

Synthesis of IR-sensitive photoswitchable molecules: photochromic 9'-styrylquinolinedihydroindolizines

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ABSTRACT: New mono- (**5a–t, w**) and biphotochromic (**5u, v**) 9'-styrylquinolinespirodihydroindolizines (DHIs) with IR-absorbing colored forms (**4**) were prepared. The conformation and configuration of these new DHIs were investigated by NMR studies and the structure was proved by x-ray analysis. The kinetics of the fast cyclizing process of betaine **4** to DHI **5** takes place in the millisecond range and were studied by flash photolysis. The absorption bands of the betaines **4** were recorded at low temperature by FT-UV/VIS/near-IR spectroscopy. Large solvent effects on the absorption maxima of betaines **4** were observed. Copyright © 2000 John Wiley & Sons, Ltd.

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KEYWORDS: IR-sensitive photoswitchable molecules; photochromic compounds; 9'-styrylquinolinedihydroindolizines

INTRODUCTION

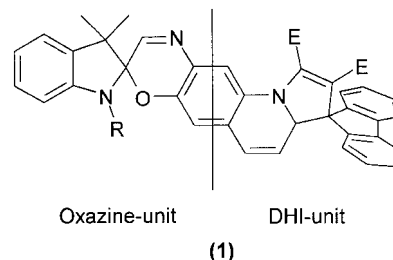
Low-intensity cheap GaAs Lasers are used in the infrared region in highly interesting commercial materials such as in video recorders and related systems.^{1–3} In addition, light-switchable materials possessing absorption in the infrared region are also of great interest. The possibility of switching back materials between two states, i.e. in the UV/VIS and the near-IR regions, provides another incentive to prepare materials with new properties.^{4–7}

We reported recently on a new material containing two photochromic units showing different photochemical reactions in one molecule.^{7,8} These molecules, based on spiro[fluorene-9,1'-((3,3-dimethylspiro[indolino-2,2'-(2H)[1,4]benzoxazino)][6,5e]indolizine)] (**1**), contained both a photochromic spirooxazine and a dihydroindolizine that generated a system absorbing at long wavelengths stretching to the near-IR region beyond 900 nm.⁷

Owing to the short half-life ($\tau_{1/2} = 150$ ms) of the open form of the spirooxazine part,³ the infrared absorption fades faster than the 9-styrylquinolinespirodihydroindolizine (DHI) colored betaine form that has a much longer lifetime (a factor of 40, $\tau_{1/2} = 6$ s).

The need for a material showing infrared absorption

and only one decay for the colored form led us to investigate simple DHI compounds again.^{9,10}

