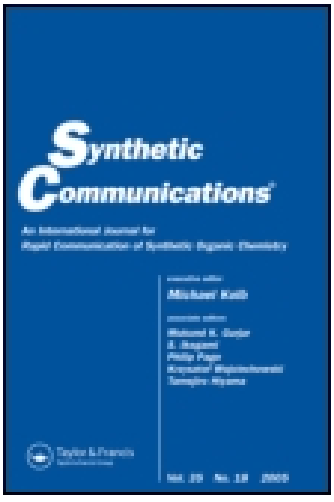

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Synthesis of Novel Photochromic 6-Benzyloxo-spirobenzopyran Compounds

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Synthesis of Novel Photochromic 6-Benzyloxo-spirobenzopyran Compounds

Luis E. Elizalde, Gladys de los Santos, Aída E. García, Diana I. Medellín, and Ricardo Acosta
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Abstract: The synthesis of four novel derivatives of 1′,3′,3′-trimethylspiro-[2H-1]-benzopyran-6-benzyloxo-2,2′-indoline is reported. The synthetic approach to these compounds involves the preparation of the key compound, 3-formyl-4-hydroxybenzophenone, by means of the Reimer–Tiemann reaction. The photochromic compounds were isolated and characterized by ^{1}H and ^{13}C NMR as well as FT-IR and UV-VIS spectrometry. Comparative studies performed in these compounds showed a higher molar extinction coefficient and red shift of maximum absorption wavelength when the benzyloxo group is introduced in the spirobenzopyran molecule.

Keywords: 3-Formyl-4-hydroxybenzophenone, optical materials, photochromism, spiropyrans

INTRODUCTION

The application of photochromic compounds in areas such as data storage, ophthalmic lenses, and security devices, among others, have attracted the interest of many researchers throughout the world. The high commercial value of these compounds has resulted in the publication of a plethora of patents and papers dealing with either new synthetic methods for the preparation of these compounds or determination of their photochemical and photophysical properties.

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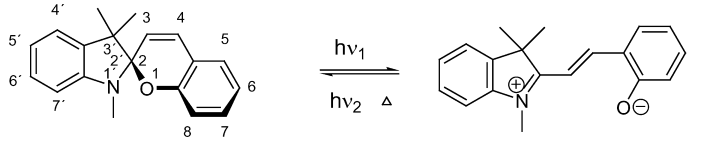
Photochromic compounds undergo a reversible transformation induced by ultraviolet light, which causes a change in the molecular structure. This is detected by a change in the coloration of the original molecule. When the excited molecule is subjected again to white light or heat, it returns to its original state. Therefore, a photochromic system has two different molecular structures, each of them with different properties, namely, absorption spectra, refractive indexes, dielectric constants, oxidation/reduction potentials, and molecular geometries.

However, the photochromism can be affected by side reactions that result in the formation of products unable to return to the original molecular structure. This effect is called fatigue, and it reduces the half-life of the active compound. Another drawback of these molecules is the color stability of the photochromic transition. In some applications (e.g., optical storage) it is very important that the secondary state has a definite transition period. Thus, many studies have focused on improving the stability and the half-life of photochromic compounds.

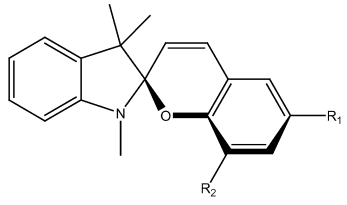
Although there are several families of compounds that exhibit photochromism, such as spiropyrans, spirooxazines, fulgides, diarylethenes, viologens, and azo compounds, the spiropyrans derived from 1′,3′,3′-trimethylspiro[2H-1] benzopyran-2,2′-indoline are especially attractive because they have applications in electronic storage media as well as in optoelectronic devices.[1–3] These molecules were first studied by Hirshberg and Fisher[4] and basically consist of two orthogonal systems linked by a tetrahedral spiro carbon. These compounds, commonly called BIPS, are numbered according to the International Union of Pure and Applied Chemistry (IUPAC), as shown in Scheme 1.

In optical device applications, the merocyanine requires a reasonable thermal stability at room temperature once the material is no longer irradiated (back thermal reaction on Scheme 1). By changing the electronic character of the substituents at the benzopyran ring, the thermal stability can be modified.[5]

We now report the synthesis of novel spirobenzopyrans derivatives **1** of 1′,3′,3′-trimethylspiro-[2H-1]benzopyran-6-benzyloxo-2,2′-indoline. These compounds can develop a colored form with maximum absorption wavelength beyond 560 nm. Such novel molecules **1a**–**d** contain a benzyloxo group in position 6 (Scheme 2) to improve the thermal stability on the merocyanine, which results from increase of the resonance effect.



