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Sensitivity and Resolution Development of Spiropyran-based Molecular Photoswitches

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The phenylazo moiety and its donor- and acceptor-substituted derivatives are studied as effective auxochromes to improve their sensitivity and resolution for distinguishing between the spiro (SP; OFF) and mero (ON) forms in molecular photoswitching applications. Thus, 13 azospiropyran derivatives were synthesized and their spectroscopic and photokinetic behaviors were studied. The quality of photochromic reactions of the synthesized photochromic compounds were compared using a dose–response model. Interestingly, by replacing the nitro group in 6-nitrospiropyran ($\varepsilon = 0.42 \times 10^4$ M^{-1} cm^{-1}) with a simple phenylazo moiety, the SP form is still colorless and the color intensity of the merocyanine (MC) form is improved desirably by extending the conjugation length (**1a**, $\varepsilon = 1.35 \times 10^4$ M^{-1} cm^{-1}). The presence of a hydrophilic OH group or a CH_3 group at the para position of phenylazo moiety revealed more or less the same photochromic properties as **1a**. The OCH_3 group substituted at position 6 of the phenylazo moiety at the para position of the azobenzene moiety effectively increased the photochromic properties with the maximum *k*-value for SP to MC switching. Meanwhile, Cl, Br, COOH, and NO_2 groups at the para position of the azobenzene moiety revealed the reduction in photochromic properties compared to **1a**.

Keywords: Azospiropyran; Photoresponsive; Photochromic dye; Spiropyran; Absorption.

INTRODUCTION

The design and synthesis of fine-tunable photoresponsive molecules are of great scientific interest and intense activity in different fields of chemistry. In fact, photoresponsive systems with controllable light-induced color have a variety of applications due to their potential use in state-of-the-art technologies.[1–10]

Photochromic molecules reversibly respond to light by the photoisomerization process, in which some physicochemical properties, such as absorption and emission spectra, electrochemical property, magnetic properties, dipole interaction, and refractive index, can be tuned.[11–14] These photoinduced tunable properties give rise to different applications in photooptical switching devices,[15–19] sensors,[20] biology,[21–23] optical storage,[8,24] displays,[25] and nonlinear optics.[26]

Among the molecular photoswitches, spiropyrans as a family of photochromic compounds constitute an important class mostly due to their molecular binding abilities and the sharp distinction between the molecular properties of their photoinduced states.[16,27] Spiropyrans reversibly switch between the colorless spiro (SP) form which is nonpolar and uncharged, and a colored merocyanine (MC) form with a polar, conjugated, zwitterionic structure.[28,29]

It has been known that the introduction of electron-withdrawing substituents at positions 6 and 8 on the chromene part lowers the energy of MC form and makes it long-lived at room temperature and so enhances the photochromic properties.[30,31] Consequently, the majority of the investigations of molecular switches based on spiropyran have focused on various derivatives of spiropyrans containing a nitro group in the chromene part.[32]

Recently, we synthesized and studied the photoresponse of bis-azospiropyrans connected with a conjugated aromatic bridge.[33–35] These photoswitches showed a high molar absorption coefficient in the MC form.[33] Such a high molar absorption coefficient improves the sensitivity and contradistinction between the two ON (MC) and OFF (SP) levels of finely photoresponsive molecules. Previous to that study, there were

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only a few studies on using an azo chromophore as a part of photochromic spiropyran molecule.[36–39] Hence, there is a lack of systematic study on azospiropyrans aimed at taking advantage of the electron-withdrawing character of phenylazo moiety to lower the energy state of the MC form and deepening the color of the solution at the photostationary state by extending the conjugation system.

This achievement persuaded us to study azospiropyrans' photoresponses and figure out the substitution effects on mono azospiropyrans-based molecular switches. Accordingly, azospiropyran derivatives were synthesized using several *p*-substituted anilines with electron donor or acceptor groups for azo moieties, and then coupling them with salicylaldehyde, 5-nitrosalicylaldehyde, or 3-methoxysalicylaldehyde. The photophysical properties of the synthesized photochromic molecules were also investigated. Thus, in this study we present the spectroscopic and kinetic results of 13 azospiropyran derivatives. Eight derivatives (**1a–h**) contain a group at position 6 of the phenylazo moiety; four (**2a–d**) possess two groups, one in position 6 of the azo moiety and a NO_2 group on chromene moiety; and the last derivative (**3**) possesses an NO_2 group in the phenylazo part and a methoxy group on the chromene moiety. Spectroscopic studies of all synthesized azospiropyran photochromic molecules were compared with those of two spiropyrans terminated with NO_2 or H groups at position 6 of the chromene moiety (**7a** and **7b**).

RESULTS AND DISCUSSION

Diazotization of *p*-substituted anilines with subsequent coupling with any of the salicylaldehyde, 5-nitrosalicylaldehyde, or 3-methoxysalicylaldehyde led to the corresponding **4a–h**, **5a–d**, and **6** in high yields (70–90%). Afterward, azospiropyrans **1a–h**, **2a–d**, and **3** were obtained in good yields (50–90%) by the coupling reaction of the synthesized azo-salicylaldehyde derivatives **4** to **6** with Fischer's base, i.e., 1,3,3-trimethyl-2-methyleneindoline (Scheme 1).

