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Photochromism of dihydroindolizines. Part II—Synthesis and photophysical properties of new photochromic IR-sensitive photoswitchable substituted fluorene-9′-styrylquinolinedihydroindolizines[†]

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epoc ABSTRACT: Twenty-nine new photochromic 2,4,7-substituted fluorene-9′-styrylquinolinedihydroindolizines (DHIs) **4a–χ** were prepared in 45–75% yield via nucleophilic addition of 4-styrylquinolines **2a–k** to substituted spirocyclopropenes **1a–c**. The absorption maxima (λ_{max}) of the colored betaines **3a–χ** were detected by flash photolysis measurements. All betaines **3a–χ** showed two absorption maxima, one in the visible region (450–525 nm) and another in the IR region (825–950 nm). Absorption spectra of betaines **3a–χ** were also recorded at low temperature (77 K) by FT-UV–Vis–near-IR spectroscopy. The kinetics of the fast cyclizing process of betaines **3a–χ** to DHIs **4a–χ** were studied by millisecond flash photolysis and were found to take place in the millisecond range (35–310 ms in dichloromethane solution and 50–425 ms in methanol solution). A transient lifetime (ca 1 ms), measured using laser flash photolysis, was attributed to the transformation of (*Z*) to (*E*)-betaines **3**. Large solvatochromic effects on the absorption maxima (λ_{max}) and a substantial increase in the half-lives ($t_{1/2}$) with solvent polarity of betaines **3a–χ** were also observed. Copyright © 2002 John Wiley & Sons, Ltd.
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KEYWORDS: photochromism; dihydroindolizines; IR-sensitive photoswitches; flash photolysis; thermal stability; solvatochromism

INTRODUCTION

In recent years, photochromic organic compounds have attracted much attention because of their potential use as active material in erasable high-density optical memories,[1–3] optical switches[4–6] and optically switchable gratings.[7–9] Extensive research has been devoted to the study of molecules whose physical properties can be reversibly switched using light. This is due to the possibility of such materials giving a high lateral resolution and short switching time in addition to having an almost instant verification of written data and photooptical technology.[10] The design of light-driven molecular switches is an active area of research, since they are crucial for devices that operate at the molecular and supramolecular levels.[10] A photochromic material is characterized by its ability to undergo reversible transitions between two states that have different optical properties. The transition in at least one direction should occur when the material is exposed to electromagnetic radiation while the transition in the other direction could be accomplished by either electromagnetic radiation of different wavelength or by some other processes (e.g. thermally). Various types of dihydroindolizines (DHIs)[1b,11,12] seem especially promising candidates as photochromic materials owing to their fatigue resistance and short switching time.

Inexpensive, low-intensity GaAs lasers are used in the IR region in many interesting commercial products such as in video recorders and related systems.[1,2,5] In addition, light-switchable materials possessing absorption in the IR region are also of great interest from a device standpoint because the emission wavelengths of semiconductor lasers usually cover this wavelength range. The possibility of switching materials between two states, i.e. in the UV–VIS and near-IR regions, provides another incentive to prepare materials with new properties.[13]

In continuation of our work dealing with the preparation of photochromic materials with absorption colored from (betaines) in the IR region,[1b,11,12] we have undertaken the study of the photophysical properties of some of these materials. In order to provide the best fatigue

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[†] Dedicated to Professor Dr Heinz Dürr on the occasion of his 67th birthday.

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Table 1. Substituent pattern of the 29 DHI derivatives **4a**–χ and their melting-points and reaction yields

Compound **4**	R_1	R_2	R_3	R_4	R_5	M.p. (°C)	Yield (%)
a	Cl	H	H	H	H	167	59
b	Br	H	H	H	H	182	52
c	H	$COOCH_3$	H	H	H	132	60
d	Cl	H	H	H	$N(CH_3)_2$	193	47
e	Br	H	H	H	$N(CH_3)_2$	179	46
f	H	$COOCH_3$	H	H	$N(CH_3)_2$	155	52
g	Cl	H	H	F	H	160	70
h	H	$COOCH_3$	H	F	H	137	75
i	Br	H	H	H	F	141	62
j	H	$COOCH_3$	H	H	F	109	67
k	Cl	H	Cl	H	H	170	66
l	Br	H	Cl	H	H	161	58
m	H	$COOCH_3$	Cl	H	H	139	67
n	Cl	H	Cl	H	Cl	167	72
o	Br	H	Cl	H	Cl	150	63
p	H	$COOCH_3$	Cl	H	Cl	123	74
q	Cl	H	H	Cl	Cl	180	74
r	Br	H	H	Cl	Cl	169	69
s	H	$COOCH_3$	H	Cl	Cl	146	74
t	Cl	H	H	NO_2	Cl	205	49
u	H	$COOCH_3$	H	NO_2	Cl	169	54
v	Cl	H	NO_2	H	H	186	44
w	Br	H	NO_2	H	H	177	43
x	H	$COOCH_3$	NO_2	H	H	162	49
y	Cl	H	H	H	NO_2	215	55
z	H	$COOCH_3$	H	H	NO_2	186	60
α	Cl	H	H	H	$COOCH_3$	122	74
β	Br	H	H	H	$COOCH_3$	112	64
χ	H	$COOCH_3$	H	H	$COOCH_3$	88	75