Scheme 1. Isomerization reaction for spirobenzopyrane indoline molecules.



1 (a-d)

a	$R_1 = H$	$R_2 = C(O)C_6H_5$
b	$R_1 = Cl$	$R_2 = C(O)C_6H_5$
c	$R_1 = Br$	$R_2 = C(O)C_6H_5$
d	$R_1 = NO_2$	$R_2 = C(O)C_6H_5$

Scheme 2. Synthesized derivatives of 6-benzyloxospirobenzopyrane molecules.

EXPERIMENTAL

All inorganic reagents and solvents were analytical grade and used as purchased (Aldrich, Merck). Sulfuryl chloride, 2-methylene-1,3,3-trimethyl-indoline 97%, and 4-hydroxybenzophenone 98% were purchased from Aldrich. The reference photochromic compounds **3a**–**d** were synthesized and purified according to reported methods.[6,7] ^{1}H and ^{13}C NMR spectra were obtained using a 300-MHz Jeol-JNM-ECP300 spectrometer, using $CDCl_3$ as solvent and tetramethyl silane as standard, at room temperature. Routine infrared spectra were obtained on a Magna Nicolet 550 infrared spectrometer. Elemental analyses were determined on a Perkin Elmer 2400 series analyser and UV-Vis spectra on an HP 8452 spectrometer. The chromatograms were run on a GC-MS Hewlett Packard HP-5971.

Synthesis of 3-Formyl-4-hydroxybenzophenone (2a)

A mixture of 1 g (5 mmol) of 4-hydroxybenzophenone and 20 mL of an aqueous solution containing 3.2 g (80 mmol) of sodium hydroxide was heated under inert atmosphere in a three-necked round-bottomed flask. Once the solution reached 70°C, 0.87 mL (10.86 mmol) of chloroform was added dropwise over 30 min. This temperature was maintained for at least 2 h. After this time, the reaction mixture was acidified by addition of 10% HCl aqueous solution and extracted with ether. KOH aqueous solution (50 mL, 7.5% w/w) was added to the organic layer and extracted twice with 50 mL of chloroform. The basic phase was acidified and extracted with ethyl ether. The extract was dried over $MgSO_4$. After the solvent evaporation, 0.74 g of a white powder was recovered (65% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.08 (d, 1H, $J = 9$ Hz), 7.53 (m, 2H), 7.61 (tt, 1H, $J = 6$ Hz, $J = 1.38$ Hz), 7.76 (m, 2H), 8.06 (dd, 1H, $J = 2$ Hz, $J = 9$ Hz), 8.13 (d, 1H, $J = 2$ Hz), 9.95 (s, 1H), 11.48 (s, 1H). ^{13}C (50 MHz, $CDCl_3$) δ: 196, 165, 161, 138, 136, 133, 132.65, 132, 129.78, 129.6, 128.5, 128.2, 117.97, 115. FTIR (KBr) ν_{max} (cm^{-1}): 1642, 1600; EI-MS m/z 226 (M^+). Anal. calcd. for $C_{14}H_{10}O_3$: C, 74.03%; H, 4.45%. Found C, 74.09%; H, 4.55%.

Synthesis of 2-Chloro-3-formyl-4-hydroxybenzophenone (2b)

3-Formyl-4-hydroxybenzophenone (**2a**) (1.51 g, 6.7 mmol) dissolved in 20 mL of dry CH_2Cl_2 was placed in a reactor. Then, carefully and under vigorous stirring, 0.65 mL (8 mmol) of sulfuryl chloride was added. The reaction mixture was kept at 25°C for 24 h. Then, it was washed with 20 mL of distilled water and 10% $NaHCO_3$ aqueous solution. The organic layer was finally dried over $MgSO_4$. The product was recovered by precipitation in ether. Yield 30%, mp 156°C, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.53 (m, 2H), 7.61 (tt, 1H, $J = 6$ Hz, $J = 1.38$ Hz), 7.76 (m, 2H), 8.06 (d, 1H, $J = 2$ Hz,), 8.13 (d, 1H, $J = 2$ Hz), 9.95 (s, 1H), 11.92 (s, 1H). ^{13}C (50 MHz, $CDCl_3$) δ: 198.17, 198.5, 161.51, 141.83, 138.56, 137.65, 136.42, 130.32, 129.12, 127.63, 120.1, 112.96. FTIR (KBr) ν_{max} (cm^{-1}): 1631, 1605; EI-MS m/z 260 (100), 262 (30) (M^+, $M^+ + 2$). Anal. calcd. for $C_{14}H_9ClO_3$: C, 64.5%; H, 3.5%, Cl, 13.6%. Found C, 64.75%; H, 3.43%, Cl, 13.57%.