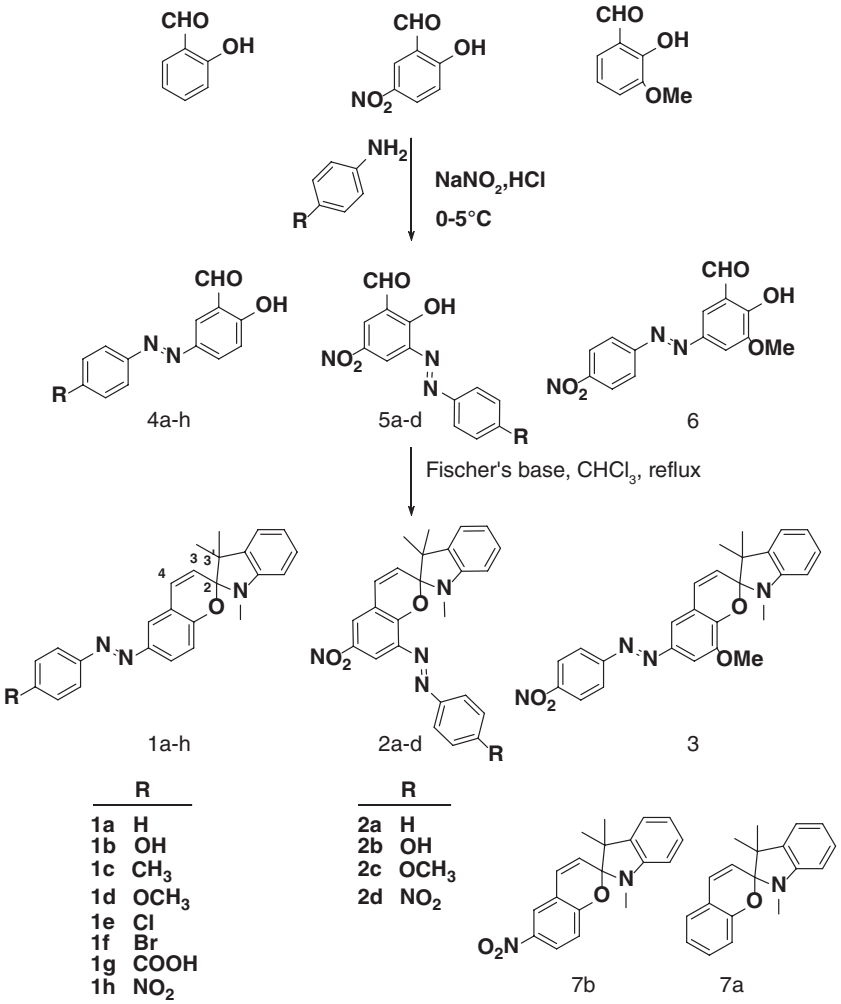
The structures of the synthesized azospiropyrans **1–3** were characterized using FT-IR and ^{1}H-NMR spectroscopic data. Since the patterns of **4–6** are of known azo structures in the literature, they were purified and characterized by FT-IR to confirm the expected functional groups as aldehyde, hydroxide, and NO_2.

The peaks at 3150–3465 cm^{-1} in the FT-IR spectra of **4a–h** were assigned to O–H stretch, and those of the azo groups were observed at 1454–1481 cm^{-1}. The peaks at 2856–2927, 1616–1668, and 2675–2867 cm^{-1} are related to C–H aromatic (Ar), C═O, and C─H stretch of the aldehyde functional groups, respectively.

The absorption at 1452–1488 cm^{-1} in the FT-IR spectra of **1a–h** revealed azo groups; the peak at 2960–2968 cm^{-1} was due to C─H, Ar, and the peak at 1602–1606 cm^{-1} was related to C(3)═C(4) stretch. The stretching vibration of the C(2)─N was observed at 1278–1317 cm^{-1}, and the C(2)─O stretching frequency occurred at 1016–1037 cm^{-1}. The ^{1}H-NMR spectra for **1a–h** clearly showed singlet signals at 1.25–1.35 ppm (3H) and 1.35–1.65 ppm (3H) for two CH_3 at C(3)─$(CH_3)_2$ (Scheme 1). The proximity of two CH_3 of indoline moieties (C(3)─$(CH_3)_2$) to the olefinic proton or oxygen moiety of the pyranyl group made them magnetically nonequivalent.[40] A singlet signal appeared at 2.70–3.02 ppm (3H) for the N─CH_3 protons of **1a–h**. The olefinic protons of **1a–h** revealed two doublets, one at 4.20–5.81 ppm for H─C(3) with large coupling constants (J = 10.2–10.4 Hz), and the other for H─C(4) at the aromatic regions. The former doublet for olefinic protons with large coupling is very characteristic of the spiropyran system.

For **5a–d**, the peaks at 3120–3130 cm^{-1} in the FT-IR spectra refer to the O─H stretch; the peaks at 2852–2933, 2692–2921, and 1612–1623 cm^{-1} correspond to C─H (Ar) , C─H, and C═O stretch of the aldehyde functional groups, respectively, and the peaks at 1510–1546 and 1332–1348 cm^{-1} were related to the N═O stretch. The peaks due to the azo groups were observed at 1440–1488 cm^{-1}.

For **2a–d** structures, the absorption frequencies in FT-IR spectra occurred at 2966 cm^{-1} for aromatic C─H; the peak at 1604–1606 cm^{-1} was related to C(3)═C(4) stretch; the peak at 1487–1488 cm^{-1} was due to the azo groups; and the peaks at 1494–1510 and 1322–1338 cm^{-1} corresponded to the N═O stretch. The stretching vibration of C(2)─N was observed at 1259 cm^{-1}, and the C(2)─O stretching frequency occurred at 1012–1014 cm^{-1}. The ^{1}H-NMR spectra for **2a–d** clearly showed two singlet signals at 1.25–1.35 ppm (3H) and 1.35–1.65 ppm



Scheme 1. Synthesis of azospiropyran photochromic dyes **1a–h**, **2a–d**, and **3**.

(3H) for two CH_3 at C(3)—$(CH_3)_2$ protons (Scheme 1). A singlet signal appeared at 2.80–3.11 ppm (3H) for N—CH_3 protons of **2a–d**. The olefinic protons of **2a–d** revealed two very characteristic doublets, one at 4.13–4.31 ppm for H—C(3) with large coupling constants (J = 10.1–10.2 Hz), and the other for olefinic protons H—C(4) at the aromatic regions.

The peaks at 3145 cm^{-1} in the FT-IR spectrum of **6** refers to O—H stretch. The peaks at 2958, 2852, and 1654 cm^{-1} were due to the aromatic C—H, C—H, and C═O stretch of the aldehyde functional groups, respectively. The azo groups were observed at 1456 cm^{-1}, and the peaks at 1514 and 1338 cm^{-1} were related to N═O stretch.

The absorption frequencies in FT-IR spectra of **3** revealed an aromatic C–H at 2964 cm^{-1}. The peak at 1606 cm^{-1} was related to C(3)═C(4) stretch, the peak at 1488 $cm^{-1}$was due to the azo groups, and the peaks at 1465 and 1340 cm^{-1} corresponded to N═O stretch. The stretching vibration of the C(2)—N was observed at 1280, and the C(2)—O stretching frequencies occurred at 1020 cm^{-1}. The ^{1}H-NMR spectra for **3** clearly showed two singlet signals at 1.31 ppm (3H) and 1.57 ppm (3H) for magnetically nonequivalent CH_3 at C(3)—$(CH_3)_2$ protons (Scheme 1). A singlet signal appeared at 2.70 ppm (3H) for N—CH_3 protons, and a singlet signal appeared at 3.01 ppm (3H) for OCH_3 protons of **3**. The olefinic protons of **3** revealed two characteristics of the spiropyran system doublets: one at 4.25 ppm for H—C(3) with large coupling constants (J = 10.1 Hz), and the other olefinic protons H—C (4) at the aromatic regions.

