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Photochromism of tetrahydroindolizines. Part XIV: synthesis of *cis*-fixed conjugated photochromic pyridazinopyrrolo[1,2-*b*]isoquinolines incorporating carbon-rich linkers

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ABSTRACT

New carbon-rich photochromic tetrahydroindolizines (THIs) bearing dihydroisoquinoline derivatives as heterocyclic bases (region B) have been synthesized via different chemical and photochemical pathways. Three alternative pathways for the synthesis of the target photochromic THI-based pyridazinopyrrolo[1,2-*b*]isoquinolines via in situ trapping with hydrazine hydrate have been established. In order to obtain high product yields, different Sonogashira-mediated coupling reactions have been optimized. Low temperature multichannel UV–vis and flash photolysis techniques were used to detect the photochromic and kinetic properties of the synthesized system.

Because of the potential applications of photochromic compounds in erasable optical memories and photoswitches, they have attracted significant attention.[1–10] Upon light irradiation, photochromic molecules exhibit reversible color and structural changes. Photochromic molecules can be employed to modulate various physicochemical properties upon light irradiation, and they have received remarkable attention for their potential applications as photoswitches and optical memory systems.[11–16] Since the pioneering discovery of Dürr on photochromic dihydroindolizines (DHIs) and tetrahydroindolizines (THIs), they have been considered as very interesting photochromic families because of their specific properties such as high photo-fatigue resistance, broad absorption spectra in the visible region, high sensitivity to activation with light, and high photochromic reactivity.[17–20] The exploration of new di- and tetrahydroindolizine structures with improved properties has received significant attention in organic materials science.[18–22] It is well known that suitable functionalization in both regions (region A is fluorene, region B is the ester or cyano groups, and region C is the heterocyclic base part) of the DHI skeleton with different substituents can modify effectively the photochromic behavior of dihydroindolizines.[23–26] The position of the substituents is also important for fine-tuning of their optoelectronic properties.[20–26] So far, our related research has been mainly focused on the effects of subsitutents on the fluorene and pyridazine moieties in the dihydroindolizine photochromes.[18–31]

To the best of our knowledge, there are not many reports on photochromic tetrahydroindolizines (THIs). Such molecules undergo a photoinduced change of color in solution, solid state, and in polymer matrices when exposed to UV irradiation or direct sunlight, and return to their initial state when the illumination ceases, normally via a thermal pathway. The photochromic behavior of THIs (Fig. 1) is based on a reversible pyrroline ring-opening, induced by light, which converts a colorless form (usually named the ‘closed form’) into the colored form (betaine form).[23,24] Few reports on photochromic THIs showed that the thermal reverse reaction, the 1,5-electrocyclization from the ring-open betaine to the THI shows rates extending from milliseconds to several weeks,[23,24] depending on the substituents and structure of the molecule involved. This interesting wide range in the lifetime of the colored form allows these molecules to find many versatile applications as shown by DHI photochromes.[30,31]

In continuation of our previous work dealing with the synthesis and properties of photochromic tetrahydroindolizines (THIs),[23,24] in this Letter, the synthesis of new, highly conjugated, photochromic

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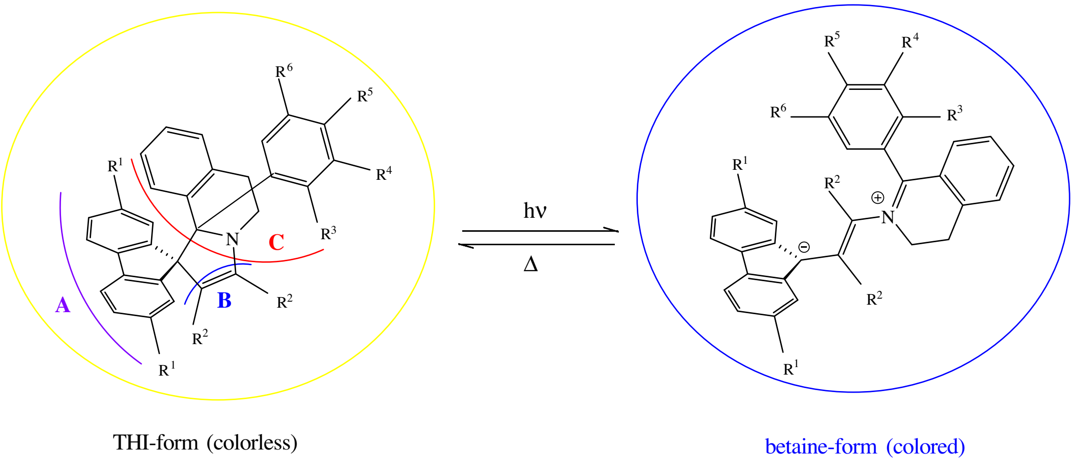
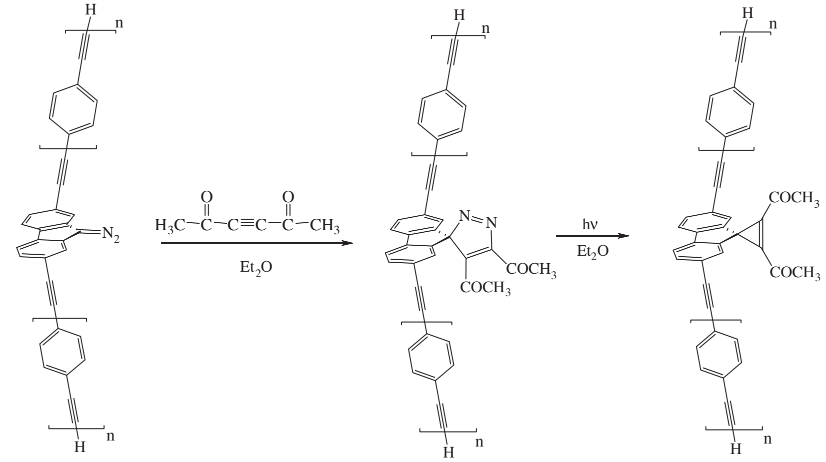