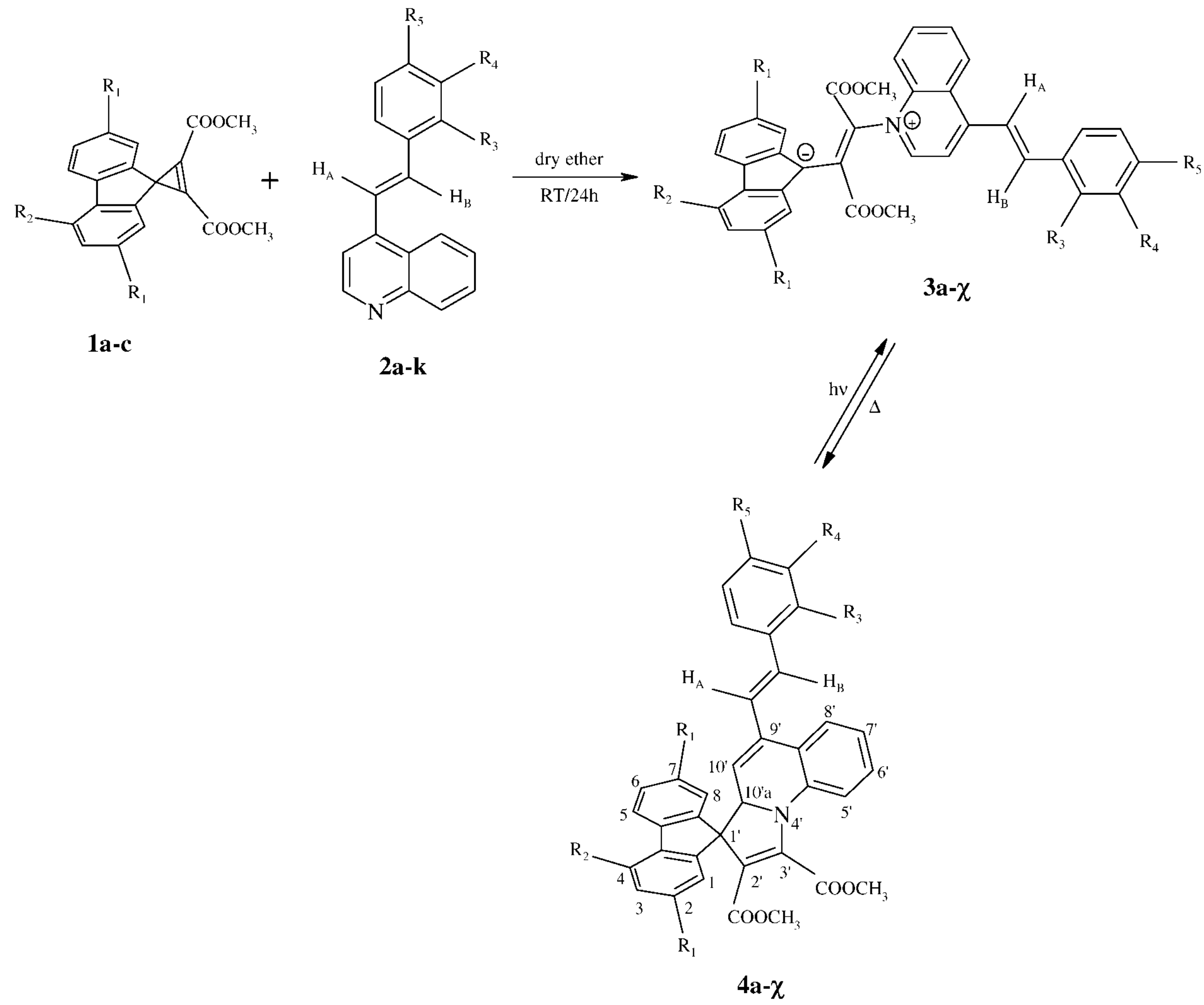
resistance, fluorene was selected as ‘region A’ of the parent molecule **4** (Scheme 1; $R_1 = R_2 = R_3 = R_4 = R_5 = H$) as shown in a previous publication.[1b] A large variety of electron-donating and electron-withdrawing substituents have been introduced on the fluorene and phenyl ring, respectively (F, Cl, Br, NMe_2, COOR, NO_2, etc.; see Scheme 1 and Table 1) taking into account the availability of starting materials and the known ability to generate ‘stable’ betaines. In preceding work, the fluorene substrate was not substituted and the 2′ and 3′ substituents were CN or $CO_2CH(CH_3)_2$. With the new homogeneous family of DHIs **4**, an improvement in the half-lives and a bathochromic effect were expected. Here we report the synthesis of new 2,4,7-substituted fluorene-9′-styrylquinoline DHIs **4a**–χ (see Scheme 1) by the well established spirocyclopropene route[1,2,11,12,14] and describe the absorption spectra and the kinetic properties of the betaines **3a**–χ.

RESULTS AND DISCUSSION

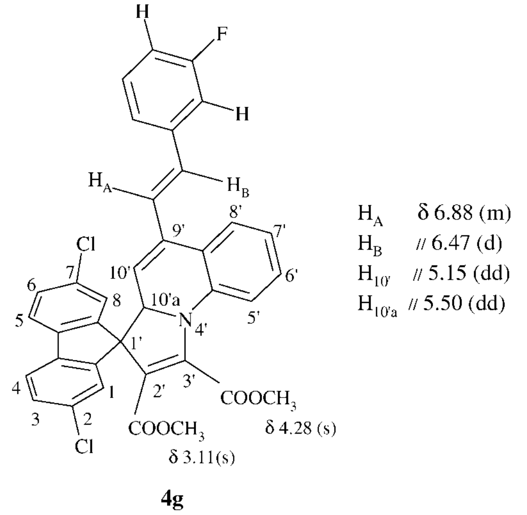
Synthesis of substituted fluorene-9′-styrylquinolinedihydroindolizines 4a–χ

Substituted fluorene spirocyclopropenes **1a**–**c** were obtained via the pyrazole route[14,15] by photolysis of the substituted fluorene pyrazoles using a 125 W high-pressure mercury lamp in dry diethyl ether at room temperature. Products were used without further purification. The different substituted 4-styrylquinoline precursors **2a**–**k** were prepared in moderate to high yields (52–90%) via zinc chloride-catalyzed aldol condensation of 4-methylquinoline with substituted benzaldehydes.[1b,16–18] Reacting the substituted fluorene spirocyclopropenes **1a**–**c** with substituted 4-styrylquinoline derivatives **2a**–**k** in dry diethyl ether at ambient temperature for 24 h under a dry nitrogen atmosphere in the absence of light gave the substituted fluorene-9′-styrylquinolinedihydroindolizines (DHIs) **4a**–χ (Scheme 1) in moderate to high yields (45–75%) (Table 1). This reaction occurs through the nucleophilic addition of the nitrogen of the *N*-heterocyclic quinolines **2a**–**k** to the electron-deficient cyclopropenes **1a**–**c**, leading to colored betaines **3a**–χ via a cyclopropyl–allyl conversion. A subsequent ring closure to DHIs **4a**–χ results in a fast 1,5-electrocyclization reaction (Scheme 1) which can be reversed upon exposure to light. Pure 2,4,7-substituted fluorene-9′-styrylquinoline DHIs **4a**–χ were obtained in all cases by column chromatography on silica using dichloromethane as the eluent (Table 1).

The chemical structures for all the synthesized styryl-



Scheme 1. Synthetic scheme for preparation of photochromic 2,4,7-substituted fluorene-9′-styrylquinoline DHIs **4a–χ** via the spirocyclopropene route



Scheme 2. ^{1}H NMR data for structure determination of DHI **4g**

DHIs **4a–χ** were established by elemental analysis, ^{1}H, ^{13}C, ^{1}H, ^{1}H-COSY, ^{1}H, ^{13}C-COSY and ^{1}H, ^{1}H-NOESY NMR experiments, IR and mass spectrometry (see Experimental). For example, it is worth commenting upon some typical features of the NMR spectra, illustrated by that of **4g** (Scheme 2). The ^{1}H–^{1}H-correlation of **4g** showed that both 2′,3′-methyl ester groups experience no coupling with other protons and appear as two singlets at 3.11 and 4.28 ppm, respectively. The four protons, $H_{10'a}$, $H_{10'}$, H_A and H_B are the most characteristic. The chemical shifts for $H_{10'a}$ [5.50, dd, J ($H_{10'}$, $H_{10'a}$) = 0.95 Hz, ^5J ($H_{10'a}$, H_A) = 4.2 Hz] and $H_{10'}$ [5.13, dd, ^4J ($H_{10'}$, H_A) = 5.6 Hz, J ($H_{10'}$, $H_{10'a}$) = 0.95 Hz] are noticeable; the first is observed downfield owing to the electronegative neighborhood of a nitrogen and a double bond and also the anisotropic effect of the fluorene ring.[1b,11e,19] In contrast, the diamagnetic current of the aromatic nucleus induces a large high-field shift for the $H_{10'}$ signal. The peaks for H_A and H_B were found to be at 6.88 and 6.47 ppm, respectively, with $J(H_{AB})$ = 15.9 Hz, indicating a *trans*