Synthesis of 2-Bromo-3-formyl-4-hydroxybenzophenone (2c)

Dry CH_2Cl_2 (15 mL) and 1.51 g (6.74 mmol) of 3-formyl-4-hydroxybenzophenone (**2a**) were placed in a three-neck round-bottom flask under inert atmosphere. The flask was cooled in an acetone–CO_2 bath at −70°C. Then, 8.11 mmol of bromine were added through a dropping funnel. As soon as the addition was completed, some crystals of anhydrous $FeCl_3$ were added. After 30 min, the temperature was allowed to reach room temperature, and the mixture was stirred for 6 h. The reaction mixture was then washed with distilled water. The organic phase was extracted with 10% NaOH aqueous solution to remove the product as the sodium salt. The aqueous phase was acidified and extracted with chloroform, and then dried over anhydrous $MgSO_4$. After evaporation of the solvent, the final product was crystallized in ethyl ether yielding 0.78 g (38%) of a white solid with a melting point of 166°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.53 (m, 2H), 7.61 (tt, 1H, $J = 6$ Hz, $J = 1.38$ Hz), 7.76 (m, 2H), 8.06 (d, 1H, $J = 2$ Hz), 8.32 (d, 1H, $J = 2$ Hz), 9.95 (s, 1H), 12.08 (s, 1H). ^{13}C (50 MHz, $CDCl_3$) δ: 196.07, 193.15, 151.51, 141.33, 135.32, 135.55, 132.07, 130.70, 128.84, 128.5, 120.49, 111.32. FTIR (KBr) ν_{max} (cm^{-1}): 1655, 1618 EI-MS m/z 304 (50), 306 (50). Anal. calcd. for $C_{14}H_9BrO_3$ C, 55.1%; H, 3.0%; Br, 26.2%. Found C, 54.37%; H, 2.98%; Br, 26.37%.

Synthesis of 2-Nitro-3-formyl-4-hydroxybenzophenone (2d)

A mixture of 0.3 g of ammonium nitrate (3.7 mmol), 0.42 g of 3-formyl-4-hydroxybenzophenone (1.85 mmol), and 25 mL of dry chloroform was

placed in an inert atmosphere. After complete dissolution of the reactants, 3.25 g (15.5 mmol) of trifluoroacetic anhydride were added. The mixture was refluxed in chloroform for 2 h. Then, it was washed with distilled water. The organic phase was separated and dried over anhydrous magnesium sulfate, after purification by column chromatography (hexanes–ethyl acetate 7:3), and 0.29 g of a yellow powder was recovered. Mp 96°C (57% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.53 (m, 2H), 7.61 (tt, 1H, $J = 6$ Hz, $J = 1.38$ Hz), 7.76 (m, 2H), 8.55 (d, 1H, $J = 2$ Hz), 8.83 (d, 1H, $J = 2$ Hz), 9.95 (s, 1H), 12.08 (s, 1H). ^{13}C (50 MHz, $CDCl_3$) δ: 189.67, 188.15, 158.51, 138.47, 136.32, 133.64, 133.07, 130.70, 129.92, 129.15, 125.49, 116.32. FTIR (KBr) ν_{max} (cm^{-1}): 1650, 1595, 1534; EI-MS m/z; 271 (M^+). Anal. calcd. for $C_{14}H_9NO_5$ C, 62.0%; H, 3.3%; N, 5.2%. Found C, 61.01%; H, 3.29%; N, 5.48%.

General Procedure for Preparation of Derivatives of 1′,3′,3′-Trimethylspiro-[2H-1] Benzopyrane-8-benzyloxo-2,2′-indoline (Benzyloxo-BIPS)

A mixture of 3 g of 3-formyl-4-hydroxybenzophenone (**2a**), 2.475 mL of 2-methylene-1,3,3-trimethylindoline, and 50 mL of distilled ethanol was boiled for 4 h. The reaction mixture was filtrated and washed with cold ethanol. The precipitate was recovered, washed with cold ethanol, and then recrystallized in ethanol.