The synthesized photochromic molecules revealed interesting substitution-dependent photophysical

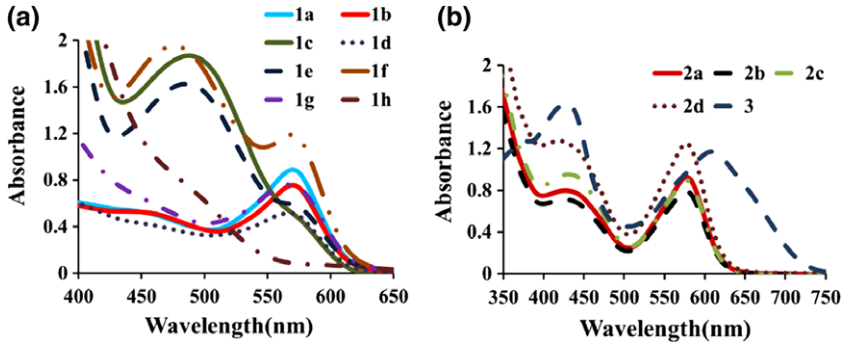


Fig. 1. UV/Vis spectra of **1** (a), and **2**, **3** (b) in CH_2Cl_2 ($C = 10^{-4}$ mol/L) after 3 min exposure to UV light at room temperature.

responses to UV light as presented in the following sections.

Photophysical studies of the photochromic dyes

Absorption spectra of the synthesized photochromic compounds **1**, **2**, and **3** in CH_2Cl_2 ($C = 10^{-4}$ mol/L) were studied after being exposed to 254 nm UV light for less than 3 min until reaching steady state (Figure. 1).

To study the substitution effect, the molar absorption coefficients of azospiropyrans **1a–h**, **2a–d**, and **3**, and also nonsubstituted spiropyran **7a** and 6-nitro BIPS **7b** (Scheme 1), which were synthesized according to the literature,[34,41] were measured and compared. The results revealed that azo substitution increases the color strength of the mero forms. Donor or acceptor groups have significant effects on the photophysical properties. The results are presented in Table 1. Two λ_{max} values are reported for **1c**, **1e**, and **1f** because both affect their related MC colors.

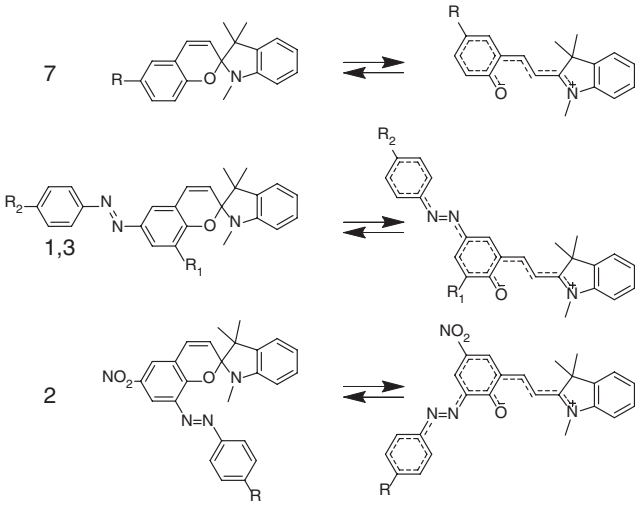
In this study, the apparent molar absorption coefficient of the simple spiropyrans, when the color of solutions reached the steady state, was 0.31×10^4 M^{-1} cm^{-1} for **7a** and 0.42×10^4 $M^{-1}cm^{-1}$ for **7b**. At the same irradiation, depending on the substitutions, ε increased to $0.84–2.2 \times 10^4$ M^{-1} cm^{-1} in the presence of an azo moiety in the mero form of the synthesized azospiropyrans. The high color strength of azospiropyrans in the MC form arises from the extension of the conjugation system of the spiropyran backbone with an azo moiety (Scheme 2). It is well known that a higher molar absorption coefficient leads to higher sensitivity and resolution, which in turn provides better distinction between the SP and MC forms in photoswitching applications.

Azospiropyrans **1a–h** were exposed to 254 nm UV light at room temperature, and their photochromic behaviors were studied using UV/Vis spectroscopy. The difference between the wavelength of maximum absorbance of azospiropyrans **1a–h** in closed and open forms was in the range 200–250 nm (Figure. 2). To investigate the ability to get the irradiated azospiropyrans back to their former SP state, thermal back reaction of **1a–h** was performed at 120–146°C in DMF (Figure. 2). It is worth noting that, due to the stability of the MC form of azospiropyrans, the spontaneous thermal back reaction in the dark and therefore photochemical bleaching

Table 1. Wavelength of maximum absorbance (λ_{max}) and molar absorption coefficients of azospiropyrans **1a–h**, **2a–d**, and **3**, and also **7a**, **b** at the same concentration 10^{-4} M in CH_2Cl_2

Compounds[1]	R	λ_{max}[1] (nm)	ε ($M^{-1}cm^{-1}$) × 10^4
1a	H	570	1.35
1b	OH	570	1.12
1c	CH_3	494, 580	1.76,0.80
1d	OCH_3	569	1.1
1e	Cl	484, 580	1.71,0.40
1f	Br	472, 565	1.76,0.72
1g	COOH	568	1.44
1h	NO_2	510	0.82
2a	H	577	1.30
2b	OH	577	1.08
2c	OMe	569	1.02
2d	NO_2	577	1.54
3	NO_2	608	2.2
7a	H	569	0.31
7b	NO_2	577	0.42

[1] For some dyes, two wavelengths of maximum absorbance at visible light are mentioned due to their effects on the final colors.



Scheme 2. Spiropyran (**7**) and azospiropyrans (**1–3**), and their differences in mero form's conjugation length

by common low-energy light sources is not possible. However, the repetition of ON and OFF cycles of an azospiropyran molecule by a laser source was shown elsewhere,[33] and this will be investigated later.

Within the synthesized azospiropyrans, **1a–h**, **1b**, and **1d** were produced in colorless SP forms due to electron-donor groups such as OH and OMe at the para position of the azo moiety. Similar to nonsubstituted azospiropyran **1a**, these spiropyrans switched to highly colored mero forms ($\lambda_{max} \geq 550$ nm) too. The electron-acceptor groups such as Cl (**1e**) and Br (**1f**) in this series gave yellow azospiropyrans and revealed a blue shift in their mero form color ($\lambda_{max} \leq 484$ nm). The SP form of compound **1 h** showed more stability than the other synthesized derivatives and was not easily switched to MC form in common polar solvents like chloroform, dimethyl sulfoxide, DMF, DCM, acetone, acetonitrile, and ethyl acetate. It also did not have enough solubility in ethanol and methanol. Only the SP form of this compound easily turned to the red MC form in the presence of the highly polar silica gel medium (Figure. 2, **1 h**). However, in the absence of silica gel, a red solution in dichloromethane was obtained only after 22 min of UV irradiation. 5-Nitrosalicylaldehyde was coupled and diazotized with *p*-substituted anilines possessing either highly electron donor (OH, **2b**, and OMe, **2c**) or acceptor (NO_2, **2d**) groups. These azospiropyrans are almost colorless in the SP form and easily switched to the highly colored mero form, with λ_{max} = 550–573 nm (Figure 3).