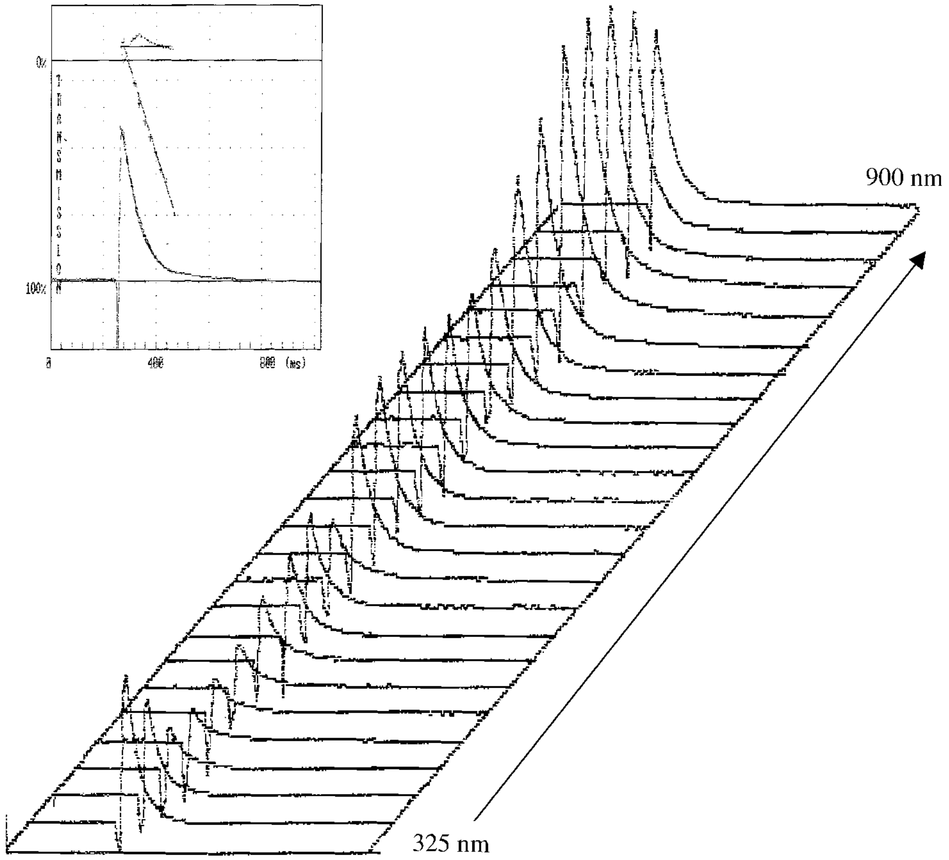


Figure 1. Absorbance decay curves and half-life determination of betaine **3t** at different wavelengths (325–900 nm every 25 nm). Inset: analysis of the curve at 500 nm ($t_{1/2}$ = 55 ms with correlation coefficient = 0.9960)

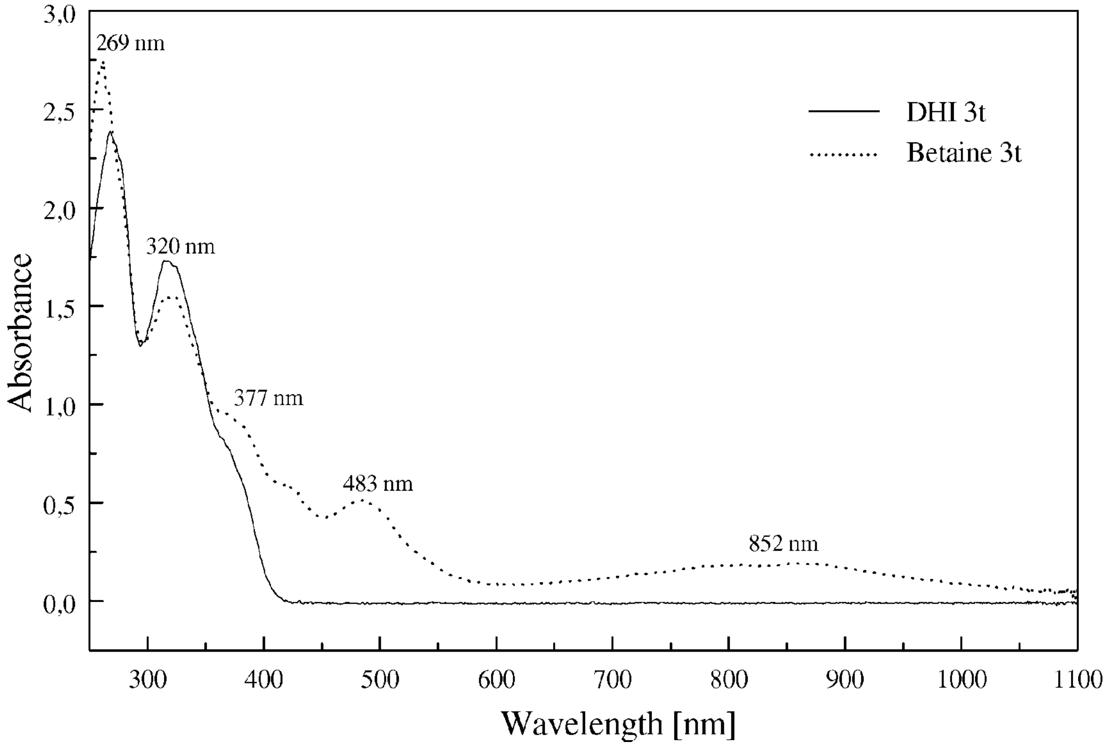


Figure 2. FT-UV spectrum of betaine **3t** and corresponding DHI **4t** ($c = 2 \times 10^{-5}$ mol l^{-1}) at 77 K

Table 2. UV–Vis absorption of DHIs **4a–χ** and betaines **3a–χ** and kinetic data for betaines **3a–χ** in the millisecond range (recorded by millisecond flash photolysis) in CH_2Cl_2 solution (23 °C, $c = 2 \times 10^{-5}$ mol l^{-1})