Figure 1. Ring-opening upon UV irradiation and ring-closure in tetrahydroindolizine (THI) photochromes.

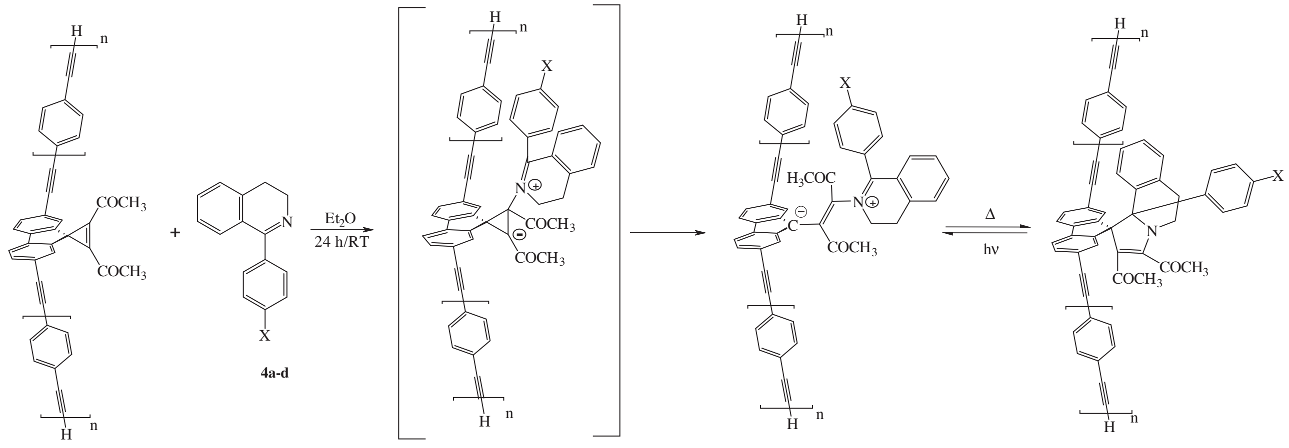


1a, n = 0
1b, n = 1
1c, n = 2

2a, n = 0
2b, n = 1
2c, n = 2

3a, n = 0
3b, n = 1
3c, n = 2

Scheme 1. Preparation of spirocyclopropene precursors **3a–c**.



3a-c

4a-d

5`a-l

5a-l

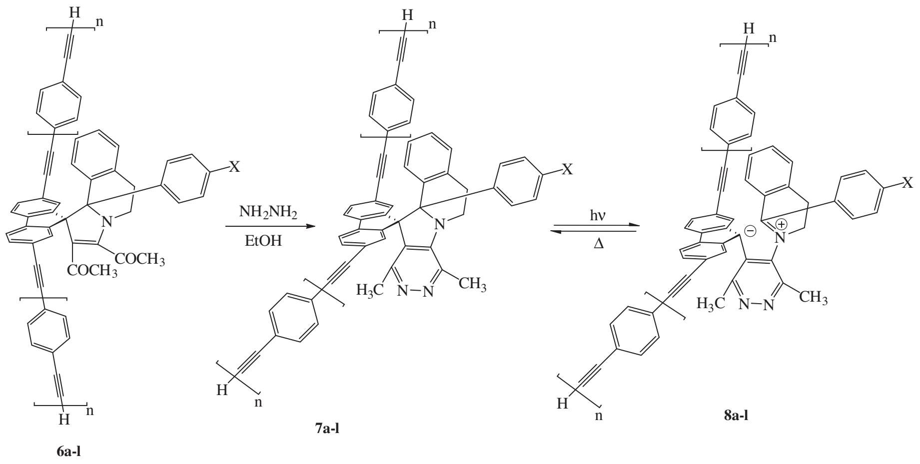
6a-l

Scheme 2. Preparation of photochromic THIs **6a–l** from spirocyclopropenes **3a–c**.