A diazotized 4-nitroaniline was also coupled with 3-methoxy salicylaldehyde for synthesizing azospiropyran **3**. The presence of the electron-donor group (OMe) on the salicylaldehyde moiety and also the acceptor group (NO_2) on the azo substituent produced yellowish azospiropyrans in the SP form, which turned into green (Figure 4). The produced green color was obtained from a mixture of the yellow SP form (λ_{max} 416 nm) and the blue mero form (λ_{max} 608 nm). Most often, spiropyrans produce red shade in colored form and produce blue color with the spiropyran-based structure **3**, which can be very interesting (Figure 4).

The quality of photocoloration reactions of the synthesized photochromic compounds is compared empirically with a dose–response model fitting. Preliminary evaluations showed that developing the visible peaks of all compounds cannot be explained by a simple exponential model. This suggests that the coloration mechanism of all compounds is not unimolecular. Knowing that photocoloration of spiropyrans is complex and is due to short- and medium-lived transient species to reach the final stable merocyanin isomer,[42] for the case of azo-spiropyrans a sigmoidal model can be fitted relatively well with the lack of random residuals. Photokinetic examination of the 13 synthesized spiropyran derivatives were studied by the fitting of the obtained absorbances at the λ_{max} of their MC form during irradiation with 254 nm UV light to an exponential model (Equation 1). The data points were fitted adequately in view of the adjusted r^2 (Table 2) and as illustrated in Figure 5. While the dose–response model (Eq. (1)) is not a mechanistic model, as a mathematical framework that simulates the trends of time vs. absorbance curves for all compounds, the derived parameters (Table 2) are practical for comparing the kinetics as well.

$$\mathrm{Abs} = \mathrm{Abs}_0 + \frac{(\mathrm{Abs}_1 - \mathrm{Abs}_0)}{1 + 10^{(t_m - t)k}} \quad (1)$$

where, k is the kinetic of SP to MC photo isomerization, Abs_0 and Abs_1 are the absorbance at λ_{max} of the MC forms before irradiation (time = 0) and at photostationary state,respectively, t is irradiation time, and t_m is the time of the middle of the curve.

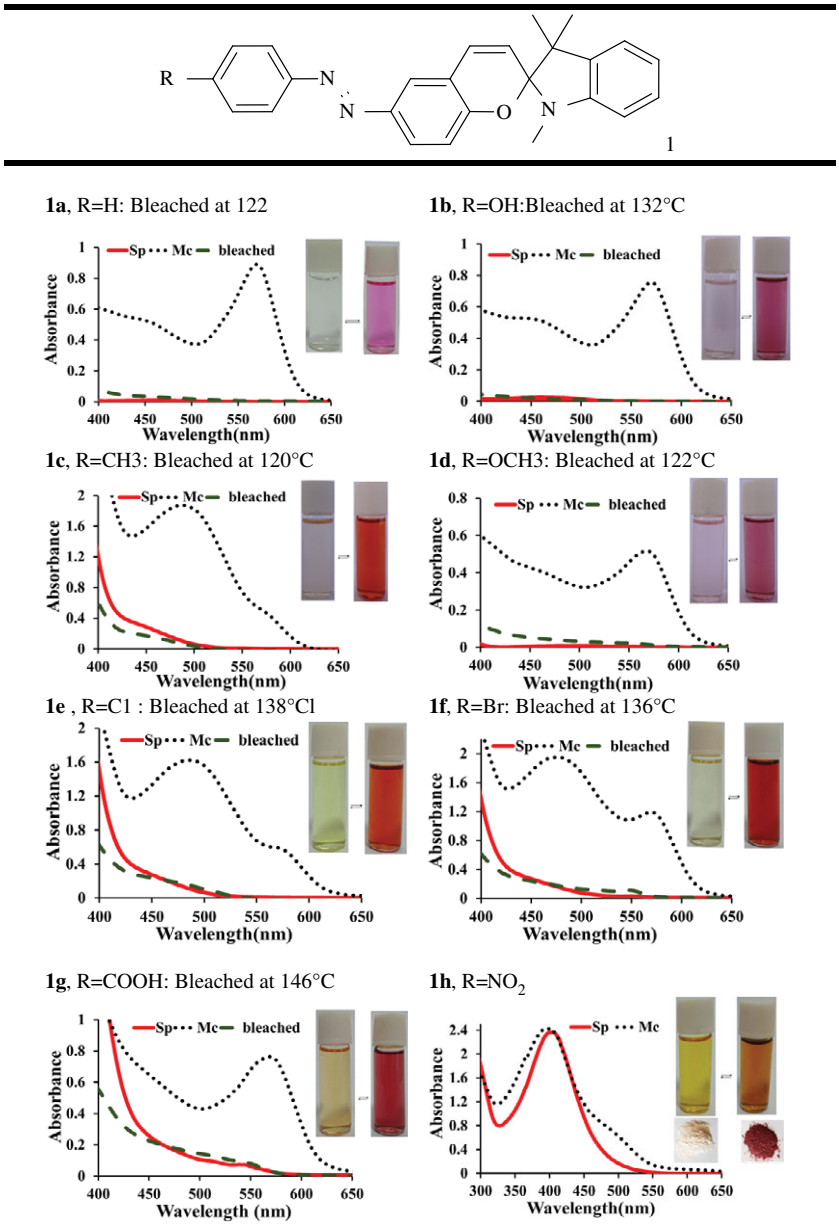


Fig. 2. UV/Vis spectra of **1a–h** (C = 10^{-4} mol/L in CH_2Cl_2) before (SP) and after (MC) 3 min exposure to 254 nm UV light at room temperature. The mero forms were transformed to spiro forms at 120–146°C in DMF.

According to Table 2, the maximum *k*-value for SP to MC switching was obtained for **1d** with OMe substitution at position 6 of the phenylazo moiety. The minimum *k* belongs to **1c** possessing the Me group at the same position.