3/4	λ_{max}(DHI) (nm)	log ε	λ_{max}(betaine) (nm)	$k \times 10^{-3}$ (s^{-1})	$t_{1/2}$ (ms)	Color of betaine
a	330; 365	4.12	475; 800	4.10	169	Orange–brown
b	335; 367	4.15	475; 800	6.13	113	Orange–brown
c	342; 372	4.01	500; 800	2.24	310	Orange–brown
d	272; 350	4.18	475; 525; 775	6.42	108	Blue–violet
e	271; 352	4.21	475; 525; 775	9.12	76	Blue–violet
f	284; 362	4.08	475; 525; 800	4.03	172	Blue–violet
g	330; 366	4.08	500; 825	8.06	86	Orange–brown
h	335; 369	3.99	500; 825	4.65	149	Orange–brown
i	342; 354	4.11	525; 850	15.40	45	Orange–brown
j	348; 360	4.01	525; 850	5.98	116	Orange–brown
k	333; 353	4.10	525; 850	9.00	77	Orange–brown
l	336; 352	4.13	525; 850	12.60	55	Orange–brown
m	272; 357	4.06	550; 850	5.73	121	Orange–brown
n	322; 352	4.16	500; 800	8.56	81	Orange–brown
o	323; 354	4.20	500; 800	13.33	52	Orange–brown
p	329; 359	4.03	525; 825	5.10	136	Orange–brown
q	322; 350	4.13	500; 800	8.45	82	Orange–brown
r	323; 350	4.15	500; 800	12.16	57	Orange–brown
s	328; 352	4.08	525; 825	5.21	133	Orange–brown
t	320; 377	4.00	525; 850	12.60	55	Orange–brown
u	334; 373	3.92	500; 800	19.80	35	Orange–brown
v	339; 382	3.92	475; 800	8.56	81	Orange–brown
w	339; 381	3.96	475; 800	15.40	45	Orange–brown
x	340; 382	3.89	500; 800	5.55	125	Orange–brown
y	338; 379	3.99	475; 800	9.00	77	Orange–brown
z	339; 381	3.90	500; 800	5.55	125	Orange–brown
α	322; 361	4.12	500; 825	7.00	99	Orange–brown
β	323; 362	4.16	500; 825	10.66	65	Orange–brown
χ	321; 364	4.07	525; 850	3.67	189	Orange–brown

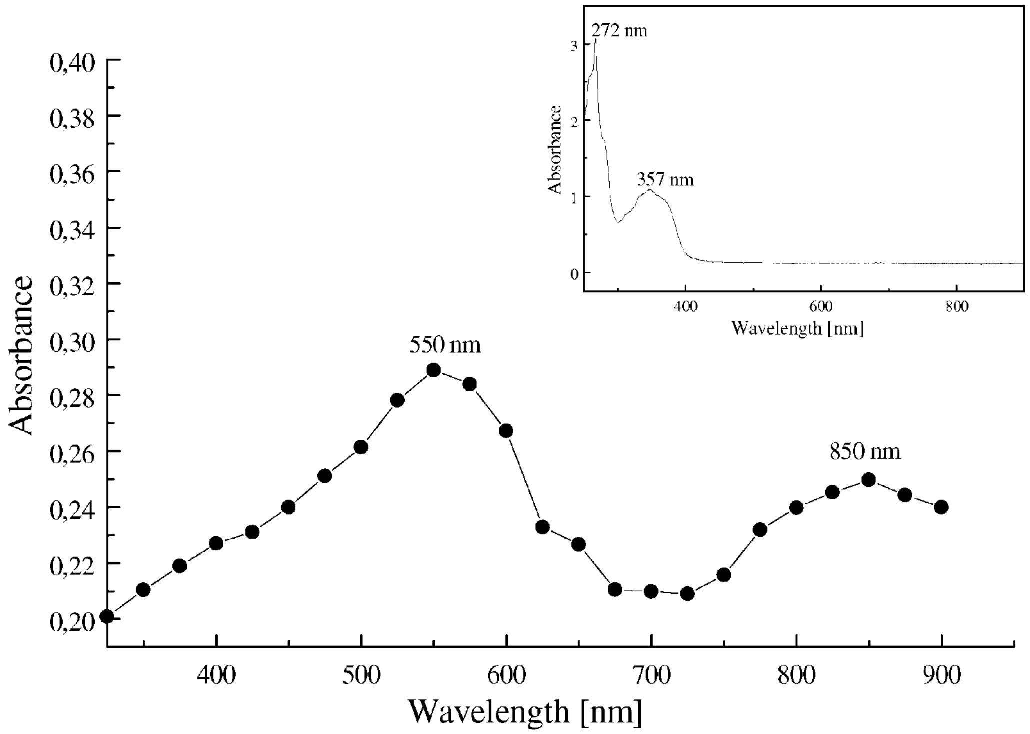


Figure 3. UV–Vis spectrum of betaine **3m** recorded by flash photolysis and plotted using the Origin program at ambient temperature in CH_2Cl_2. The spectra of the other betaines are similar except for **3d–f**, which display three bands (see Table 2). Inset: absorption spectrum of DHI **4m**

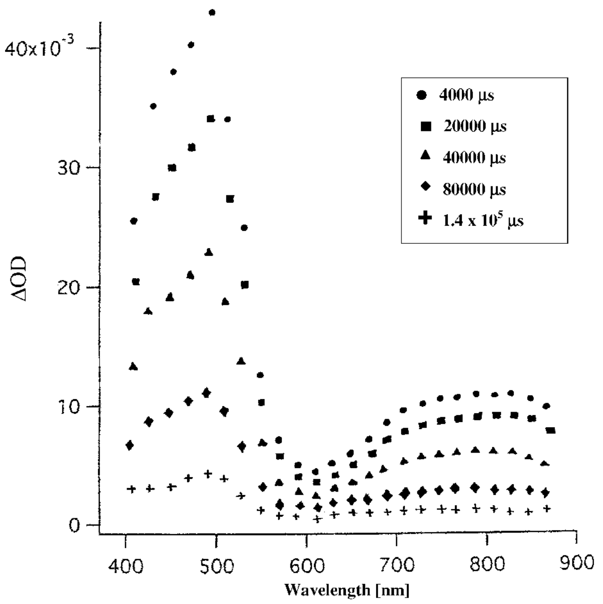


Figure 4. Transient absorption spectra of **3y** in dichloromethane generated by exciting **4y** at 340 nm with a ruby laser and analyzed at different times after the laser pulse at ambient temperature

configuration; H_A is further coupled with $H_{10'}$ and $H_{10'a}$ as indicated above. This coupling proves that the signal at 6.88 ppm is for H_A-styryl and the signal at 6.47 ppm is for H_B-styryl. The other possibility would be that the signal at 6.88 ppm belongs to H_B-styryl; then the couplings would be ^5J and ^6J, which is less likely.

Photophysical properties

Electronic spectra of DHIs **4** and betaines **3** were measured in solution using a UV–Vis spectrometer. However, as compounds **3** are thermally unstable, it was convenient to use the technique of millisecond flash photolysis (Fig. 1), which allowed us to determine, in addition, the kinetics of the thermal back-reaction (**3** → **4**). To investigate more deeply the mechanism of the fast decay of **3**, it was necessary to employ laser flash photolysis equipment (see below).