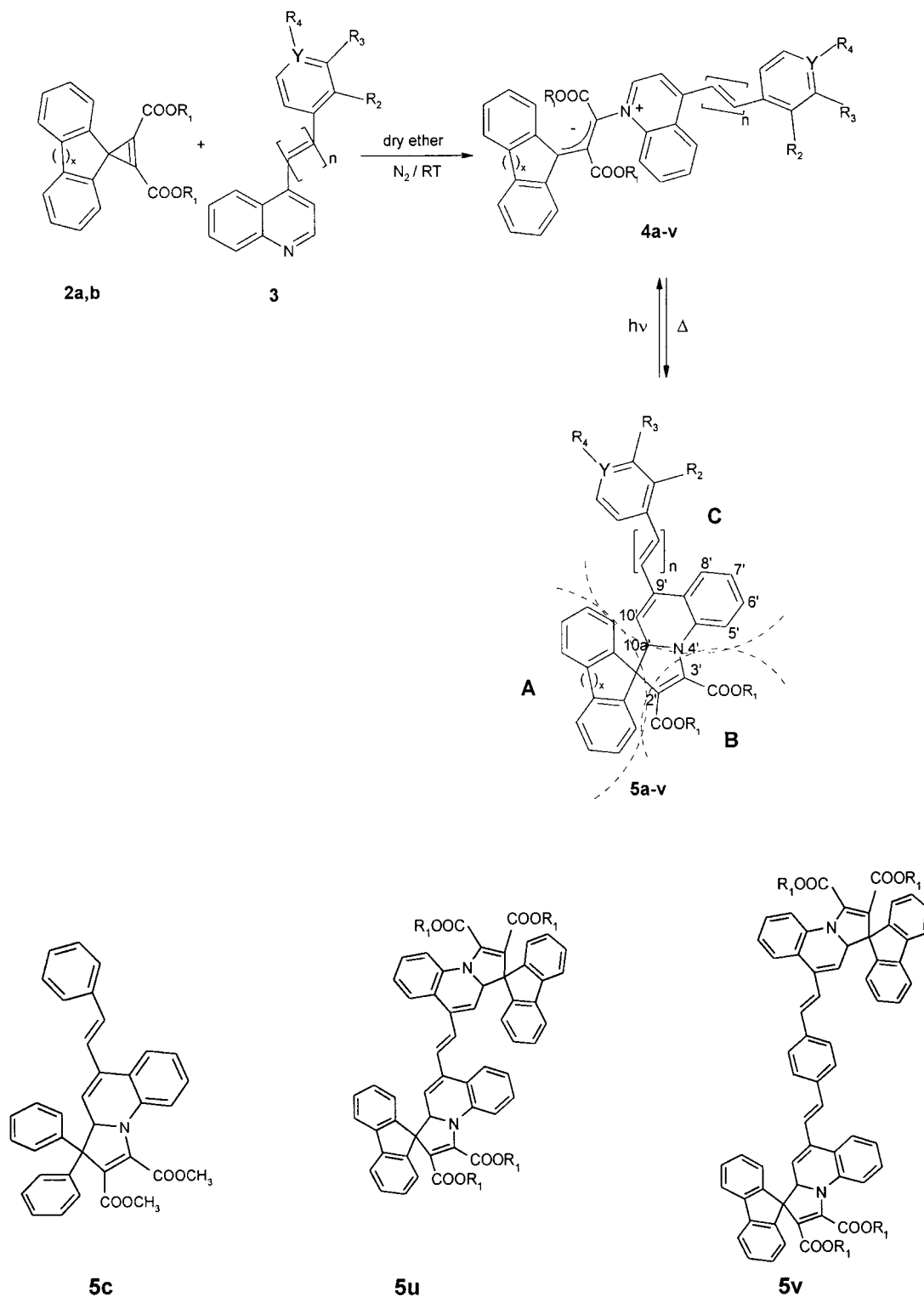


In this paper, we describe (1) the syntheses of new 4-styrylquinolinespirodihydroindolizines (**5**) by the well established spirocyclopropene route,^{10,11} (2) structural proof for the new molecules (**5**) by spectral and x-ray data and (3) irradiation of the DHI **5** to ring-open betaines **4** with absorptions in the IR region.

SYNTHESIS OF 9'-STYRYLQUINOLINEDIHYDROINDOLIZINES

The 4-styrylquinoline precursors **3** were obtained in moderate to good yield via aldol condensation of lepidine with substituted benzaldehydes using zinc chloride as condensing agent.^{12,13} The 4,4'-bisstyrylquinoline precursors for DHI (**5u, v**) were obtained by condensation of lepidine with 4-quinolinecarboxaldehyde and terephthalaldehyde in the presence of methanesulfonic acid.¹⁴

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Scheme 1. Preparation of diester DHI **5a-v** (regions A, B and C are indicated)

Spirene route

The photochromic systems **5a-v** were formed by reacting various substituted 4-styrylquinolines (**3**) with fluorene-spirocyclopropenes (**2**) in good to moderate yields.