According to Figure 5, as expected, nonsubstituted spiropyran **7b** revealed low color intensity in the MC form (maximum absorbance 0.6, $\varepsilon = 0.31 \times 10^4$ M^{-1} cm^{-1}) compared to 6-nitro BIPS (**7a**, maximum absorbance 1.4, $\varepsilon = 0.42 \times 10^4$ M^{-1} cm^{-1}). Interestingly, by replacing the nitro group with a simple azobenzene (**1a**), the SP form is still colorless but the color intensity of the MC form is improved considerably by long conjugation (**1a**, maximum absorbance 1.25, $\varepsilon = 1.35 \times 10^4$ M^{-1} cm^{-1}).

It should be noted that the obtained data presented in Table 2 is at the same concentration (5×10^{-5} M). However, for better kinetic examination, the solutions of **7a** and **7b** were more concentrated (2×10^{-4} M).

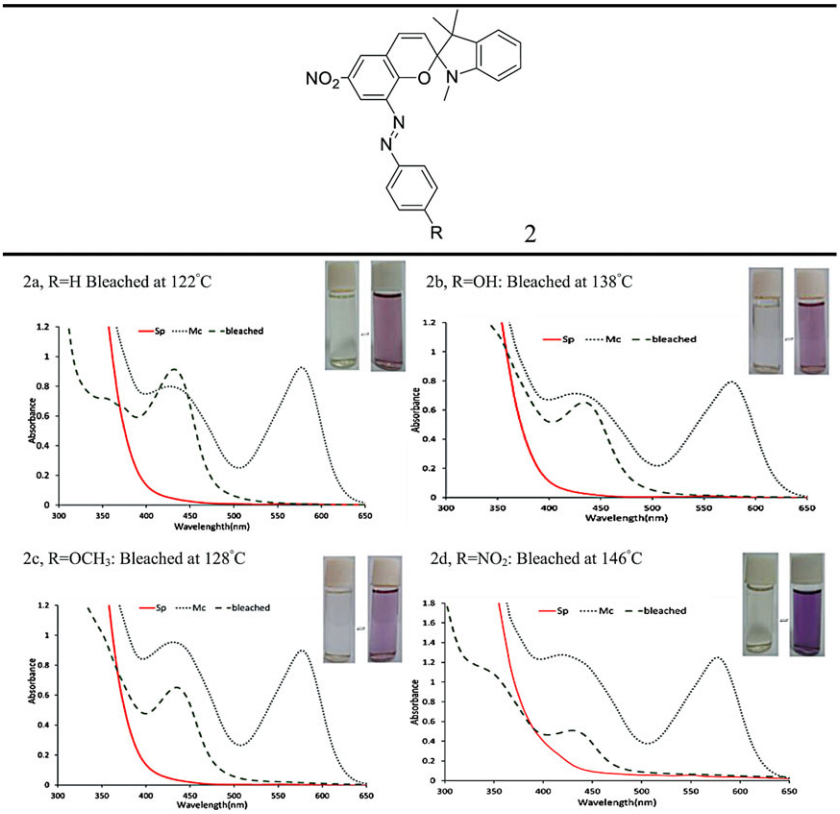


Fig. 3. UV–Vis absorption of **2a–d** ($C = 10^{-4}$mol/L in CH_2Cl_2) after 3 min exposure to 254 nm UV light at room temperature. The mero forms are reversible to spiro forms at 128–146°C at the same concentration 10^{-4} M in DMF.

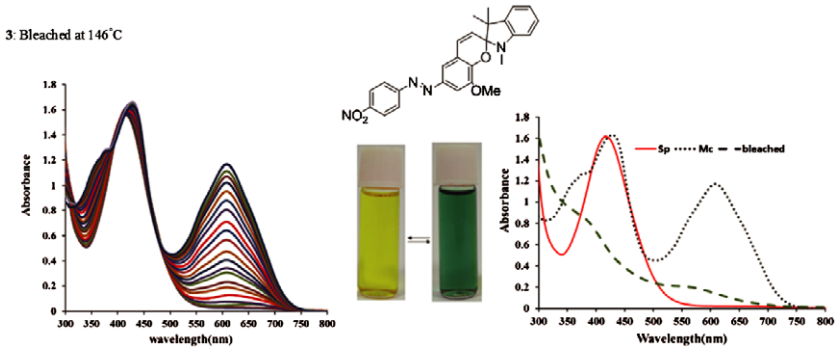


Fig. 4. UV/Vis spectra of **3** ($C = 5 \times 10^{-5}$ mol/L in CH_2Cl_2), after 3 min exposure to 254 nm UV light at room temperature. The mero form was transformed to spiro form at 146°C in DMF.

The presence of a hydrophilic OH group or a CH_3 group at the para position of azobenzene moiety, **1b** and **1c** respectively, revealed more or less the same photochromic properties as **1a**. However, OCH_3 group at the para position of the azobenzene moiety (**1d**) increased the photochromic properties more effectively than **1a**, while Cl, Br, COOH, and NO_2 groups at the para position of azobenzene moiety, **1e**, **1f**, **1g**, **1h**, respectively, revealed reduced photochromic properties compared to **1a**.

Table 2. Derived parameters from dose–response curve fitting on azospiropyrans **1a–h**, **2a–d**, and **3**, and also nonsubstituted spiropyrans **7a**, **b** using time vs. absorbance data

	k	Span[1]	Adj. r^2
1a	0.015	2.22	0.9985
1b	0.013	1.10	0.9945
1c	0.009	3.65	0.9994
1d	0.055	1.89	0.9968
1e	0.013	3.27	0.9985
1f	0.018	5.68	0.9991
1h	0.016	0.51	0.9962
1g	0.029	1.97	0.9948
2a	0.024	1.00	0.998
2b	0.011	1.07	0.9985
2c	0.036	1.54	0.9971
2d	0.010	1.39	0.9985
3	0.018	0.99	0.9954
7a	0.067	0.053	0.9102
7b	0.024	0.176	0.9852

[1] Span = $Abs_1 - Abs_0$.

The other possibility for the photochemical process is the well-known *cis–trans* isomerization of the azo bonds, which would lead to a decrease in color intensity.[24,26,33,34,43–46] However, such isomerization of the azobenzene moieties should have a negligible impact on the resulting immensely increased color intensities resulting from the mero forms spiropyrans. Therefore, the *cis–trans* isomerization of the azo bonds is discounted.

To better understand the new aspects of the photochromic properties of azospiropyrans, more investigations on solvatochromism and photokinetics, e.g., photochromic quantum yield determination, are in progress and the results will be published soon.