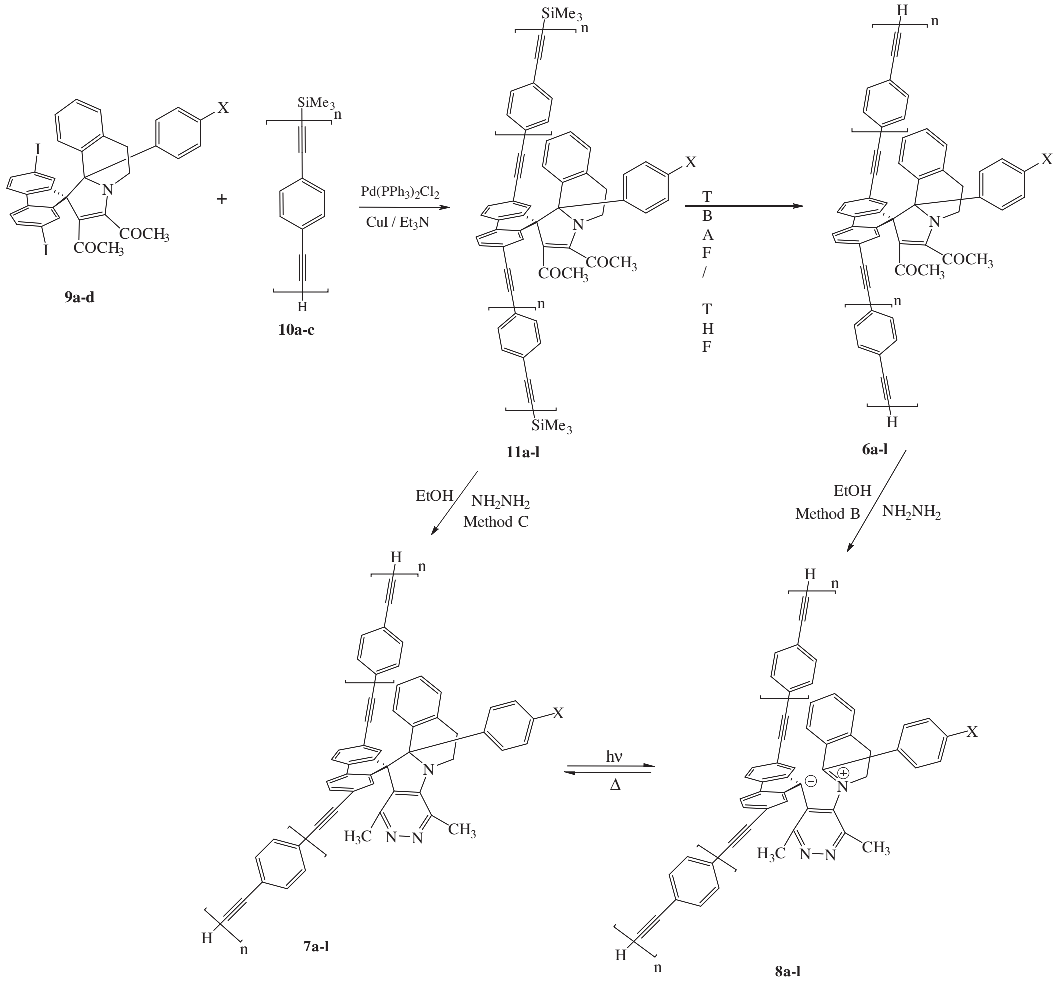
tetrahydroindolizines via palladium-mediated Sonogashira coupling is reported. The kinetics of the 1,5-electrocyclization to obtain different fading rates to suit some industrial applications are the main motivation behind this work.

The diazo derivatives **1a**–**c** have been prepared previously.[30,31] The cycloaddition of hex-3-yne-2,5-dione to the 9-diazofluorene derivatives **1a**–**c** in dry ether in the dark for 24 h led to the formation of the pyrazoles **2a**–**c** in low yields (23%, 29% and 36%, respectively) (Scheme 1).

Photolysis of the pyrazole derivatives **2a**–**c** was carried out in a Schlenck[30–34] photochemical reactor made from Pyrex (λ >290 nm). The source of irradiation was a high-pressure mercury lamp (HPK 125 W, Philips). Solutions to be photolyzed were flushed with dry nitrogen for 30 min before switching on the lamp. Photolysis was



Scheme 3. Method A for the preparation of photochemical THIs **7a**–**l** from THIs **6a**–**l** in ethanol at ambient temperature.