Photophysical data pertinent to their photochromic properties were obtained from the absorption features of 9′-styrylquinoline-DHI **4a**–χ. The absorption spectra of the new photochromic DHIs **4a**–χ along with the corresponding betaines **3a**–χ were measured in dichloromethane at 23 °C at a concentration of 2×10^{-5} mol l^{-1} using UV–Vis (for the absorption maxima of DHIs, see Figs 2 and 3) and flash photolysis (for the absorption maxima of betaine forms). All the DHIs **4a**–χ are colorless to pale yellow in both the solid state and in solution (Table 2). The absorption maxima of **4a**–χ were observed in the UV region, between 330 and 370 nm, depending on the substituent on the 9′-styryl group. The intensities (log ε) of these bands were found to be between 3.92 and 4.49. As established previously,[1] these absorption bands can be assigned to the locally excited π–π^* transition (LE) located in the butadienylvinylamine chromophore[1,11,19,20] of the DHIs **4**.

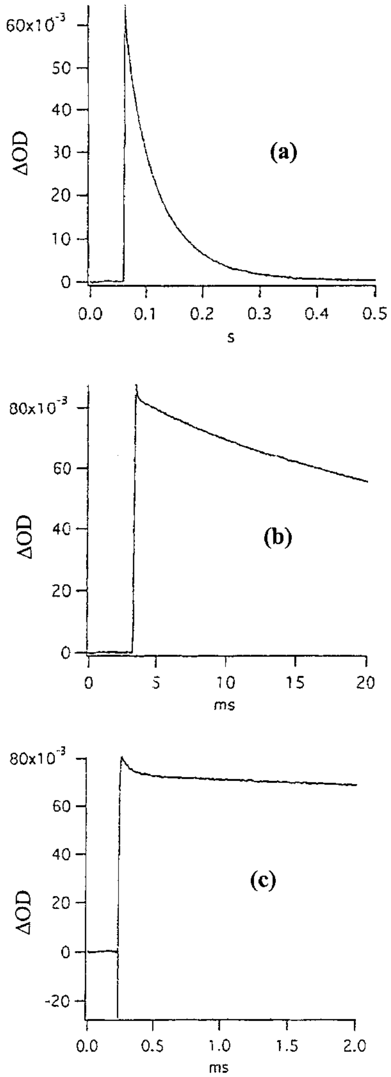
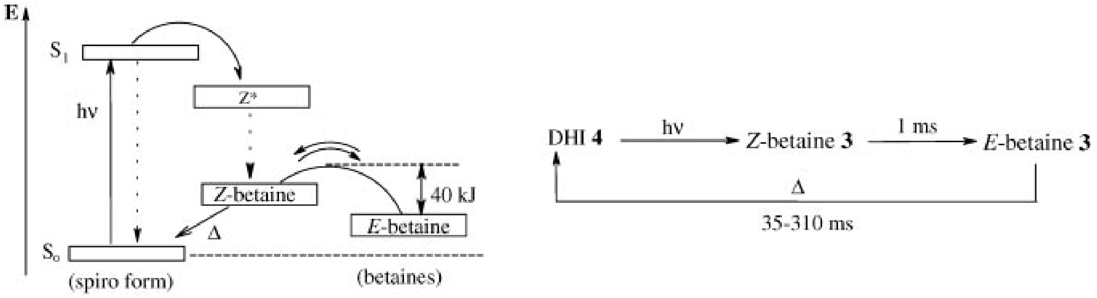


Figure 5. Oscilloscope trace of the growing-in and the decay of the transient absorption at 470 nm of **3y** in dichloromethane analyzed at different laser energies: (a) 1025 µJ and 500 ms sweep rate, (b) 1241 µJ and 20 ms sweep rate and (c) 1101 µJ and 200 ms sweep rate at ambient temperature

The DHIs **4a**–χ could not be colorized by irradiation at room temperature owing to the fast 1,5-electrocyclization of the betaines **3** back to DHIs **4**, but after cooling to low temperature (−20 °C), irradiation of **4a**–χ afforded orange–brown to blue–violet solutions with two absorption bands ranging (Table 2) between 450 and 550 nm and between 800 and 950 nm, respectively (Fig. 2) with a tail extending beyond 1050 nm. To examine the absorption maxima in the IR region, the relationship between the absorbance and wavelength recorded by flash photolysis was plotted (Fig. 3); for instance, the UV–