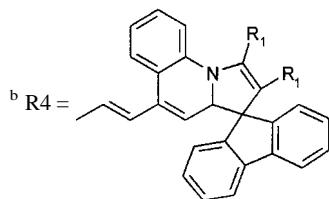
Employing diphenylspirocyclopropene, however, gave a low yield of **5c**.

The biphotocromic systems **5u** and **v** were synthesized in low yield by reacting 2 mol of spirene **2b** with 1 mol of the corresponding 4,4'-bisquinoline bases. The

Table 1. 9'-Styryldihydroindolizines: yields and melting-points

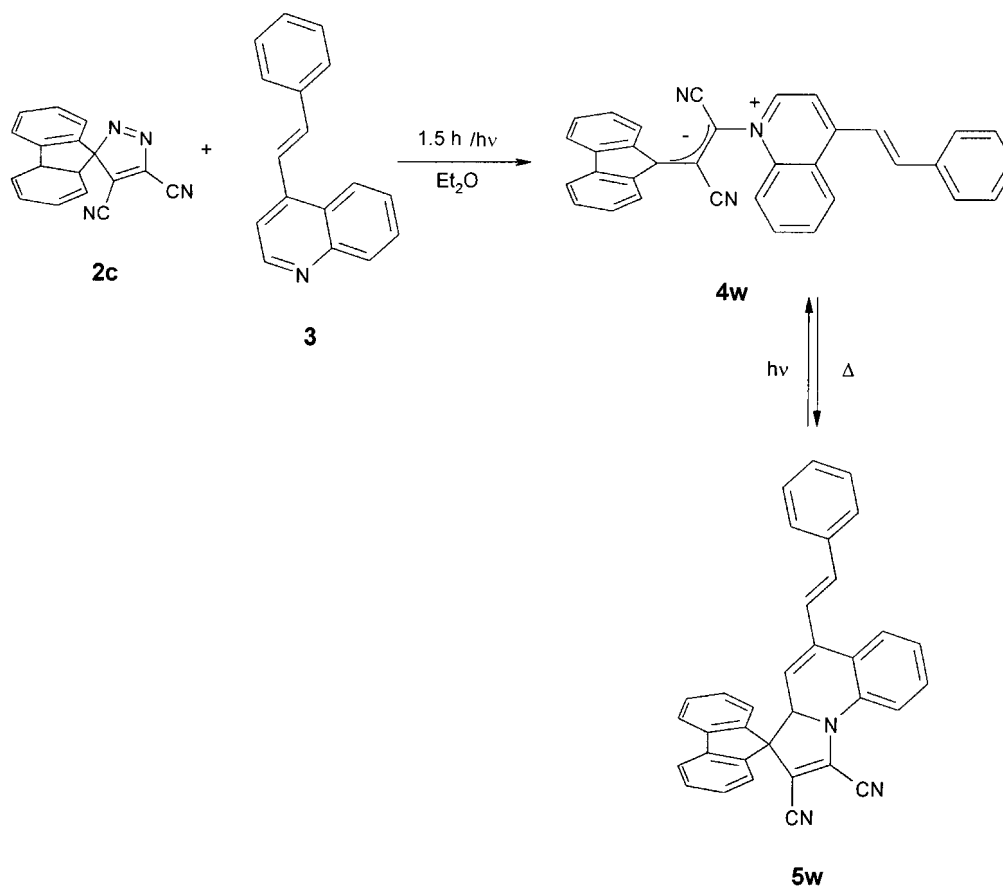
5	R1	R2	R3	R4	n	x	y	Yield (%)	M.p. (°C)
a	CH ₃	H	H	H	1	1	C	68.1	135
b	CH ₃	H	H	H	2	1	C	54.3	128
c	CH ₃	H	H	H	1	0	C	25.7	132
d	iPr	H	H	H	1	1	C	62.2	106
e	iPr	H	H	H	2	1	C	60.6	147
f	iPr	H	H	OCH ₃	1	1	C	15.4	128
g	iPr	H	H	N(CH ₃) ₂	1	1	C	21.7	153
h	iPr	H	F	H	1	1	C	45.6	117
i	iPr	H	H	F	1	1	C	48.1	124
j	iPr	Cl	H	H	1	1	C	45.2	161
k	iPr	H	Cl	H	1	1	C	23.5	123
l	iPr	H	H	Cl	1	1	C	53.1	212
m	iPr	Cl	H	Cl	1	1	C	42.4	202
n	iPr	H	Cl	Cl	1	1	C	66.2	122
o	iPr	H	NO ₂	Cl	1	1	C	56.4	144
p	iPr	H	H	Br	1	1	C	52.1	142
q	iPr	NO ₂	H	H	1	1	C	55.8	149
r	iPr	H	NO ₂	H	1	1	C	58.9	140
s	iPr	H	H	NO ₂	1	1	C	41.4	148
t	iPr	H	H	COOCH ₃	1	1	C	46.2	147
u	iPr	H	— ^a	— ^a	1	1	N	23.2	154
v	iPr	H	H	R4 ^b	1	1	C	6.1	122
w	CN	H	H	H	1	1	C	24.5	193