Scheme 4. Methods B and C for the preparation of the targets **7a**–**l** and **8a**–**l**.

performed in dry ether for three hours under a nitrogen atmosphere to give the target diacetyl spirocyclopropene derivatives **3a**–**c** in low yields (29%, 20%, and 14%, respectively).[32–34] The structures of the diacetyl spirocyclopropenes **3a**–**c** were established on the basis of analytical and spectroscopic data.[35]

Nucleophilic addition of substituted 1-aryl-3,4-dihydroisoquinolines **4a**–**d** to spirocyclopropene derivatives **3a**–**c** using the cyclopropene route,[19–27] (Scheme 2) in dry ether at room temperature under a dry nitrogen atmosphere in the absence of light, afforded the new photochromic tetrahydroindolizines (THIs) **6a**–**l**. The reaction occurred through electrophilic addition of the electron-deficient spirocyclopropene derivatives **3a**–**c** to the nitrogen of the *N*-heterocyclic isoquinoline derivatives **4a**–**d**, which led to ring-opening via a cyclopropyl-allyl conversion of **5′a**–**l** to the colored betaines **5a**–**l** (Scheme 2).

Table 1

Substituent patterns, yields, and melting points of the target photochromic THIs **7a**–**l** synthesized by three alternative methods A–C

THI	X	*n*	Method	Yield (%)	mp (°C)
7a	H	0	A	24	191
7a	H	0	B	28	192–193
7a	H	0	C	46	192
7b	H	1	A	28	180
7b	H	1	B	33	182
7b	H	1	C	47	181–182
7c	H	2	A	20	166–168
7c	H	2	B	30	165–167
7c	H	2	C	50	166–167
7d	CH_3	0	A	18	146
7d	CH_3	0	B	23	145–146
7d	CH_3	0	C	41	147
7e	CH_3	1	A	29	136
7e	CH_3	1	B	31	133–135
7e	CH_3	1	C	40	134
7f	CH_3	2	A	30	119
7f	CH_3	2	B	34	121
7f	CH_3	2	C	51	120
7g	F	0	A	44	172
7g	F	0	B	32	173
7g	F	0	C	48	172
7h	F	1	A	41	165
7h	F	1	B	29	164–165
7h	F	1	C	46	166
7i	F	2	A	46	153
7i	F	2	B	33	153
7i	F	2	C	44	152
7j	CN	0	A	52	211
7j	CN	0	B	34	210
7j	CN	0	C	49	209
7k	CN	1	A	49	191
7k	CN	1	B	33	190–191
7k	CN	1	C	40	192
7l	CN	2	A	48	179
7l	CN	2	B	27	178
7l	CN	2	C	43	177–178

Subsequent ring-closure to give THIs **6a**–**l** resulted in a partial slow thermal 1,5-electrocyclization reverse reaction (Scheme 2), which can be reversed upon exposure to light. The prepared THIs **6a**–**l** showed low photostability and decomposition can occur during purification and also on standing for a few days at ambient temperature.[19,23] The decomposition was apparent as a gradual loss of photochromic properties. The THIs **6a**–**l** reach the t_{30} value (a decrease of 30% of the initial absorbance) within the range of 67–92 min depending on both the substituents on the fluorene and isoquinoline moieties. In addition, compared with those THIs bearing ester groups, the THIs under investigation showed a decrease in the t_{30} values by a factor of 7–9. It was found necessary to react them directly after work-up, with hydrazine in absolute ethanol at room temperature for eight hours to afford *cis*-fixed conjugated photochromic THIs **7a**–**l** (Scheme 3). The pure products were obtained as white powders in low to moderate yields (18–52%) after two successive column chromatographic purifications on silica gel using dichloromethane as the eluent.

A successful alternative pathway for the synthesis of the target photochromic THIs **7a**–**l** was achieved through palladium-mediated Sonogashira coupling of THIs **9a**–**d** with alkynes **10a**–**c** in the presence of palladium diphenylphosphinedichloride (5%) and CuI/Et_3N in dry THF to afford the desired photochromic trimethylsilyl THIs **11a**–**l** in 23–42% yields after purification by flash chromatography on silica gel with CH_2Cl_2 as the eluent. Treatment of THIs **11a**–**l** with tetrabutylammonium fluoride (TBAF) in dry THF for 12 h afforded the desilylated products **6a**–**l** in 39–54% yields. Rapid treatment of the THIs **6a**–**l** with hydrazine hydrate in absolute ethanol at ambient temperature for eight hours afforded the target THIs **7a**–**l** in 52–68% yields (Method C, Scheme 4).