EXPERIMENTAL

General remarks

Chemicals were purchased from Merck and used without further purification. Melting points were measured by a Büchi B-545 apparatus, and the values are uncorrected. UV/Vis spectra were recorded on a Multispec-1501-Shimadzu UV/Vis spectrophotometer. IR spectra were recorded on a Perkin-Elmer Spectrum-One-BX FT-IR spectrometer in KBr, and the ν values are reported in cm^{-1}. ^{1}H-NMR spectra were recorded on a Bruker-400-Avance Fourier transform (FT) NMR instrument, at 400 MHz in $CDCl_3$; δ is reported in ppm relative to $SiMe_4$, J in Hz. A 254 nm UV hand-held lamp (8 watt/cm^2) was used as the excitation light source for the photochromic ring-opening reactions.

Preparation of compounds 4a–h, 5a–d, and 6

General procedure A solution of $NaNO_2$ (1.6 g, 23.2 mmol) in H_2O (5 mL) was added to salicylaldehyde (21.8 mmol) in H_2O (10 mL) including NaOH (1.8 g) at 5°C. The resulting solution was added dropwise to the solution of amine derivatives (23.2 mmol) in HCl (10 mL, 1%) at 0°C. The mixture was stirred for 30 min at 0°C and then for 30 min at room temperature. Afterward, it was filtered and washed three times with distilled water. The products were crystallized in EtOH several times to afford pure **4a–h**, **5a–d**, and **6** (Scheme 1).

(*E*)-5-(2-Phenyldiazenyl)-2-hydroxybenzaldehyde (4a). Yield (90%). m.p. 127–129°C. IR (KBr): 3217 (OH), 2852 (C—H aldehyde), 2971 (CH═), 1634 (C═O), 1477 (N═N), 1274 (C—N).

(*E*)-2-Hydroxy-5-((4-hydroxyphenyl)diazenyl)benzaldehyde (4b). Yield (90%). m.p. 135–136°C. IR (KBr): 3407 (OH), 2852 (C—H aldehyde), 2927 (CH═), 1616 (C═O), 1456 (N═N), 1257 (C—N).

(*E*)-5-(2-*p*-Tolyldiazenyl)-2-hydroxybenzaldehyde (4c). Yield (90%). m.p. 151–152°C. IR (KBr): 3191 (OH), 2860 (C—H aldehyde), 2923 (CH═), 1650 (C═O), 1454 (N═N), 1271 (C—N).

(*E*)-5-(2-(4-Methoxyphenyl)diazenyl)-2-hydroxybenzaldehyde (4d). Yield (90%). m.p. >300°C. IR (KBr): 3404 (OH), 2840 (C—H aldehyde), 2962 (CH═), 1620 (C═O), 1458 (N═N), 1280 (C—N), 1029 (C—O).

(*E*)-5-(2-(4-Chlorophenyl)diazenyl)-2-hydroxybenzaldehyde (4e). Yield (90%). m.p. 207–209°C. IR (KBr): 3184 (OH), 2925 (CH═), 2867 (C—H aldehyde), 1668 (C═O), 1477 (N═N), 1284 (C—N).

(*E*)-5-(2-(4-Bromophenyl)diazenyl)-2-hydroxybenzaldehyde (4f). Yield (90%). m.p. 214–216°C. IR (KBr): 3188 (OH), 2871 (CH═), 2867 (C—H aldehyde), 1668 (C═O), 1475 (N═N), 1286 (C—N).

(*E*)-4-((3-Formyl-4-hydroxyphenyl)diazenyl)benzoic acid (4g). Yield (70%). m.p. >300°C. IR (KBr): 2817–3055 (COOH), 2677 (CH═), 2675 (C—H aldehyde), 1679 (C═O), 1454 (N═N), 1286 (C—N).

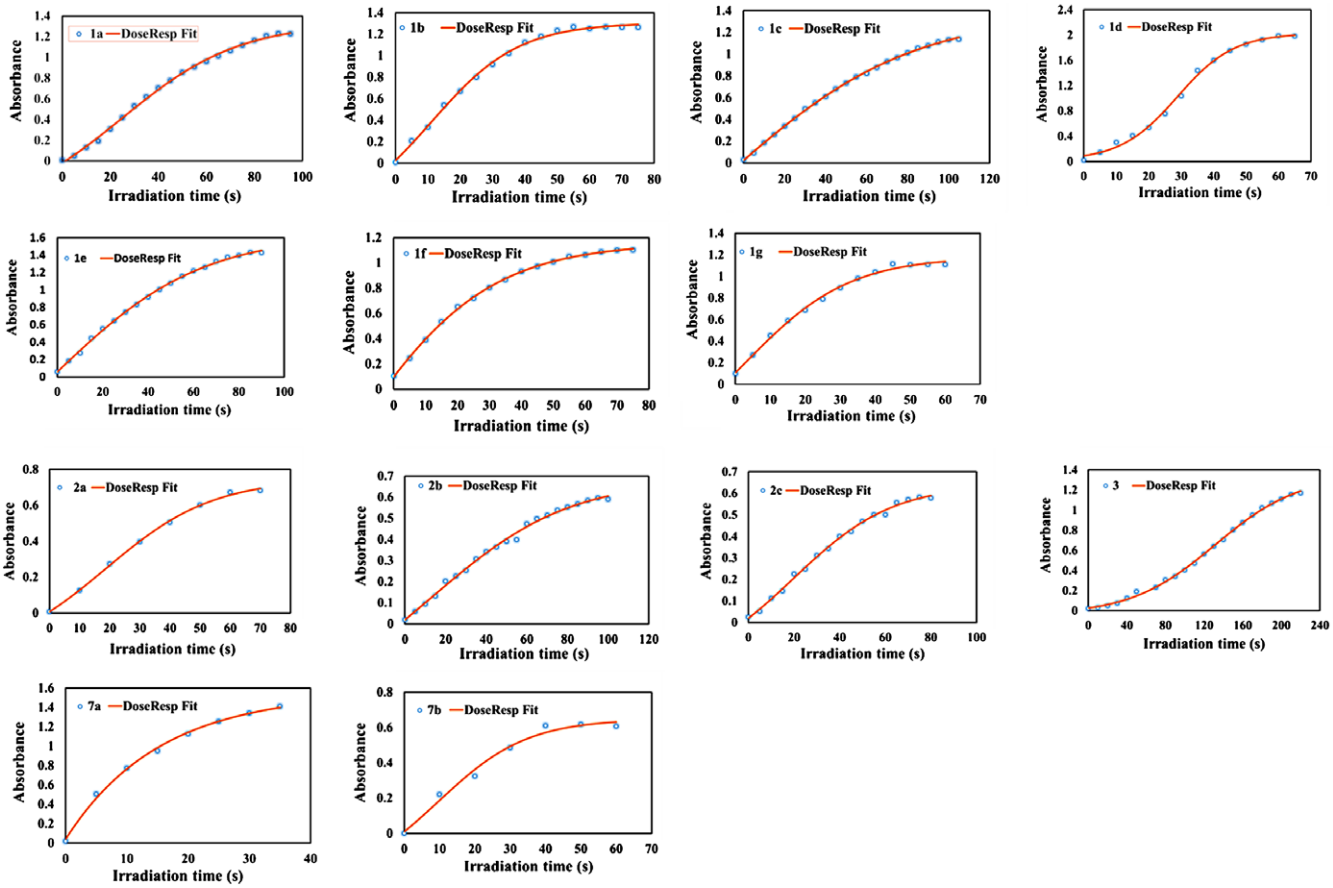


Fig. 5. Kinetic study of UV/Vis spectra of a dose–response model for absorbance at the λ_{max} of the dichloromethane solutions of **1–3** against irradiation time (s) at 254 nm UV light.