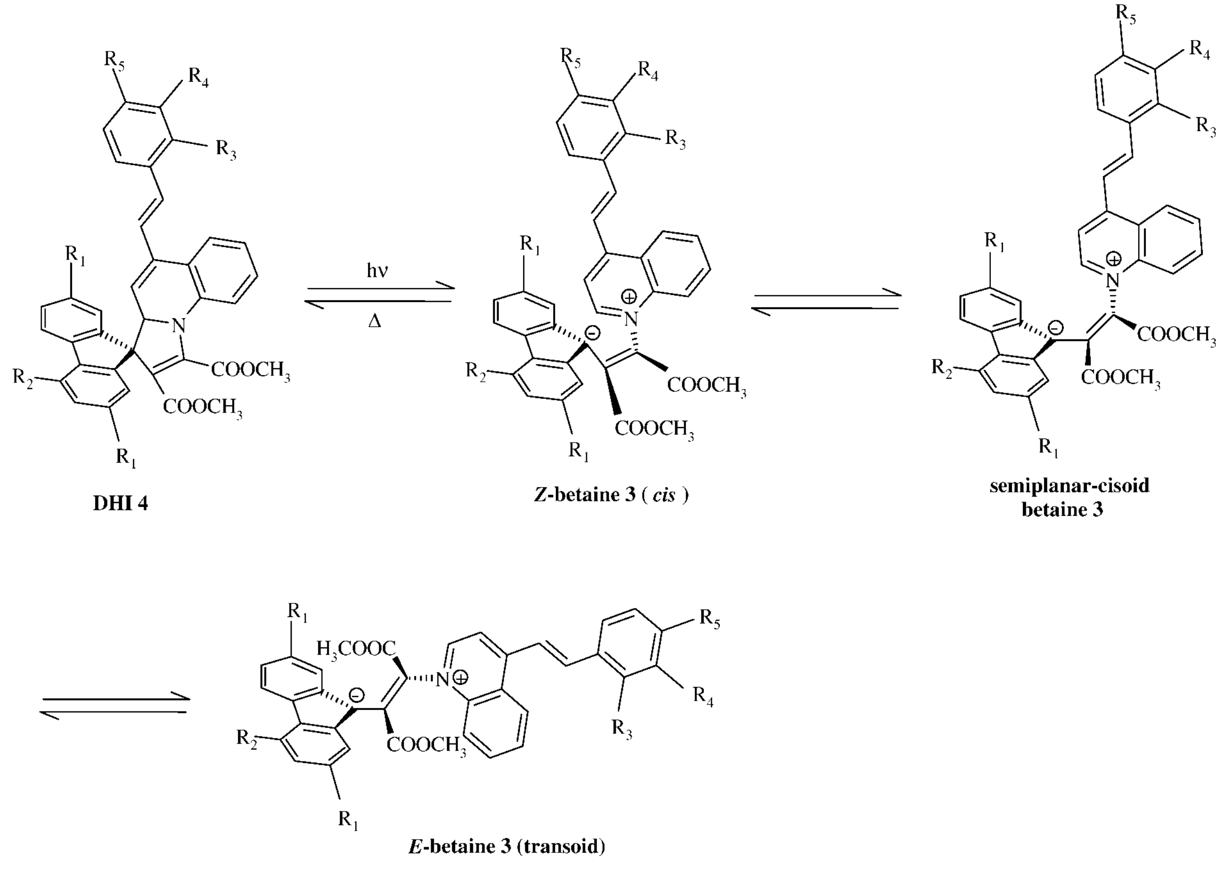


Scheme 3. Simplified representation (not to scale) of the formation of betaines **3** (*Z* and *E* forms) and back thermal cyclization to spiro form **4**; data are for CH_2Cl_2 (see Ref. 19). More details will be given in a forthcoming paper (S. A. Ahmed, Th. Hartmann, H. Dürr, P. Valat, V. Wintgens and J. Kossanyi, in preparation)

Vis spectrum of betaine **3m** (Fig. 3) revealed two maxima, one at 550 nm and the other at 850 nm.

It is noticeable that the *N,N*-dimethyl-substituted phenylstyrylbetaines **3d**–**f** exhibited an additional absorption maximum at 535 nm resulting in a blue–violet color and showed the strongest colorability of all the betaines. This could be attributed to the strong electron-donating ability of the $N(CH_3)_2$ group. Irradiating DHI **4a**–**χ** in CH_2Cl_2 at 77 K (liquid nitrogen) gave the orange–brown to blue–violet colors immediately (Fig. 2). The resulting betaines **3a**–**χ** could be stored at this temperature for several weeks without color decay.

In addition to the photophysical properties of betaines **3a**–**χ** obtained by millisecond flash photolysis at room temperature (Fig. 1) and UV–Vis at 77 K (Fig. 2), a time-resolved transient absorption spectrum was obtained using laser flash photolysis (Nd:YAG laser flash photolysis).[19f,21] Two maxima in the visible and near-IR regions could be detected for the betaines **3a**–**χ** which ranged between 450 and 950 nm. A typical example is



Scheme 4. Proposed structures for the successive betaine forms appearing after light-induced ring opening of the spiro DHIs **4** (see also Scheme 3)

Table 3. Half-lives ($t_{1/2}$) of thermal 1,5-electrocyclization of selected betaines **4a–χ** and E_T (30) values of 10 different solvents ($c = 2 \times 10^{-5}$ mol l^{-1}) at 23 °C

	Betaines $t_{1/2}$ (ms)									
Solvent	**3c**	**3f**	**3i**	**3l**	**3o**	**3q**	**3s**	**3w**	**3χ**	E_T (30)
Pentane	246	134	33	42	41	64	104	34	151	32
Toluene	257	142	37	44	42	66	108	35	154	34
Dioxane	274	149	39	46	46	73	116	40	167	36
Tetrahydrofuran	281	156	42	50	47	76	121	43	174	37
Chloroform	296	164	43	53	51	80	126	44	181	39
Dichloromethane	310	172	45	55	52	82	133	45	189	41
Acetonitrile	349	191	51	59	58	93	150	50	213	46
2-Propanol	370	202	52	62	61	99	156	55	223	49
Ethanol	394	215	58	70	66	106	167	58	238	52
Methanol	423	240	64	75	75	117	188	65	260	56

depicted in Fig. 4. The transient spectrum of **3y** was obtained in dichloromethane by excitation of **4y** at 340 nm with a ruby laser. This can be seen as a spectrum evolving with time.

The change in the transient absorption is better visualized by examining the spectral changes at different wavelengths (Fig. 4). One observes a biexponential decay at 470 nm; the fast decay has a lifetime of 1 ms; it can be found also in the growing-in of the transients with different laser energies (Fig. 5). The biexponential decay is due to two species corresponding to the *Z* and *E* forms of the betaine, respectively (Scheme 3), the latter being more stable[19b,f,22] (S. A. Ahmed, Th. Hartmann, H. Dürr, P. Valat, V. Wintgens and J. Kossanyi, in preparation). The slow decay was not measured under these conditions[22] (S. A. Ahmed, Th. Hartmann, H. Dürr, P. Valat, V. Wintgens and J. Kossanyi, in preparation). A simplified representation of the formation of (*Z*)- and (*E*)-betaines is given in Scheme 3; it takes into account the energy barrier between the (*E*)-betaine and the (*Z*)-betaine estimated previously[19b,f] to be of the order of 40 kJ mol^{-1}. It seems that previous results[11,19] favor an adiabatic process to an open excited intermediate (*Z**) which gives the *cis*-betaine through a diabatic process (comprehensive details on the fluorescence and transient spectroscopic data of these series of compounds will be discussed in a separate paper) (S. A. Ahmed, Th. Hartmann, H. Dürr, P. Valat, V. Wintgens and J. Kossanyi, in preparation). The proposed structures of the light-induced intermediates between spiro-DHIs and (*E*)-betaine forms are represented in Scheme 4.

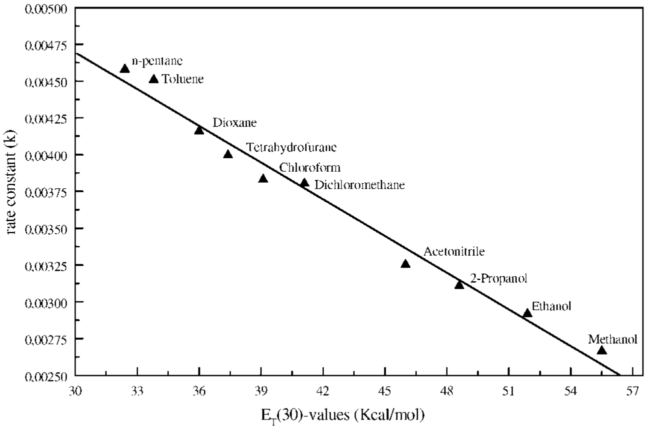


Figure 6. Plot of the decay rate constant (*k* in s^{-1}) for betaine **3χ** ($c = 2 \times 10^{-5}$mol l^{-1}) at 296 K as a function of solvent polarity E_T(30). Correlation coefficient $r^2 = 0.9913$

Solvatochromism

A strong effect of the solvent polarity on the λ_{max} and the half-lives of betaine **3a–χ** was observed. Changing the solvent from dichloromethane to ethanol causes hypsochromic shifts of $\Delta\nu \approx +400$ cm^{-1} in the visible region, and markedly larger shifts of $\Delta\nu \approx +900$ cm^{-1} in the near-IR region. This solvatochromic effect is in agree-