On the other hand, deprotection of the silyl groups and reactions of the acetyl groups were achieved in one step when photochromic trimethylsilyl THIs **11a**–**l** were treated with hydrazine hydrate in ethanol for six hours to afford the desired THIs **7a**–**l** in 40–51% yields (Method C, Table 1). Thus, rigid acetylenic bridged THIs **7a**–**l** could be successfully prepared as shown in Scheme 4. The three products obtained from the different pathways showed the same analytical and spectroscopic data as well as the same melting points and mixed melting points (Table 1). The chemical structures of all the synthesized THIs were confirmed on the bases of spectroscopic and analytical methods.[36]

The electronic spectra of the newly synthesized THIs **6a**–**l** and **7a**–**l** were measured in dichloromethane at a concentration of 1×10^{-5} mol/L at 23 °C using a UV–vis spectrophotometer. All the THIs showed yellow color in both the solid state and in dichloromethane (Table 2). The intensities (log ε) of these bands were found to be between 4.01 and 4.46 depending on the number of

Table 2

Absorption spectral data of THIs **6a**–**l** and **7a**–**l** and their corresponding betaines **5a**–**l** and **8a**–**l**, and their kinetic data (monitored by UV–vis-spectrophotometry at ambient temperature for betaines **5a**–**l** and at −30 °C for betaines **8a**–**l**) in CH_2Cl_2 ($c = 1 \times 10^{-5}$ mol/L)

THI/ Betaine	λ_{max} (THI) [nm]	λ_{max} (betaine) [nm]	Color of betaine	$t_{1/2}$ (s) Betaine	THI/ Betaine	λ_{max} (THI) [nm]	λ_{max} (betaine) [nm]	Color of betaine	$t_{1/2}$ (ms) Betaine
6a/5a	389	528	Red	210	**7a/8a**	386	443, 628	Blue	30
6b/5b	388	532	Red	235	**7b/8b**	387	446, 630	Blue	37
6c/5c	395	536	Red–violet	246	**7c/8c**	398	447, 630	Blue	46
6d/5d	387	526	Red	1245	**7d/8d**	385	346, 638	Blue	96
6e/5e	386	528	Red	1394	**7e/8e**	386	346, 640	Blue	106
6f/5f	392	531	Red	1463	**7f/8f**	386	447, 650	Blue-green	117
6g/5g	394	533	Red	968	**7g/8g**	385	440, 623	Blue	79
6h/5h	389	538	Red–violet	1007	**7h/8h**	356	441, 628	Blue	88
6i/5i	390	537	Red–violet	1120	**7i/8i**	388	441, 630	Blue	97
6j/5j	391	542	Red–violet	1369	**7j/8j**	391	450, 625	Blue	119
6k/5k	394	544	Red–violet	1527	**7k/8k**	391	448, 628	Blue	102
6l/5l	395	545	Red–violet	1798	**7l/8l**	392	443, 632	Blue	130

alkyne groups and substitution on the isoquinoline moiety. The absorptions of THIs **6a**–**l** and **7a**–**l** were observed in the far UV-region and showed absorption maxima between 387 and 395 nm (Figs. 2 and 3, Table 2). This absorption is dependent on the number of phenylethyne (n) substituents on the fluorene (region A). As established previously,[26–34] these absorption bands can be assigned to the locally excited π–π^*-transition (LE) located in the butadienyl-vinyl-amine chromophores[29–34] of the THIs **6a**–**l** and **7a**–**l** (Table 2).

Irradiation of THIs **6a**–**l** with ultraviolet light for two minutes with an approximate 7 cm distance between the light and the probe, led to ring-opened betaines **5a**–**l** (Fig. 2). The colored betaine forms **5a**–**l** varied from red to red–violet in CH_2Cl_2 (concentration of 1×10^{-5} mol/L) at room temperature because of their slower 1,5-electrocyclization, which refers to the stabilization of the charged zwitterionic betaines. All the absorption maxima of the colored betaines **5a**–**l** were found to be in the visible region and lie between 528 (betaines **5a**,**e**) and 545 nm (betaine **5l**). The UV–vis spectra of the colored betaines containing a cyano-substituted isoquinoline, as in THIs **5j**–**l**, exhibit a red–violet color and were shifted bathochromically by about 17 nm compared with non-substituted betaine **5a**. This can be attributed to the electron-attracting property of the cyano group.