(*E*)-5-(2-(4-Nitrophenyl)diazenyl)-2-hydroxybenzaldehyde (4h). Yield (80%). m.p. 192–194°C. IR (KBr): 3404 (OH), 2856 (CH═), 2852 (C—H aldehyde), 1664 (C═O), 1456 (N═N), 1286 (C—N), 1521, 1348 (N═O).

(*E*)-2-Hydroxy-5-nitro-3-(phenyldiazenyl)benzaldehyde (5a). Yield (80%). m.p. 112–115°C. IR (KBr): 3217 (OH), 2920 (CH═), 2692 (C—H aldehyde), 1623 (C═O), 1515, and 1348 (N═O), 1477 (N═N), 1274 (C—N).

(*E*)-2-Hydroxy-3-((4-hydroxyphenyl)diazenyl)-5-nitrobenz-aldehyde (5b). Yield (80%). m.p. 277–278°C. IR (KBr): 3122 (OH), 2692 (C—H aldehyde), 2852 (CH═), 1612 (C═O), 1546 and 1332 (N═O), 1440 (N═N), 1286 (C—N).

(*E*)-3-(2-(4-Methoxyphenyl)diazenyl)-2-hydroxy-5-nitrobenz-aldehyde (5c). Yield (70%). m.p. 169–170°C. IR (KBr): 3130 (OH), 2921 (CH═), 2844 (C—H aldehyde), 1623 (C═O), 1510 and 1342 (N═O), 1485 (N═N), 1299 (C—N), 1020 (C—O).

(*E*)-3-(2-(4-Nitrophenyl)diazenyl)-2-hydroxy-5-nitrobenz-aldehyde (5d). Yield (70%). m.p. >300°C. IR (KBr): 3118 (OH), 2971 (CH═), 2921 (C—H aldehyde), 1622 (C═O), 1515 and 1340 (N═O), 1488 (N═N), 1284 (C—N).

(*E*)-3-(2-(4-Nitrophenyl)diazenyl)-6-hydroxy-2-methoxybenz-aldehyde (6). Yield (80%). m.p. 225–226°C. IR (KBr): 3145 (OH), 2958 (CH═), 2852 (C—H aldehyde), 1654 (C═O), 1514 and 1338 (N═O), 1456 (N═N), 1265 (C—N), 1130 (C—O).

Preparation of compounds 1a–h, 2a–d, and 3

General procedure A solution of **4a–h**, **5a–d**, or **6** (1 mmol) in 50 mL $CHCl_3$ was heated under reflux conditions, and then 2- methylene-1,3,3-trimethylindoline (1 mmol) in 5 mL $CHCl_3$ was added dropwise. The mixture was refluxed for 2 h and then cooled to room temperature. The precipitate was

filtered and crystallized in EtOH to afford pure **1a–h**, **2a–d**, and **3**, respectively (Scheme 1).

(*E*)-1',3',3'-Trimethyl-6-(phenyldiazenyl)spiro[chromene-2,2'-indoline] (1a). Yield (90%). m.p. 206–207.5°C. IR (KBr): 2968 (CH═), 1606 (C(3)═C(4)), 1485 (N═N), 1311 (C(2)─N), 1018 (C(2)─O).

(*E*)-4-((1',3',3'-Trimethylspiro[chromene-2,2'-indolin]-6-yl)diazenyl)phenol (1b). Yield (90%). m.p. 193–195°C. IR (KBr): 2966 (CH═), 1606 (C(3)═C(4)), 1487 (N═N), 1259 (C(2) –N), 1012 (C(2) –O). ^{1}H-NMR ($CDCl_3$) δ ppm: 1.33 (s, Me); 1.62 (s, Me); 2.84 (s, NMe); 4.20 (d, $^3J_{HH}$ = 10.2, H-C(3)); 6.53–7.25 (m, 11 H, Ar, and H─C(4)).

(*E*)-1',3',3'-trimethyl-6-(*p*-tolyldiazenyl)spiro[chromene-2,2'-indoline] (1c). Yield (90%). m.p. 181–182°C. IR (KBr): 1456 (N═N), 2960 (CH═), 1604 (C(3)═C(4)), 1317 (C(2)─N), 1016 (C(2)─O). ^{1}H-NMR ($CDCl_3$) δ ppm: 1.32 (s, Me); 1.70 (s, Me); 2.67 (s, NMe); 2.34 (s, Ph-Me); 4.26 (d, $^3J_{HH}$ = 10.2, H─C(3)); 6.57–7.92 (m, 11 H, Ar, and H─C(4)).

(*E*)-6-((4-Methoxyphenyl)diazenyl)-1',3',3'-trimethyl-spiro- [chromene-2,2'-indoline] (1d). Yield (50%). m.p. 193.5–195°C. IR (KBr): 2966 (CH═), 1604 (C(3)═C(4)), 1452 (N═N), 1307 (C(2)─N), 1018 (C(2)─O). ^{1}H-NMR ($CDCl_3$) δ ppm: 1.32 (s, Me); 1.70 (s, Me); 2.67 (s, NMe); 3.4 (s, OMe); 4.26 (d, $^3J_{HH}$ = 10.2, H─C(3)); 6.57–7.92 (m, 11 Ar···H, and H─C(4)).

(*E*)-6-((4-Chlorophenyl)diazenyl)-1',3',3'-trimethyl-spiro-[chromene-2,2'-indoline] (1e). Yield (90%). m.p. 176–178°C. IR (KBr): 2962 (CH═), 1602 (C(3)═C(4)), 1454 (N═N), 1317 (C(2)─N), 1016 (C(2)─O). ^{1}H-NMR ($CDCl_3$) δ ppm: 1.37 (s, Me); 1.67 (s, Me); 2.90 (s, NMe); 4.20 (d, $^3J_{HH}$ = 10.2, 2H─C(3)); 6.57–7.95 (m, 11 H, Ar, and H─C(4)).