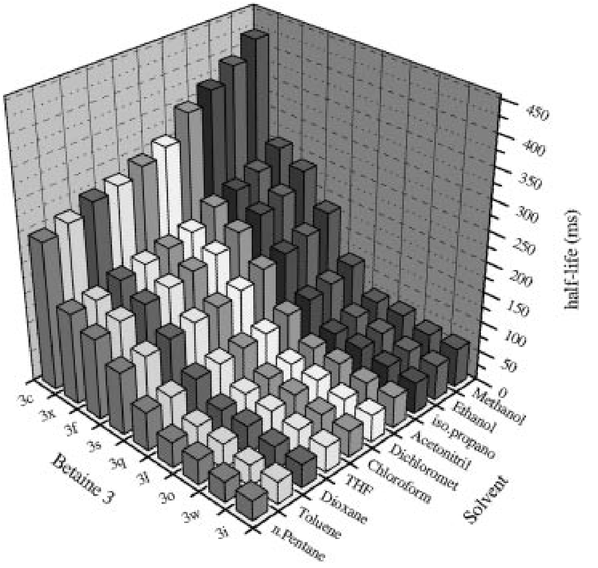


Figure 7. Balcony diagram showing the relationship between the half-lives ($t_{1/2}$) of betaines **3c**, **f**, **i**, **l**, **o**, **q**, **s**, **w**, **χ** with differing solvent polarity ($c = 2 \times 10^{-5}$mol l^{-1}) at 296 K

ment with previous observations on DHIs.[23] These two solvatochromic shifts are ascribable to π–π^* transitions in the visible region and charge-transfer transitions in the near-IR region.[24]

The effect of solvent polarity was also studied by using flash photolysis to determine the half-life ($t_{1/2}$) of betaines **3a**–$\boldsymbol{\chi}$ in 10 different solvents (Table 3). As expected, the half-lives increase with increasing solvent polarity (Figs 6 and 7). This is due to the partial charge transfer from the betaine form to the solvent and vice versa, as a result of the weak Coulombic exchange effects. Therefore, the charged zwitterionic structure was stabilized by increasing solvent polarity due to these electrostatic interactions.[25]

CONCLUSION

New photochromic compounds **4a**–$\boldsymbol{\chi}$ derived from 9′-styrylquinolinedihyroindolizines (DHIs) based on 1,5-electrocylization having absorption in the Vis–IR region were prepared. The chemical structures of **4a**–$\boldsymbol{\chi}$ were assigned by NMR, IR, MS and elemental analysis. Interestingly, ^4J and ^5J couplings between $H_{10'}$, $H_{10'a}$ and H_A, H_B, respectively, were detected using 2D-NMR spectroscopy. Irradiation of compounds **4a**–$\boldsymbol{\chi}$ led to colored betaines **3a**–$\boldsymbol{\chi}$ showing two main absorption maxima, one in the visible and the other in the IR region, which were observed using millisecond flash photolysis and UV–Vis spectrometry at low temperature (77 K). Of note, the *N,N*-dimethyl-substituted styrylphenylbetaines **3d**–**f** show specific absorption in the visible region and may potentially be used as non-linear optical materials. The photochromism of the fast electrocyclization process of the colored betaines **3a**–$\boldsymbol{\chi}$ in the millisecond range was recorded by millisecond flash photolysis at ambient temperature. This series of substituted DHIs show improved physical properties compared with previous related compounds:[1b] longer half-lives and further bathochromic shifts in the IR region (more than 750 cm^{-1}). The transient absorption lifetime recorded by laser flash photolysis was found to be about 1 ms. An increase in the half-lives of selected betaines **3a**–$\boldsymbol{\chi}$ with increasing solvent polarity was observed. The betaines **3a**–$\boldsymbol{\chi}$ can be used as IR-sensitive recording or storage materials at 77 K for several weeks without any color decay.

EXPERIMENTAL

The solvents used (Aldrich or Merck, spectroscopic grade) were dried, according to standard procedures,[26] over sodium or potassium metal (diethyl ether, toluene, THF, pentane, -hexane), CaH_2 (ethanol, methanol, 2-propanol) and P_2O_5 (CH_2Cl_2, $CHCl_3$, acetonitrile) and were all stored over sodium wire or molecular sieve (5 Å) in brown bottles under a nitrogen atmosphere.

Spirocyclopropene derivatives were obtained via photolysis of the corresponding pyrazoles prepared according to reported procedures. Photolysis was carried out in a Schenck[27] photochemical reactor made from Pyrex ($\lambda > 290$ nm). The source of irradiation was a Philips HPK 125 W high-pressure mercury lamp. Solutions to be photolyzed were flushed with dry nitrogen for 30 min before switching on the UV lamp. The progress of the reaction and the purity of the products isolated were monitored using TLC. Separation and purification of all synthesized photochromic materials were carried out using column chromatography (1 m × 2 cm i.d. column) on silica gel with CH_2Cl_2 as eluent. Melting-points were measured on a Gallenkamp or a Büchi (Smp-20) melting-point apparatus.

All NMR spectra were collected on a Bruker DRX 500 spectrometer (500 MHz) in $CDCl_3$ using TMS as the internal standard. Chemical shifts (δ) are reported in ppm. IR spectra were measured on a Bio-Rad Excalibur series FTS 3000 instrument. Mass spectra were recorded on a Mat-90 mass spectrometer (Finnigan MAT). Elemental analyses (CHN) were carried out on a LECO CHNS-932 analyzer. UV spectra were recorded on an HP 6543 FT-UV–Vis computer–spectrometer. Millisecond flash photolysis was carried out with a Photoflash (METZ 32 Z-1) 12 V (50 W) halogen lamp. The laser flash photolysis experiments were carried out with frequency-double-pulsed ruby laser excitation and an Nd:YAG laser.[19f,21] A detailed description of the experimental set-up has been published[19f,21,22] (S. A. Ahmed, Th. Hartmann, H. Dürr, P. Valat, V. Wintgens and J. Kossanyi, in preparation).

Full spectroscopic and elemental analysis data for DHIs **4a**–**c** as reference compounds are listed below. NMR, IR, MS and elemental analysis data for **4d**–$\boldsymbol{\chi}$ are provided as supplementary material at the epoc website at http://www.wiley.com/epoc.

Preparation of dimethyl 9′-(substituted styryl)-spiro(substituted fluorene-9,1′-pyrrolo[1,2-a]quinoline)-2,3-dicarboxylate 4a–χ

General procedure. To a solution of spirene **1a**–**c** (0.001 mol) in dry diethyl ether (50 ml) was added a solution of substituted 4-styrylquinolines **2a**–**k** (0.001 mol) in dry diethyl ether (10 ml) over 15 min under a dry nitrogen atmosphere. The mixture was stirred at room temperature for about 24 h (TLC controlled) in the dark. The solvent was evaporated under reduced pressure and the pure products were obtained by column chromatography on silica gel using CH_2Cl_2 as eluent and recrystallized from the appropriate solvent to give DHIs **4a**–χ as white to yellow needles in 45–75% yield.

