The structure of the open merocyanine form of a benzothiazolinic spiropyran was reported by Miler-Srenger and Guglielmetti [18]. In this work, the crystal structure of





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Fig. 1. Photochromism of the benzothiazolinic spiropyran 1; the colorless closed form 1 is interconverted with the colored open form.



Fig. 2. Representative spiropyran compounds with correlations between photochromism and C_{spiro}–O bond length. Left: spiroindolinopyran; Right: spirooxazine.

1 (Fig. 5) is compared with the equilibrium geometry obtained using density functional calculations shown in Fig. S4 (B3LYP/6-31G*) as well as certain structural reported and calculated features of related photochromic and nonphotochromic spiropyran scaffolds shown below (Fig. 3).

2. Experimental and computational

The compounds **2**, **7** and **8** were synthesized according to the procedure reported in Guglielmetti et al. [19]. The procedure was adapted to synthesize compound **1** as described below and in Scheme 1.

Compound **1** (60% yield). A mixture of **8** (0.28 g, 0.80 mmol) and of 5-nitrosalicylaldehyde (0.14 g, 0.83 mmol) were added to a

50 mL round bottom flask. The reaction flask was evacuated and filled with N₂ (gas). Ethanol (15 mL) and piperidine (0.1 mL) were added to the reaction flask. The reaction mixture was refluxed for 1 h. The solvent was evaporated and impure product was purified using flash column chromatography (10% Ethyl acetate in hexane) to give **1** (0.12 g, 60%) as a pure product. ¹H NMR (CDCl₃, 400 MHz, δ): 8.05 (dd, *J* = 8.88 Hz, 1H), 7.98 (d, *J* = 2.24 Hz, 1H), 7.20–7.14 (m, 2H), 6.91–6.84 (m, 2H), 6.84–6.64 (m, 2H), 3.04 (s, 3H), 2.10 (s, 3H); ¹³C NMR (CDCl₃, 400 MHz, δ): 155.8, 144.6, 142.4, 131.6, 125.9, 125.6, 125.0, 122.1, 121.7, 121.6, 121.0, 120.5, 117.1, 114.8, 108.0, 30.5, 19.62. HRMS (*m/z*): Calcd.: 326.0725; found: 326.0725. Crystals suitable for single-crystal X-ray determinations were grown by keeping a solution of **1** in THF for several weeks in the dark.

Compound **2** (51% yield). ¹H NMR (CDCl₃, 400 MHz, δ): 7.68 (d, J = 3.2 Hz, 1H), 7.63 (d, J = 3.6 Hz, 1H), 7.154 (m, 2H), 6.86 (t, J = 10 Hz, 1H), 6.66 (d, J = 10 Hz, 1H), 6.59 (d, J = 1.60 Hz, 1H), 3.81 (s, 3H), 3.07 (s, 3H), 2.07 (d, J = 2.0 Hz, 3H); ¹³C NMR (CDCl₃, 400 MHz, δ): 148.7, 145.4, 144.7, 142.0, 131.7, 125.8, 122.2, 121.5, 121.0, 119.8, 114.9, 114.3, 107.8, 107.6, 56.5, 30.4, 19.4.

Photochemistry: A 30 mL solution of **1** $(3.68 \times 10^{-5} \text{ M})$ or **2** $(6.17 \times 10^{-5} \text{ M})$ was prepared in the appropriate solvent in a 3-neck flask containing a stir bar. The flask was cooled to -30 °C in a thermostatted cryobath. Light from a 200 W Mercury Xenon lamp, filtered by water and an Oriel #59800, 330 nm bandpass filter, was directed via a 3 foot fiber optic bundle into the top of a 3-neck flask while the solution was stirred. UV–Vis observations were made using a Hellma 10 mm immersion probe connected to a Varian Cary 50 spectrophotometer. Rates are reported as averages of three runs, except for **1** in isopropanol and acetonitrile, in which the reaction was performed once and the rate was averaged from five different wavelengths.