(*E*)-6-((4-Bromophenyl)diazenyl)-1',3',3'-trimethyl-spiro-[chromene-2,2'-indoline] (1f). Yield (90%). m.p. 173.5–175°C. IR (KBr): 2964 (CH═), 1606 (C(3)═C(4)), 1454 (N═N), 1317 (C(2)─N), 1016 (C(2)─O). ^{1}H-NMR ($CDCl_3$) δ ppm: 1.31 (s, Me); 1.54 (s, Me); 2.84 (s, NMe); 4.20 (d, $^3J_{HH}$ = 10.4, H─C(3)); 6.53–7.70 (m, 11 H, Ar, and H─C(4)).

(*E*)-4-((1',3',3'-Trimethylspiro[chromene-2,2'-indolin]-6-yl)dia-zenyl)benzoic acid (1g). Yield (50%). m.p. 157–159°C. IR (KBr): 2962 (CH═), 1606 (C(3)═C(4)), 1452 (N═N), 1313 (C(2)─N), 1016 (C(2)─O). ^{1}H-NMR ($CDCl_3$) δ ppm: 1.33 (s, Me); 1.54 (s, Me); 2.84 (s, NMe); 4.20 (d, $^3J_{HH}$ = 10.2, H─C(3)); 6.53–7.26 (m, 11 H, Ar, and H─C(4)).

(*E*)-1',3',3'-Trimethyl-6-((4-nitrophenyl)diazenyl) spiro-[chromene-2,2'-indoline] (1h.Yield (90%). m.p. 202–203°C. IR (KBr): 2962 (CH═), 1606 (C(3)═C(4)), 1521and 1346 (N═O), 1456 (N═N), 1278 (C(2)─N), 1022 (C(2)─O). ^{1}H-NMR ($CDCl_3$) δ 1.20 (s, Me); 1.33 (s, Me); 2.77 (s, NMe); 5.80 (d, $^3J_{HH}$ = 10.3, H─C(3)); 6.56–8.37 (m, 11 H, Ar, and H─C(4)). ^{13}C-NMR ($CDCl_3$) δ 20, 25, 28 (CH_3); 52, 53 (C(3'), C(2)); 121, 127 (C(4), C(3)); 106–158 (18 C, Ar)

(*E*)-4-((1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indolin]-8-yl)diazenyl)phenol (2b). Yield (70%). m.p. 168–168.5°C. IR (KBr): 2970 (CH═), 1604 (C(3)═C(4)), 1508 and1338 (N═O), 1487 (N═N), 1259 (C(2)─N), 1012 (C(2)─O)). ^{1}H-NMR ($CDCl_3$) δ ppm: 1.29 (s, Me); 1.54 (s, Me); 2.80 (s, NMe); 4.20 (d, $^3J_{HH}$ = 10.2, H─C(3)); 6.53–7.25 (m, 10 H, Ar, and H─C(4)).

(*E*)-8-((4-Methoxyphenyl)diazenyl)-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (2c). Yield (90%). m.p. 169–170°C. IR (KBr): 2962 (CH═), 1606 (C(3)═C(4)), 1510 and 1322 (N═O), 1488 (N═N), 1311 (C(2)─N), 1018 (C(2)─O). ^{1}H-NMR ($CDCl_3$) δ ppm:1.28 (s, Me); 1.63 (s, Me); 2.86 (s, NMe); 3.4 (s, OMe); 4.15 (d, $^3J_{HH}$ = 10.1, H─C(3)); 6.57–8.24 (m, 10 H, Ar, and H─C(4)).

(*E*)-1',3',3'-Trimethyl-6-nitro-8-((4-nitrophenyl)diazenyl)spiro[chromene-2,2'-indoline] (2d). Yield (50%). m.p. 169.5–170°C . IR (KBr): 2968 (CH═), 1604 (C(3)═C(4)), 1494 and 1338 (N═O), 1488 (N═N), 1259 (C(2)─N), 1014 (C(2)─O). ^{1}H-NMR ($CDCl_3$) δ ppm: 1.38 (s, Me); 1.55 (s, Me); 2.86 (s, NMe); 4.15 (d, $^3J_{HH}$ = 10.1, H─C(3)); 6.53–7.25 (m, 10 H, Ar, and H─C(4)).

(*E*)-5-Methoxy-1',3',3'-trimethyl-6-((4-nitrophenyl) diazenyl)-spiro[chromene-2,2'-indoline] (3). Yield (80%). m.p. 192–194°C . IR (KBr): 2964 (CH═), 1606 (C(3)═C(4)), 1488 (N═N), 1465 and 1340 (N═O), 1280 (C(2)─N), 1020 (C(2)─O). ^{1}H-NMR ($CDCl_3$) δ ppm: 1.33 (s, Me); 1.65 (s, Me); 2.90 (s, NMe); 3.7 (s, OMe); 4.25 (d, $^3J_{HH}$ = 10.1, H─C(3)); 6.53–7.25 (m, 10 H, Ar, and H─C(4)).

CONCLUSIONS

Electron-donor substitution on the azo moiety in azospiropyrans made colorless SP and purple mero forms with high color strength. However, electron-acceptor substitution on azo moiety were made yellowish SP and red mero forms, with more stable SP forms. The presence of

electron-acceptor group on the azo moiety and the electron donor on the salicylaldehyde moiety effected a red shift to longer absorption wavelengths in comparison with the reverse condition, i.e., the electron-donor group on the azo and the acceptor on the salicylaldehyde moiety. Increasing the molar absorption coefficient of nonsubstituted spiropyrans in mero forms in the presence of an azo moiety was effective in improving the spiropyran structures, which led to higher sensitivity and resolution, and hence better distinction between the SP (OFF) and mero (ON) forms in photochromic applications. In azospiropyrans, electron-donor groups at the para position of the azo moiety produced colorless SP forms (OFF) switching to highly colored MC forms ($\lambda_{max} \geq 550$ nm). In contrast, electron-acceptor substitutions reduced the possibility of SP–MC color differentiation.

Colorless azospiropyrans obtained by coupling of 5-nitrosalicylaldehyde with diazotized *p*-substituted anilines switched to highly colored mero forms (λ_{max}: 550–573 nm).

Possessing an electron-donor group (OMe) on the salicylaldehyde moiety and also an acceptor group (NO_2) on azo substitute produced yellowish azospiropyrans in SP form, which switched to green color. Spiropyrans usually produce red shade in their colored form, so producing a green color can be very interesting.

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