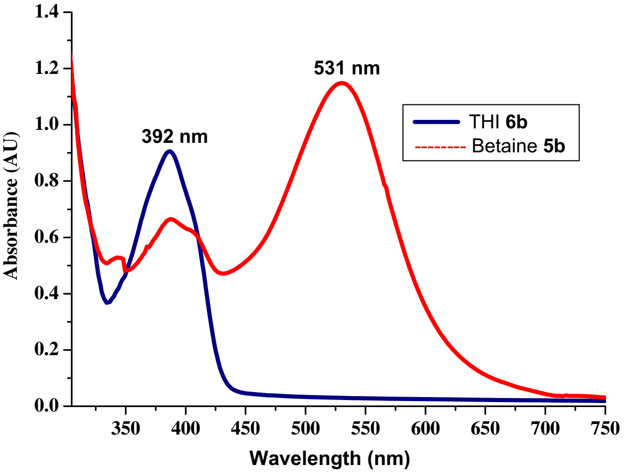


Figure 2. UV–vis spectra of photochromic THI **6f** and the corresponding betaine **5f** in dichloromethane at ambient temperature ($c = 1 \times 10^{-5}$ mol/L).

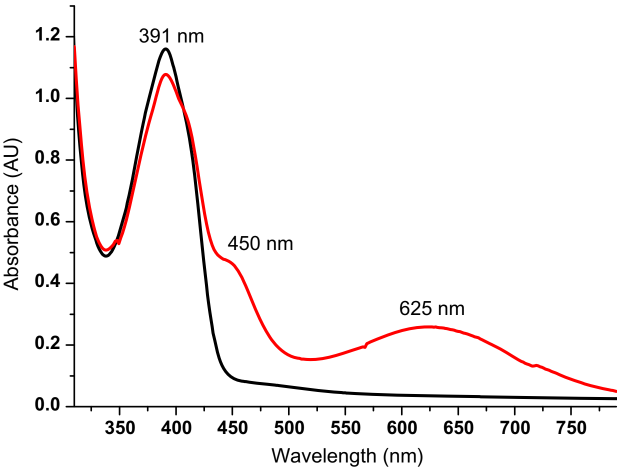


Figure 3. UV–vis spectra of photochromic THI **7j** at ambient temperature and the corresponding betaine **8j** at −30 °C in dichloromethane ($c = 1 \times 10^{-5}$ mol/L).

Furthermore, a noticeable bathochromic shift of about 2–6 nm was observed upon increasing the number of bridged phenyl acetylenic groups from $n = 0$ to $n = 3$, with no dependency on the substituted or non-substituted isoquinoline moiety. This may be attributed to the increasing aromaticity of the fluorene unit conjugated with the aromatic phenyl rings through the bridged acetylenic bond. Additional spectroscopic data on the UV–vis measurements of the colored betaines under investigation are listed in Table 2.

On the other hand, irradiation of the target THIs **7a**–**l** at ambient temperature did not afford the colored betaines **8a**–**l**, and no photochromic properties were evident. This can be attributed to the 1,5-electrocyclic reaction to THIs **7a**–**l**. This phenomenon motivated us to study further the conditions for obtaining the photochromic properties of this class of THI system. Thus, the colored betaines **8a**–**l** were analyzed using an FT–UV–vis photospectrometer after irradiation of the THIs **7a**–**l** at low temperature (−30 °C). The blue to blue–green colored betaines showed two absorption maxima around 440–450 and 620–750 nm depending on the subsitutents on both fluorene and isoquinoline regions (Fig. 3).

The kinetics of the thermal 1,5-electrocyclization of betaines **5a**–**l** were studied by using multichannel FT–UV–vis spectrophotometry (Fig. 4). The kinetic measurements showed that the

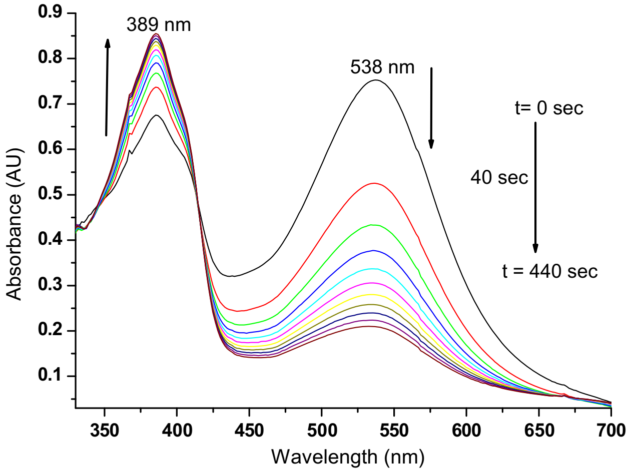


Figure 4. Kinetics of the thermal fading of the 1,5-electrocyclization of betaine **6h** to THI **5h** (cycle time = 40 s, and run time = 440 s) in CH_2Cl_2 ($c = 1 \times 10^{-4}$ mol/L) at 25 °C.