^a See special formula **5u** in Scheme 1.

**Table 2.** ¹H NMR characteristic signals for **5a–w**

5	2'-Ester	3'-Ester	2'-CH	3'-CH	10'-CH	10'a-CH	1H-styryl	2H-styryl
a	3.21	4.02	—	—	5.03	5.47	6.41	6.76
b	3.15	3.95	—	—	4.95	5.39	6.09	6.18
c	3.14	3.99	—	—	5.04	5.55	6.44	6.71
d	0.54	1.44	4.52	5.43	5.14	5.53	6.48	6.82
e	0.45	1.35	4.45	5.33	5.03	5.43	6.27	6.32
f	0.45	1.35	4.46	5.33	5.02	5.43	6.33	6.72
g	0.51	1.37	4.44	5.35	5.02	5.41	6.11	6.42
h	0.52	1.45	4.53	5.43	5.14	5.52	6.46	6.83
i	0.59	1.50	4.58	5.49	5.16	5.53	6.49	6.78
j	0.45	1.35	4.44	5.33	5.09	5.45	6.71	6.77
k	0.45	1.35	4.44	5.34	5.06	5.44	6.70	6.74
l	0.56	1.44	4.55	5.45	5.16	5.54	6.44	6.74
m	0.55	1.45	4.57	5.41	5.18	5.53	6.80	7.00
n	0.54	1.44	4.53	5.41	5.10	5.49	6.33	6.44
o	0.54	1.45	4.53	5.43	5.17	5.52	6.43	7.02
p	0.55	1.45	4.53	5.43	5.14	5.51	6.40	6.80
q	0.55	1.45	4.53	5.43	5.19	5.53	6.77	6.94
r	0.55	1.45	4.53	5.43	5.18	5.53	6.51	6.95
s	0.45	1.36	4.45	5.35	5.15	5.46	6.45	6.90
t	0.54	1.44	4.53	5.40	5.18	5.53	6.50	6.93
u	—	—	—	—	5.01	5.49	6.45	6.79
v ^a	—	—	—	—	—	—	—	—
w ^a	—	—	—	—	—	—	—	—

^a See Experimental section.