Computation: The program Spartan '04 was used. AM1 was used to generate the initial geometry for **1**. The compound **1** was then



Fig. 3. Structures of related spiropyrans (1, 2, 3, 4) and spirooxazines (5, 6).



Table 1First order rate constants of thermal bleaching at -30° .

Solvent	2-Propanol	CH ₃ CN	THF	Toluene
$k_{\rm T} \min^{-1} (1) \\ k_{\rm T} \min^{-1} (2)$	$\begin{array}{l} 5.28 \pm 0.29 \times 10^{-3} \\ \text{Negligible} \end{array}$	$\begin{array}{l} \textbf{6.00 \pm 0.81 \times 10^{-3}} \\ \textbf{Negligible} \end{array}$	$\begin{array}{c} 7.40 \pm 0.54 \times 10^{-3} \\ 1.11 \pm 0.19 \times 10^{-2} \end{array}$	Insoluble photoproduct $4.14 \pm 1.33 \times 10^{-2}$

subjected to geometry optimization (B3LYP/6-31G*), and the resulting geometry was used to determine single point energy. Cartesian coordinates and energies are listed in Table S6. For compound **2**, AM1 was used to generate conformers. These conformers were then subjected to geometry optimization (B3LYP/6-31G*), and the resulting geometries were used to determine single point energies. Cartesian coordinates and energies are listed in Tables S7–S9.

2.1. Crystal data

C ₁₇ H ₁₄ N ₂ O ₃ S	Monoclinic, $P2_1/n$
<i>M</i> _r 326.36	Z = 4
MoK $lpha$ radiation	T = 100 (2) K
a = 9.1899 (4) Å	$V = 1522.24(11) \text{ Å}^3$
<i>b</i> = 11.8526 (5) Å	$0.29\times0.28\times0.28~mm^3$
<i>c</i> = 13.9833 (6) Å	μ = 0.229 mm ⁻¹
$\beta = 91.9440 \ (10)^{\circ}$	Density = 1.424 Mg/m^3

2.2. Data collection

Bruker SMART 1000	25987 measured reflections
Absorption correction: none	6105 independent reflections
$T_{\rm max} = 0.9386$	$I > 2\sigma(I)$, 4660 reflections
$T_{\min} = 0.9365$	$R_{\rm int} = 0.0777$

2.3. Refinement

$R1 (w = 1/\sigma^2(Fo^2)) = 0.0443$	S = 1.689
$wR^2 = 0.0872$	$\Delta \rho_{\rm max}$ = 0.621 e Å ⁻³
Parameters 264	$\Delta ho_{ m min}$ = -0.356 e Å ^{-3}
Restraint 0	H atom unrestrained

Data collection: Bruker *SMART* v5.630; cell refinement: Bruker *SAINT* v6.45A; data reduction: Bruker *SAINT* v6.45A; program(s) used to solve structure: *SHELXS97* [20]; program(s) used to refine structure: *SHELXL97* [21]; molecular graphics: Bruker *XP* v5.1; Ortep3 [22]; Mercury [23]; software used to prepare material for publication: Bruker XCIF v6.12.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 632419.

3. Results and discussion

3.1. Synthesis and characterization of 1 and 2

As detailed in the experimental section, the known targets **1** and **2** were prepared from a quaternized ethylbenzothiazole. Addition of piperidine generated the enamine base, which was condensed with the appropriately substituted salicylaldehyde to make the spiropyran. The reported ¹H spectrum (for **2**) and ¹³C spectra (for **1** and **2**) are consistent with those determined in this work [24].