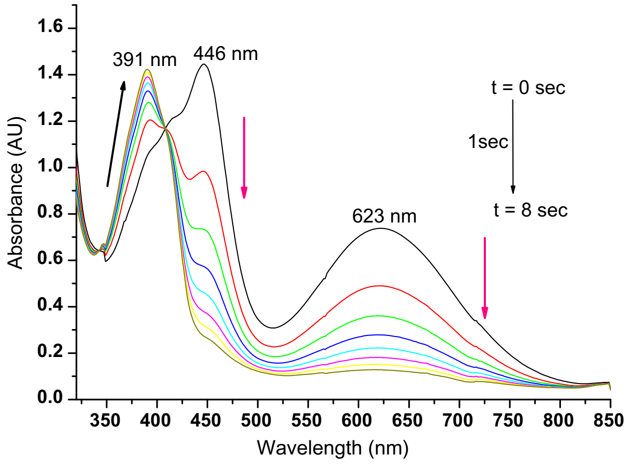


Figure 5. FT–UV–vis kinetics of the thermal fading of the 1,5-electrocyclization of betaine **8e** to THI **7e** (cycle time = 1 s, and run time = 8 s) in CH_2Cl_2 ($c = 1 \times 10^{5}$ mol/L) at −30 °C.

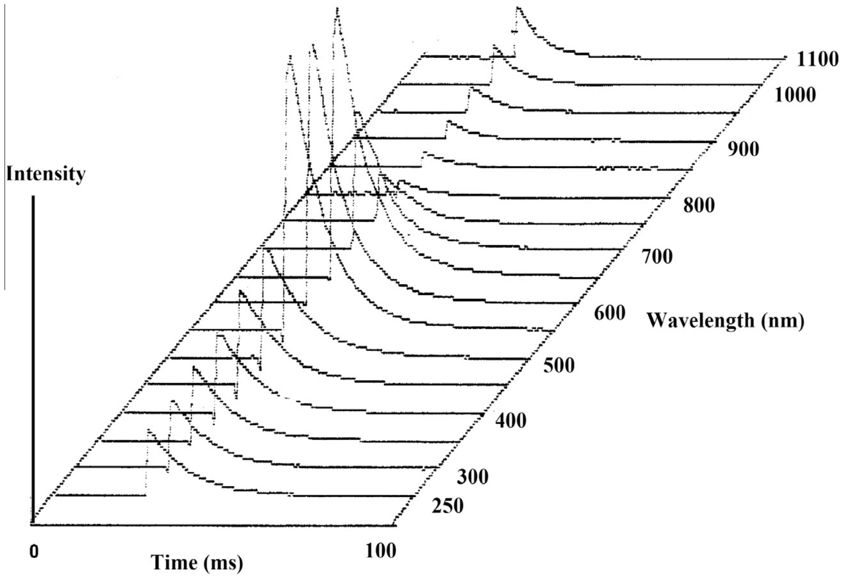


Figure 6. Flash photolysis of THI **7f** for determination of the absorption maxima and half-life time of betaine **8f** in dichloromethane at 23 °C ($c = 1 \times 10^{-5}$ mol/L).

half-lives of the colored betaines **5a**–**l** were in the second domain between 210 and 1798 s (Table 2, Fig. 4).

A highly pronounced increase in the half-lives of the betaines with a methyl substituted isoquinoline (**5d**,**e**,**f**) by approximately a factor of six was observed compared with the half-lives of the betaines **5a**–**c** bearing a non-substituted isoquinoline. This increase in the half-lives may be attributed to the stabilization of the electrostatic charges on the betaines by the electron-donating methyl group.

An increase in the half-lives of the betaines by increasing the number acetylenic bridges from one to three in the fluorene part was recorded. This may be attributed to the bulky sterically hindered phenyl rings substituted on the fluorene moiety. On the other hand, low temperature FT–UV–vis (−30 °C) and flash photolysis techniques were used for detection of both the absorption maxima and the half-lives of the betaine forms **8a**–**l** (Figs. 5 and 6). The half lives were found to be in the millisecond domain and were between 30–130 ms. The rapid 1,5-electrocyclization suggested that the betaine structure exists only in a *cis*-fixed form and cyclized back thermally from this form to the THI skeleton. The pronounced tuning of the absorption maxima and the kinetic properties by changing the substitution in the fluorene region, as well as in the dihydroisoquinoline region, should help this family of compounds to find many applications, particularly in the area of molecular electronics.

In conclusion, carbon-rich molecules based on photochromic tetrahydroindolizines (THIs) have been successfully synthesized via Sonogashira coupling reactions. The coupling reactions between fluorenes (region A) and acetylenic bridges in addition to substitution on the dihydroisoquinolines (region B) resulted in target molecules with extended photochromism. Interesting photochromic properties have been observed by tuning the chemical structure of the photochromic THI by changing the number of acetylenic bridges in the fluorene part and the substitution on the isoquinoline region. This pronounced influence of the substituents in both regions A and C showed strong effects on the UV–vis absorptions of DHIs and betaines, as well as their kinetic properties (half-lives). The *cis*-fixed betaine forms with 1,5-electrocyclization were confirmed using FT–UV–vis and flash photolysis measurements. These broad spectrum photochromic properties of the new THIs and their corresponding betaines should aid in finding suitable applications for these materials.