Characterization of 1′,3′,3′-Trimethylspiro-[2H-1] Benzopyran-6-benzyloxo-2,2′-indoline (1a)

^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.23 (d, 1H, $J = 2$ Hz), 8.059 (dd, 1H, $J = 9$ Hz, $J = 2$ Hz), 7.66 (tt, 1H, $J = 6$ Hz, $J = 1.38$ Hz), 7.55 (m, 2H), 7.78 (m, 2H), 7.28 (m, 2H), 7.15 (d, 1H, $J = 8$ Hz), 7.01 (d, 1H, $J = 9$ Hz), 6.82 (d, 1H, $J = 12$ Hz), 6.38 (d, 1H, $J = 8$ Hz), 5.75 (d, 1H, 12H), 3.05 (s, 3H), 1.25 (s, 3H), 1.15 (s, 3H). ^{13}C (50 MHz, $CDCl_3$) δ: 190.54, 156.15, 149.8, 143.47, 138.52, 136.64, 134.07, 131.70, 130.92, 129.15, 129.04, 122.49, 122.13, 119.32, 118.95, 109.53, 108.32, 97.351.8, 30.41, 18.63. EI-MS m/z 159 (100), 381 (1). FT-IR (KBr film) ν_{max} cm^{-1}: 1648, 1285, 885, 732. Anal. calcd. for $C_{26}H_{23}NO_2$: C, 81.9%; H, 6.1%; N, 3.7%. Found C, 82.10%; H, 6.23%; N, 3.25%.

Characterization of 1′,3′,3′-Trimethylspiro-[2H-1] Benzopyran-6-benzyloxo-8-chloro-2,2′-indoline (1b)

^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.18 (d, 1H, $J = 2$ Hz), 8.05 (d, 1H, $J = 2$ Hz), 7.66 (tt, 1H, $J = 6$ Hz, $J = 1.38$ Hz), 7.55 (m, 2H), 7.78(m, 2H), 7.28 (m, 2H),

7.15 (d, 1H, $J = 8$ Hz), 6.82 (d, 1H, $J = 12$ Hz), 6.38 (d, 1H, $J = 8$ Hz), 5.75 (d, 1H, 12H) 3.05 (s, 3H), 1.25 (s, 3H), 1.15 (s, 3H). ^{13}C (50 MHz, $CDCl_3$) δ: 191.50, 156.15, 149.8, 146.47, 139.32, 136.64, 134.07, 131.70, 130.92, 129.15, 129.04, 122.49, 122.13, 119.32, 115.92, 111.23, 108.32, 97.31, 51.83, 30.41, 18.63. EI-MS m/z 159 (100), 415 (5), 417 (2). FT-IR (KBr film) ν_{max}: 1649, 1286, 892, 733 cm^{-1}. Anal. calcd. for $C_{26}H_{22}ClNO_2$: C, 75.1%; H, 5.3%; Cl, 8.5%; N, 3.4%. Found C, 75.31%; H, 5.45%; N, 3.27%; Cl, 8.35%.

Characterization of 1′,3′,3′-Trimethylspiro-[2H-1] Benzopyran-6-benzyloxo-8-bromo-2,2′-indoline (1c)

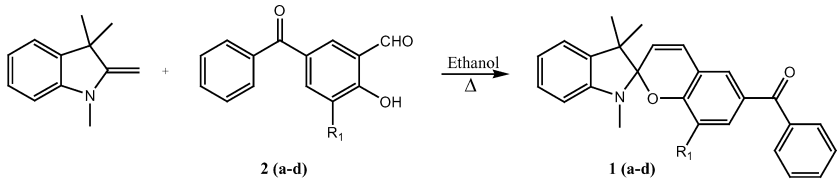
^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.33 (d, 1H, $J = 2$ Hz), 8.19 (d, 1H, $J = 2$ Hz), 7.66 (tt, 1H, $J = 6$ Hz, $J = 1.38$ Hz), 7.55 (m, 2H), 7.78(m, 2H), 7.28 (m, 2H), 7.15 (d, 1H, $J = 8$ Hz), 6.82(d, 1H, $J = 12$ Hz), 6.38 (d, 1H, $J = 8$ Hz), 5.75 (d, 1H, 12H), 3.05 (s, 3H), 1.25 (s, 3H), 1.15 (s, 3H). ^{13}C (50 MHz, $CDCl_3$) δ: 193.54, 156.15, 149.8, 146.47, 139.32, 136.64, 134.07, 131.70, 130.92, 129.15, 129.04, 122.49, 122.13, 119.32, 118.95, 111.23, 108.32, 97.31, 51.83, 30.41, 18.63. EI-MS m/z, 159 (100), 459 (2), 461 (2). FT-IR (KBr Film) ν_{max} cm^{-1}: 1648, 1285, 885, 732. Anal. calcd. for $C_{26}H_{22}BrNO_2$: C, 67.8%; H, 4.8%; Br, 17.4%; N, 3.0%. Found C, 68.23%; H, 4.91%; N, 2.85%; Br, 17.36%.