3.2. Photochemical studies

At several temperatures, solutions of 1 and 2 in a variety of solvents were irradiated with UV light, and subsequently were allowed to return to their original colorless form in the dark. Compound 1 was found to exhibit weak photochromism at room temperature only in polar solvents (isopropanol, but not in toluene or THF). Photochromism in 1 was observed in several solvents (THF, acetonitrile, isopropanol) tested at lower temperatures to slow thermal closure rates (Table 1). Closure rates had been reported earlier only for photoirradiation in toluene at 25 °C. After irradiation at low temperature, the solution is colored, as shown in Fig. 4, and then thermally bleaches to a colorless solution over time. Thermal fading rates are slower in more polar solvents, due to solvent stabilization of the polar zwitterionic open forms. The addition of an electron-donating group (2) has the effect of increasing the rate of thermal closure, as the nucleophilicity of the phenolic oxygen is enhanced, or as the stability of the zwitterionic form is decreased.

3.3. Crystallography and intermolecular contacts

The target compound **1** crystallized in the $P2_1/n$ space group from THF as yellow crystals (Fig. 5). One interesting feature of the structure is the presence of several short intermolecular distances (Table 2 and Fig. 6). For example, edge to face interactions are observed between aromatic systems, such as the intermolecular short contact observed between H₁₁ and C₄, displaced from the centroid (H₁₁-centroid distance is 3.166 Å) [25]. In addition, there is a C-H...pi interaction between the methyl H_{17A} and C₄ (H_{17A}-centroid distance is 3.307 Å). The crystal lattice is further stabilized by the presence of short intermolecular contacts between carbon atoms. For example, the C_3-C_{10} distance is 3.391 Å and the C_{10} -C₁₁ distance is 3.343 Å. Similar short contacts were reported in the crystal structure of a related compound 3-ethyl-8-methoxy-6-nitro-2H-1-benzopyran-2-spiro-2'-(3'-methylthiazolidine) (4) by Miler-Srenger and Guglielmetti [26]. However, the crystal structures of two benzothiazolinic spirooxazines (3-methyl-2,3-dihydro-l,3-benzothiazolespiro-2,2'-(3-methyl-2H-phenanthr[9,10-b] [1,4]oxazine) (5), 3-methyl-2,3-dihydro-1,3-benzothiazolespiro-2,2'-(3-methyl-2H-naphth[2,I-b][1,4]-oxazine) (6) reported earlier



Fig. 4. Absorption spectra of an irradiated solution of spiropyran 1 in THF (3.68 \times 10⁻⁵ M) at -30 °C as it thermally (without light) reverts from open to closed form.

Table 2Short intermolecular contacts.





Fig. 5. Ortep view [22] of 3-methyl-6-nitro-3'-methylspiro-[2H-l-benzopyran-2,2'-benzothiazoline] with displacement ellipsoids at the 50% probability level.

by Sun et al. [27] show no short intermolecular contacts, possibly due to the absence of electron donating or withdrawing substituents. Compound **2** did not crystallize well.

3.4. Computational studies

Table 3

Examination of various bond distances and bond angles reveals that in the solid state, the molecule **1** adopts a geometry very close to that obtained using DFT calculations (Tables 3, S1, S11, and S12). This suggests that the weak C–H…pi interactions do not affect the geometry significantly for **1**. For example, the bond distance C_{spiro} – O_1 (C_8 – O_1) is 1.458 Å in both structures. This bond distance is of particular interest, due to its potential for use in prediction of photochromic properties. For the related spiropyrans **4**, **5**, and **6**, the calculated bond lengths are slightly less accurate, but are within 0.01 Å. The calculated C_{spiro} –N bond lengths are within 0.01 Å of experimental values for **1** and **4**, but do not accurately reproduce crystallographic distances for spirooxazines **5** and **6**.