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35. For example, the ^{1}H NMR (400 MHz, CDCl$_3$) of the spirocyclopropene precursor **3b** showed the following signals: δ 7.89 (d, J = 1.82 Hz, 2H, CH-arom.), 7.80 (d, J = 1.32 Hz, 2H, CH-arom.), 7.55 (d, J = 8.9 Hz, 2H, CH-arom.); 7.61 (dd, J = 8.9, 2.2 Hz, 4H, CH-arom.), 7.48 (dd, J = 8.9, 2.3 Hz, 4H, CH-arom.), 4.02 (s, 2H, CH-acetylenic), 2.32 (s, 6H, 2CH$_3$) ^{13}C NMR (400 MHz, CDCl$_3$) of **3a** 182.9 (2C=O), 147.5 (2C), 142.2 (2C), 139.7 (2C), 135.2 (2CH), 132.5 (8CH), 129.8 (2CH), 127.4 (2CH), 123.8 (4C), 122.7 (2C), 95.2 (2C), 90.3 (2C), 83.5 (2C), 81.6 (2CH), 49.8 (C-spiro), 31.1(2CH$_3$) ; IR (KBr): v = 3028–3092 (C–H, arom.), 2900–2967 (C–H, aliph.), 2252 (acetylenic bond), 1742 (3′–C=O), 1708 (CO–CH$_3$), 1670 (2′–C=O), 1530 (C=C), 1442, 1398, 1278, 1126, 1071, 947, 861, 746 cm^{-1}; HR-MS *m*/*e* (%) 522.16 [M$^+$] (100.0%), 523.17 (44.4%), 524.17 (16.7%), 525,17 (1.4%) Elemental analysis for **3a** (C$_{39}$H$_{22}$O$_2$, 522.16): C, 89.63; H, 4.24; Found: C, 89.81; H, 4.14.
36. For example the ^{1}H NMR (400 MHz, CDCl$_3$) of THI **7k** showed the following signals: δ 7.93 (d, J = 8.1 Hz, 2H, CH-arom.), 7.72 (d, J = 1.32 Hz, 2H, CH-arom.), 7.69 (d, J = 8.1 Hz, 2H, CH-arom.), 7.63 (d, 7.8, 2H, CH-arom.), 7.62 (dd, J = 8.9, 2.2 Hz, 4H, CH-arom.), 7.53 (dd, J = 9.9, 2.6 Hz, 4H, CH-arom.), 7.41 (d, J = 7.8 Hz, 2H, CH-arom.), 7.37 (dd, J = 8.1, 1.9 Hz, 2H, CH-arom.), 7.20 (dd, J = 8.1, 1.9 Hz, 2H, CH-arom.), 4.35 (s, 2H, acetylenic CH); 3.44 (t, J = 2.3 Hz, 2H, CH$_2$), 2.95 (t, J = 2.3 Hz, 2H, CH$_2$); 2.40 (s, 3H, CH$_3$); 1.39 (s, 3H, CH$_3$) ppm; ^{13}C NMR (400 MHz, CDCl$_3$) of THI **7k** showed the following signals: δ 158.2 (C); 146.20 (C); 144.9 (C); 143.4 (C); 142.2 (2C); 141.0 (2C); 119.2 (C); 135.9 (C); 135.7 (C); 134.3 (2CH); 132.7 (2CH); 130.9 (9CH); 129.4 (2CH); 128.3 (2CH); 127.8 (2CH); 126.9 (2CH); 125.8 (2CH); 122.7 (4C); 121.5 (2C); 119.4 (2C); 92.5 (2C); 88.9 (2C); 86.0 (C); 82.7 (2C); 80.4 (2CH); 46.4 (CH$_2$); 31.9 (CH$_2$); 21.7 (CH$_3$); 19.7 (CH$_3$) ; IR (KBr): v = 3030–3059 (C–H, arom.), 2965–2998 (C–H, aliph.), 2242 (acetylenic bond), 2215 (CN), 1741 (3′–C=O), 1712 (CO–CH$_3$), 1687 (2′–C=O), 1637 (C=N), 1523 (C=C), 1421, 1387, 1282, 1174, 1071, 938, 874, 758 cm^{-1}; HR-MS *m*/*e* (%) 750.28 [M$^+$] (100.0%), 750.28 (61.7%), 750.22 (18.1%), 753.20 (2.9%); Elemental analysis for THI **7k** (C$_{55}$H$_{34}$N$_4$): C, 87.97; H, 4.56; N, 7.46; Found: C, 87.69; H, 4.62; N, 7.31.