Scheme 2. Preparation of dicyano-DHI **5w**

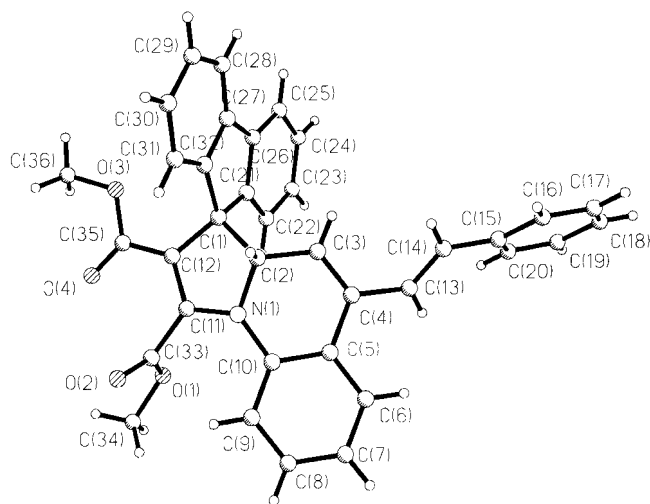
Table 3. ^{13}C NMR characteristic signals for **5a–w**

5	2'-C=O	3'-C=O	2'-Ester	3'-Ester	2'-CH	3'-CH	C-spiro	10'a-CH
a	164.08	164.35	51.16	53.73	—	—	63.16	69.82
b	163.85	164.05	50.86	53.43	—	—	62.79	69.47
c	163.34	163.65	50.48	53.17	—	—	62.51	69.26
d	163.10	163.19	21.42	21.92	66.35	71.27	63.29	69.42
e	163.10	163.13	21.40	21.88	66.35	71.26	63.26	69.41
f	163.08	163.27	21.31	21.79	66.29	71.19	63.26	69.93
g	162.61	162.82	21.20	21.22	65.64	70.54	62.09	68.37
h	163.18	163.20	21.45	21.92	66.37	71.27	63.36	69.45
i	162.76	162.96	20.94	21.12	66.03	70.94	62.38	68.97
j	163.20	163.40	21.36	21.84	66.36	71.30	63.27	69.34
k	162.72	162.94	21.05	21.54	66.06	70.96	62.98	69.06
l	163.05	163.27	21.35	21.86	66.37	71.28	63.28	69.36
m	163.11	163.31	21.32	21.81	66.39	71.28	63.30	69.34
n	163.10	163.33	21.40	21.87	66.37	71.28	63.29	69.40
o	162.98	163.21	21.32	21.87	66.26	71.19	63.20	69.23
p	162.85	162.97	21.18	21.70	66.16	71.08	63.04	69.15
q	162.80	163.00	20.03	21.52	65.93	70.99	62.96	69.02
r	163.05	163.28	21.30	21.80	66.39	71.33	63.22	69.25
s	162.73	162.95	21.00	21.51	66.15	71.06	62.88	68.94
t	163.11	163.34	21.32	21.82	66.39	71.30	63.22	69.31
u ^a								
v ^a								

^a See Experimental section.

Table 4. Mass spectrometric data for selected compounds **5**

5	MS (found)	M ⁺ (calc.)	M + 1 (calc.)
a	537.6	537.62	—
b	573.7	573.73	—
e	620.7	—	619.75
f	623.7	623.74	—
o	674.7	—	673.16
p	674.6	—	673.62
r	638.7	638.72	—
t	651.8	651.67	—

**Figure 1.** X-ray structure analysis of **5a**

addition was carried out by stirring for 96 h at room temperature in a dry diethyl ether solution in the absence of light (Scheme 1). Pure products were obtained in all cases by column chromatography on silica gel using dichloromethane as eluent (Table 1).

In this reaction, the nitrogen of quinoline **4** adds nucleophilically to the cyclopropene **2** and the intermediate opens via a cyclopropyl–allyl conversion and leads to the colored betaine form **4** that closes finally to the DHI **5** in a fast electrocyclic reaction.

Pyrazole route

A longer living IR-active molecule (**5w**) (see below) was obtained by reacting fluorenedicyanopyrazole (**2c**) and 4-styrylquinolines (**3**) according to the pyrazole route¹¹ by photolysis for 1.5 h in a degassed absolute diethyl ether solution using an HPK 125 W high-pressure mercury lamp/Pyrex filter ($\lambda > 290$ nm) (Scheme 2).