Characterization of 1′,3′,3′-Trimethylspiro-[2H-1] Benzopyran-6-benzyloxo-8-nitro-2,2′-indoline (2d)

^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.85 (d, 1H, $J = 2$ Hz), 8.55 (d, 1H, $J = 2$ Hz), 7.66 (tt, 1H, $J = 6$ Hz, $J = 1.38$ Hz), 7.55 (m, 2H), 7.78 (m, 2H), 7.28 (m, 2H), 7.15 (d, 1H, $J = 8$ Hz), 6.82 (d, 1H, $J = 12$ Hz), 6.38 (d, 1H, $J = 8$ Hz), 5.75 (d, 1H, 12H), 3.05 (s, 3H), 1.25 (s, 3H), 1.15 (s, 3H). ^{13}C (50 MHz, $CDCl_3$) δ: 190.54, 156.15, 149.8, 146.47, 139.32, 136.64, 134.07, 131.70, 130.92, 129.15, 129.04, 122.49, 122.13, 119.32, 118.95, 116.23, 108.32, 97.31, 51.83, 30.41, 18.63. EI-MS m/z 159 (100), 426 (2). FT-IR (KBr Film) ν_{max} cm^{-1}: 1650, 1595, 1279, 710. Anal calcd. for $C_{26}H_{22}N_2O_2$: C, 73.2%; H, 5.2%; N, 6.6%. Found C, 73.7%; H, 5.45%; N, 6.32%.

RESULTS AND DISCUSSION

Four substituted derivatives of 1′,3′,3′-trimethylspiro-[2H-1]-benzopyran-6-benzyloxo-2,2′-indoline compounds (**1a**–**d**) were prepared according to Scheme 3. Yields, melting points, and UV absorption data are depicted in Table 1.



2 (a-d) 1 (a-d)

2a $R_1 = H$
2b $R_1 = Cl$
2c $R_1 = Br$
2d $R_1 = NO_2$

Scheme 3. Preparation of 6-benzyloxospirobenzopyrane photochromic compounds.

The reaction involves the condensation of 2-methylene-1,3,3-trimethyl-indoline with 3-formyl-4-hydroxy-benzophenone (**2a**), in ethyl alcohol as solvent. The preparation of **2a** was attempted by direct formylation of 4-hydroxybenzophenone using several methods.[8–10] The best result was obtained when chloroform and sodium hydroxide were used as the formylating agent according to the Reimer–Tiemann reaction. This methodology involves the interaction between the 4-hydroxybenzophenone and aqueous sodium hydroxide at 70°C, followed by the addition of chloroform as the formylating agent for 0.5 h (see Scheme 4).

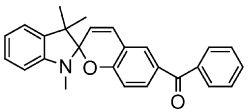
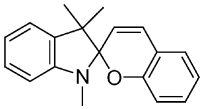
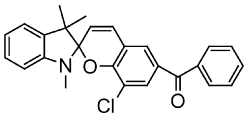
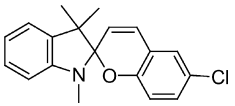
The synthesis of benzophenones **2b–d** was achieved by further functionalization of 3-formyl-4-hydroxy-benzophenone **2a**, using halogenations and nitration reactions (Scheme 5). The compounds **2b** and **2c** were prepared according to the common aromatic electrophilic substitution using sulfuryl chloride[11] or bromine[12] as electrophiles and dichloromethane as solvent (the latter catalyzed with ferric trichloride). These compounds were purified by fractional crystallization in ethyl ether, resulting in a 30% yield for **2b** (chloro substituted) and 38% yield **2c** (bromo substituted).