*Dimethyl-9′-styrylspiro(2,7-dichlorofluorene-9,1′-pyrrolo[1,2-a]quinoline)-2′,3′-dicarboxylate (**4a**).* Reactants: 375 mg (0.001 mol) spirene **1a**, 231 mg (0.001 mol) 4-styrylquinoline **2a**; yield 358 mg (59.2%) as pale yellow crystals from diethyl ether–CH_2Cl_2 (8:2); m.p. 167 °C. ^{1}HNMR ($CDCl_3$): $\delta = 7.75–7.77$ (m, 2H, CH-arom.), 7.56–7.58 (d, $J = 7.12$ Hz, 1H, CH-arom.), 7.47–7.49 (d, $J = 7.11$ Hz, 1H, CH-arom.), 7.35–7-42 (m, 2H, CH-arom.), 7.27–7.30 (m, 3H, CH-arom.), 7.17–7.22 (m, 3H, CH-arom.), 7.04–7.08 (dd, $J = 7.00$ Hz 1H, CH-arom.), 6.90–6.99 (dt, $J = 7.55$, 1H, CH-arom.), 6.75–6.79 (m, 1H, H_A), 6.40–6.43 (d, $J_{AB} = 15.92$ Hz, $H_{10'a}$1H, H_B), 5.45 (dd, 1H, $H_{10'a}$), 5.04–5.05 (dd, 1H, $H_{10'}$), 4.09 (s, 3H, 3′-CH_3), 3.25 (s, 3H, 2′-CH_3) ppm. ^{13}CNMR ($CDCl_3$): $\delta = 164.50$ (3′-CO), 164.22 (2′-CO), 69.81 (10′a-C), 63.12 (spiro-C), 53.70 (3′-CH_3), 51.14 (2′-CH_3) ppm. MS (70 eV): *m/z* (%) = 607.50 [M^+] (7.18), 43.00 [B^+] (100). IR (KBr): $v = 3070$ (CH, arom.), 2819–2989 (CH, aliph.), 1740 (3′-C=O), 1683 (2′-C=O), 1587 (C=C), 1493, 1257, 1209, 1159, 1092, 969, 722, 698 cm^{-1}. Elemental analysis for $C_{36}H_{25}Cl_2NO_4$ (MW = 606.50): calc. C, 71.29; H, 4.15; N, 2.31; Cl, 11.69; found C, 71.32; H, 4.11; N, 2.33; Cl, 11.66%.

*Dimethyl-9′-styryl-spiro(2,7-dibromofluorene-9,1′-pyrrolo[1,2-a]quinoline]-2′,3′-dicarboxylate (**4b**).* Reactants: 464 mg (0.001 mol) spirene **1b**, 231 mg (0.001 mol) 4-styrylquinoline **2a**; yield 360 mg (51.8%) as pale yellow crystals from diethyl ether–CH_2Cl_2 (8:4); m.p. 182 °C. ^{1}HNMR ($CDCl_3$): $\delta = 7.74–7.78$ (m, 2H, CH-arom.), 7.57–7.59 (d, $J = 7.12$ Hz, 1H, CH-arom.), 7.46–7.48 (d, $J = 7.11$ Hz, 1H, CH-arom.), 7.38–7-44 (m, 2H, CH-arom.), 7.25–7.29 (m, 3H, CH-arom.), 7.20–7.25 (m, 3H, CH-arom.), 7.00–7.04 (dd, $J = 7.00$ Hz, 1H, CH-arom.), 6.91–6.98 (dt, $J = 7.55$, 1H, CH-arom.), 6.77–6.80 (m, 1H, H_A), 6.44–6.47 (dd, $J_{AB} = 15.92$ Hz, 1H, H_B), 5.41 (dd, 1H, $H_{10'a}$), 5.03–5.04 (dd, 1H, $H_{10'}$), 4.11 (s, 3H, 3′-CH_3), 3.22 (s, 3H, 2′-CH_3) ppm. ^{13}CNMR ($CDCl_3$): $\delta = 164.49$ (3′-CO), 164.25 (2′-CO), 69.78 (10′a-C), 63.08 (spiro-C), 53.75 (3′-CH_3), 51.17 (2′-CH_3) ppm. MS (70 eV): *m/z* (%) = 697.43 [M^{2+}] (12.98), 43.00 [B^+] (100). IR (KBr): $v = 3076$ (CH, arom.), 2832–2998 (CH, aliph.), 1741 (3′-C=O), 1686 (2′-C=O), 1588 (C=C), 1494, 1260, 1202, 1153, 1094, 961, 721, 689 cm^{-1}. Elemental analysis for $C_{36}H_{25}Br_2NO_4$ (MW = 695.41): calc. C, 62.18; H, 3.62; N, 2.01; Br, 22.98; found C, 62.19; H, 3.65; N, 2.00; Br, 22.93%

*Dimethyl-9′-styrylspiro(4-carboxymethylfluorene-9,1′-pyrrolo[1,2-a]quinoline)-2′,3′-dicarboxylate (**4c**).* Reactants: 362 mg (0.001 mol) spirene **1c**, 231 mg (0.001 mol) 4-styrylquinoline **2a**; yield 360 mg (60.5%) as white crystals from diethyl ether; m.p. 132 °C. ^{1}H-NMR ($CDCl_3$): $\delta = 7.74–7.79$ (m, 2H, CH-arom.), 7.58–7.60 (d, $J = 7.12$ Hz, 1H, CH-arom.), 7.42–7.47 (d, $J = 7.11$ Hz, 1H, CH-arom.), 7.40–7-44 (m, 2H, CH-arom.), 7.27–7.33 (m, 4H, CH-arom.), 7.22–7.27 (m, 3H, CH-arom.), 7.15–7.18 (dd, $J = 7.25$ Hz 1H, CH-arom.), 6.90–6.96 (dt, $J = 7.70$, 1H, CH-arom.), 6.79–6.84 (m, 1H, H_A), 6.47–6.50 (d, $J_{AB} = 15.90$ Hz, 1H, H_B), 5.45–5.47 (dd, 1H, $H_{10'a}$), 5.00–5.01 (dd, 1H, $H_{10'}$), 4.27 (s, 3H, 3′-CH_3), 3.99 (s, 3H, 4-CH_3), 3.22 (s, 3H, 2′-CH_3) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 164.68$ (3′-CO), 164.35 (4-CO), 164.21 (2′-CO), 69.73 (10′a-C), 63.01 (spiro-C), 53.69 (3′-CH_3), 52.54 (4-CH_3), 51.17 (2′-CH_3) ppm. MS (eV): *m/z* (%) = 595.60 [M^+] (8.89), 43.00 [B^+] (100). IR (KBr): $v = 3120$ (CH, arom.), 2840–2985 (C-H, aliph.), 1741 (3′-C=O), 1710 (4-C=O), 1690 (2′-C=O), 1592 (C=C), 1497, 1240, 1164, 1081, 966, 715, 681 cm^{-1}. Elemental analysis for $C_{38}H_{29}NO_6$ (MW = 595.66): calc. C, 76.63; H, 4.91; N, 2.35; found C, 76.67; H, 4.90; N, 2.38%.

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