3.5. Correlating structural features with photochromism and thermochromism

As for other classes of spiropyrans and spirooxazines, efforts to correlate substituent effects with photochromism have been pur-



Fig. 6. Crystal packing diagram (Mercury [23]) of 1 showing short contacts.

sued extensively for benzothiazolinic spiropyrans by several investigators such as Vandewyer et al. [31] and Kister et al. [32]. The presence of an electron-withdrawing group in position 6 and an electron-donating group in position 8 of the benzopyran ring system is often required for good photochromic properties. Compound 1 has one nitro substituent at position 6, and it is weakly photochromic at room temperature. By comparison, a second benzothiazolinic spiropyran (2) with both nitro and methoxy substituents was synthesized and characterized. This compound did not form suitable crystals to obtain a crystal structure, however, photochemical and computational studies were pursued. Compound 2 was photochromic, and using the measure of colorability, or the steady state absorbance in the visible region upon irradiation, it was found to be more efficient at ring opening than 1 in THF at -30 °C. This substituent effect in a different solvent and at a different temperature is also documented by other investigators (Table 4). Compound 3 was reported to be not photochromic [16]. The slight shortening of the C_{spiro}-O bond length with the added methoxy group (1 versus 2) is consistent with that found for the same substituent changes in photochromic spiroindolinopyrans [9]. For spiropyrans 1–4, as the C_{spiro}–O bond increases in length, the C_{spiro}-N bond decreases, which is consistent with what is observed crystallographically for indolinospiropyrans.

3.5.1. C_{spiro} – N_1 bond length

A crystallographic C_{spiro} -N₁ bond length of 1.434 is observed for benzothiazolinic spiropyran **1**, which is slightly longer than the re-

	E _{rel} (kcal/ mol) ^a	C _{spiro} –O bond length (calc) (Å)	C _{spiro} –N bond length (calc) (Å)	C _{spiro} –O bond length (crystal) (Å)	C _{spiro} –N bond length (crystal), Å
1	-	1.458	1.437	1.458	1.434
2-a	0	1.454	1.437	-	-
2-b	1.689	1.458	1.436	-	-
2-c	2.595	1.462	1.440	-	-
3-a	0	1.437	1.443	-	-
3-b	0.652	1.440	1.442	-	-
4	-	1.462	1.436	1.469 [26]	1.421 [26]
5	-	1.436	1.438	1.422 [27]	1.402 [27]
6	-	1.436	1.438	1.430 [27]	1.409 [27]
Saturated heterocycles [12]	-	-	-	1.41-1.43	1.47-1.48

^a Relative to that of the lowest energy conformer.

Calculated bond lengths and crystallographic bond lengths.

	C _{spiro} –O (Å)	C _{spiro} -N (Å)	Colorability = (A_0/cL) ; (solvent, <i>T</i>)	k_{T}
1	1.458	1.434	4916 (THF, -30°) 700 (toluene, 25°) [28]	$1.11 \times 10^{-4} \text{s}^{-1}$ (THF, $-30^\circ)$ 1.8 s^{-1} (toluene, 25°) [26]
2	1.454 ^a	1.437 ^a	8995 (THF, -30°) 3700 (toluene, 25°) [28]	$1.85 \times 10^{-4} \text{ s}^{-1}$ (THF, -30°) 6.5 s ⁻¹ (toluene, 25°) [28]
3	1.437 ^a	1.443 ^a	0 ^b	-
4	1.469 [26]	1.421	2300 (toluene, 25°) [29]	76 s ⁻¹ (toluene, 25°) [30]
5	1.422 [27]	1.402	0 ^b	-
6	1.430 [27]	1.409	0 ^b	-

Table 4	
Bond lengths and photochemical	properties for 1 and related spiropyran compounds.

^a Calculated using DFT for the most stable isomer (Table 3).