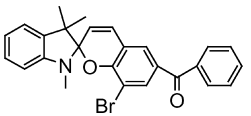
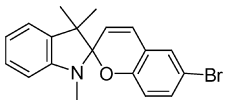
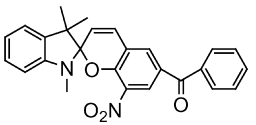
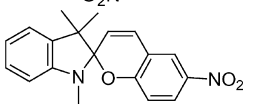
We found that the nitration of 3-formyl-4-hydroxy benzophenone **2a** can be satisfactorily performed using trifluoro acetic anhydride and ammonium nitrate in chloroform as solvent.[13] Compound **2d** was obtained in 57% yield after purification by column chromatography. All products were characterized by common spectroscopic techniques such as IR, GC-MS, ^{1}H NMR, ^{13}C NMR, and C, H, N analysis.

Once **2a–d** were obtained, the preparation of the photochromic compounds **1a–d** was completed by condensation with 2-methylene-1,3,3-trimethylindoline in ethanolic solution. Condensation occured rapidly, and the product was removed from the reaction mixture by filtration and purified by recrystallization from methanol. These novel spiropyrans **1a–b** were also characterized by the spectroscopic techniques previously mentioned.

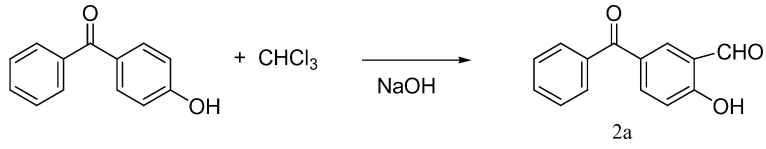
The photochemical properties of the photochromic compounds **1a–d** were measured by ultraviolet spectroscopy from 10^{-5} M solutions in dimethylsulfoxide and compared with the absorption spectra of

Table 1. Spectroscopic properties of the 6-benzyloxospirobenzopyran compounds

				Closed form		Open form	
Notation	Chemical structure	Mp (°C)	Yield (%)	λ_1 (nm)	ε_1 (L/mol cm)	λ_2 (nm)	ε_2 (L/mol cm)
1a		175	91	258	11,700	412	825
3a		205	85	256	16,500	N.A.	—
1b		140	90	260	13,500	568	2,700
3b		155	30	258	8,000	430	700

1c		144	85	260	16,000	568	2,800
3c		159	60	258	7,000	420	620
1d		162	85	272	16,500	602	5,800
3d		177	90	272	16,510	558	4,700

N.A. = No absorption in the visible region.



Scheme 4. Preparation of 3-formyl-4-hydroxybenzophenone.

Scheme 5. Preparation of 3-formyl-4-hydroxy-5-substituted-benzophenones.

1′,3′,3′-trimethylspiro-[2H-1]-benzopyran-2,2′-indoline, 6-chloro, 6-bromo, and 6-nitro derivatives **3a**–**d** in the same solvent and at the same concentration. The latter compounds were synthesized according with reported methods.[6,7] Dimethylsulfoxide was used as the solvent to prevent the solvatochromic effect.

The synthesized compounds showed absorptions in the 200–400-nm interval (Table 1) and molar absorptions coefficients up to 10,000 when they are in the closed form. When these compounds were irradiated with ultraviolet light with a Hg lamp in a quartz cell, it was observed that chemical changes resulted in a different UV pattern. We assumed that all molecules reach the open form (right side of Scheme 1) and that changes can be observed in the absorption spectra in the visible region.

The reference molecule **3a** (which does not have the benzyloxo fraction in position 6) does not develop any absorption in the visible region. However, the irradiation with UV light we detected absorptions at 412 nm for the molecule **1a**.

Molecules bearing the benzyloxo group in the 6-position and groups with strong electron-withdrawing character such as Cl, Br, and NO_2 (**1b**–**d**) showed a remarkable increase in photochromic properties when compared with the reference molecules **3b**–**d** evidenced by their ability to develop a deep purple color, maximum wavelength absorption beyond 568 nm, and molecular extinction coefficients higher than 2800 L/mol cm.

We can assume that these synthesized novel molecules **1a**–**d** derivatives of the 6-benzyloxospirobenzopyranindolines develop a deep purple color after UV irradiation and can be applied in several optoelectronic devices.

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