^b Not photochromic.

ported value 1.421 Å for the related thiazolidinic spiropyran **4** and also longer than those found for the benzothiazolinic spirooxazines **5** and **6** (Table 3). Calculated bond lengths for $C_{spiro}-N_1$ in benzo-thiazolinic spiropyrans **2** and **3** are close to that observed for **1**. Taken together, bond lengths in all six compounds are significantly shorter than $C(sp^3)-N(sp^3)$ bond lengths found in five-membered heterocycles. A shorter $C_{spiro}-N_1$ bond is an indication of donation of lone pair electrons from N_1 to C_{spiro} , which would stabilize the cation that develops on C_{spiro} when the compound is in the open form. There does not appear to be a correlation between $C_{spiro}-N_1$ bond length and either photochromism or the extent of photocolorability for the series of compounds **1–6** (Table 4). It is possible, however, that the uncertainty of the calculated $C_{spiro}-N_1$ bond lengths in the spirooxazines masks any trend that may exist.

The crystallographic bond angles around the spiro carbon atom of **1** are found to be between 106.15° and 114.01°. This distortion from the tetrahedral angle and the short $C_{spiro}-N_1$ bond length indicate that the spiro carbon possesses a degree of sp² character. The sum of the bond angles at N₁ was found to be 348.21°, which lies between the sum for sp³ hybridized bond angles (327°) and the sum for sp² hybridized bond angles (360°). The sum of the bond angles, as well as the shorter $C_{spiro}-N$ distance described above, indicates that N₁ has some sp² character to stabilize a developing positive charge on C_{spiro} , suggesting a possibility of thermochromism. This possibility was also reported by Sun et al. [27] for their nonphotochromic benzothiazolinic spirooxazines **5** and **6**. Thermochromism was not observed for **1** at room temperature, or up to 50 °C in isopropanol.

3.5.2. C_{spiro}-O bond length

As discussed in the introduction, a longer C_{spiro} –O bond is associated with photochromism in spiropyrans and spirooxazines. In addition, for spirooxazines, this bond length correlates with the degree of photocolorability. The extent to which either photochromism or the degree of photocolorability of thiazolidinic and benzothiazolinic spiropyrans and benzothiazolinic spirooxazines may also be predicted by C_{spiro} –O bond length was explored using data collected and reported for compounds **1–6**.

Taking together both the crystallographic and computational distances in Table 4, it appears that compounds with C_{spiro} –O bond distances greater than or equal to 1.454 Å (**4**, **1**, **2**) are photochromic, while compounds with C_{spiro} –O bond distances less than or equal to 1.437 Å (**3**, **6**, **5**) are not photochromic. Within the uncertainty of calculated bond C_{spiro} –O bond distances of up to 0.01 Å (Table 3), this cutoff is consistent with that observed for nonbenzo-thiazolinic or thiazolidinic spiropyrans and spirooxazines. In those classes of photochromic compounds, C_{spiro} –O bond distances were found to be greater than or equal to 1.463 Å [9]. It is interesting to note that the extent of colorability for compounds **1–6** does not correlate with longer C_{spiro} –O bonds. Clearly, many factors contribute to the colorability of a compound, including the effect of substituents on the nature of the electronic transitions that lead to the photoexcited state, rates of thermal closure, and irradiation

wavelength-dependent quantum yields for photochemical ring opening.

4. Conclusions

Few crystallographic studies have been published for this subclass of benzothiazolinic spiropyrans, and no crystal structure of the closed form of any benzothiazolinic spiropyran has been reported. Therefore, correlations between experimental molecular geometry and photochromism or the degree of photocolorability for this subclass of spiropyrans are not yet well substantiated. In this work, we confirm that for benzothiazolinic or thiazolidinic spiropyrans and spirooxazines, the crystallographic bond distances such as C_{spiro} –O can be used as an indicator of photochromism, but not for the degree of photocolorability. Moreover, for compounds such as these, the crystal structure and the computational results are similar for C_{spiro} –O bonds. Therefore, computation may also serve as a useful tool to predict photochromism from ground state structures for benzothiazolinic or thiazolidinic spiropyrans and spirooxazines.

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Appendix A. Supplementary data

CCDC 632419 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via External link http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2010.01.012.

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