The pure product dicyano-9'-styryl-DHI (**5w**) was obtained by column chromatography on silica gel with dichloromethane as eluent and recrystallization from light petroleum as yellow crystals in low yield (24.5%).

RESULTS AND DISCUSSION

The conformation and configuration of all synthesized styryl-DHIs (**5a–w**) were established by elemental analysis, ¹H and ¹³C NMR experiments, mass and IR spectroscopy (Tables 2–4).

The final structural proof of 4-styrylquinoline-DHI was provided by x-ray analysis of a single crystal of **5a**. The crystal structure (Fig. 1) corresponds very well with the structural data obtained by NMR.

The DHIs consist of three regions, A, B and C,^{10,11} that can be clearly assigned in the case of DHI **5a** from the x-ray structure. The fluorene unit is perpendicular to the pyrrole diester unit that exists in a half-boat and the quinoline part. The bond distances and angles are listed in Table 5.

The double bond [C(13)=C(14)] of length 1.317 Å is consistent with the NMR results with a coupling constant (³J_{styryl-H} = 15.9 Hz) in **5a** indicating a *trans* configuration. Notable is the unusually long bond distance C(1)—C(2) of 1.574 Å. This is the longest C—C single bond length in the structure of **5a**, hence it can be cleaved easily by irradiation with UV light, leading to the ring-open betaine form **4a**. This compares well with the long C(1)—C(2) bond in DHI¹⁵ and THI¹⁶ of 1.552 and 1.626 Å, respectively. The ester groups on C(11) and C(12) and the styryl at C(4) are found to be in free rotation. (The labeling of the x-ray crystal structure is due to apparative numerics and does not follow IUPAC conventions.)

Photophysical properties

Photophysical data from absorption of 9'-styrylquinoline-DHI^{9,17} (**5**) were investigated with regard to their photochromic properties.

All the DHIs (**5a–w**) were colorless to pale yellow. Absorption maxima were found in the UV region and ranged between 330 and 370 nm depending on the substituent in the 9'-styryl group.

The DHI **5a**, **b** and **e–v** could not be colorized by irradiation at room temperature owing to fast cyclization of the betaine **4** in all cases with lifetimes in the millisecond range (**4a**, **b** and **e–v**). Half-lives $\tau_{1/2}$ recorded by flash photolysis ranged from 50 to 200 ms (in CH₂Cl₂) (Table 6).

Irradiation of DHIs (**5a**, **b**, **e**, **f** and **h–v**) afforded after cooling to low temperature (–20 °C) orange–brownish colors. The absorption spectra at (–20 °C) in CH₂Cl₂ revealed two betaine maxima, one in the visible region at about 470 nm and the other in the near-IR region between 780 and 860 nm with tailing beyond 1000 nm (Table 6, Fig. 2).

The *N,N*-dimethyl-substituted phenylstyryl-DHI **5g**, after irradiation to **4g**, exhibited an additional absorption maximum at 540 nm that caused a blue–violet color and

Table 5. X-ray analysis data on bond lengths and bond angles for **5a**

Region	Bond	Length (Å)	Bond	Angle [°]	
5-Ring (dihydropyrrole)	N(1) — C(2)	1.486	N(1) — C(2) — C(1)	104.59	
	N(1) — C(11)	1.377	C(11) — N(1) — C(2)	107.92	
	C(11) — C(12)	1.348	C(11) — N(1) — C(10)	131.51	
	C(1) — C(12)	1.521	C(12) — C(11) — N(1)	113.15	
	C(1) — C(2)	1.574	C(12) — C(1) — C(2)	100.52	
	Quinoline	C(2) — C(3)	1.489	C(4) — C(3) — C(2)	122.02
		C(3) — C(4)	1.337	C(3) — C(4) — C(5)	119.69
		C(4) — C(5)	1.472	C(10) — C(5) — C(4)	119.79
		C(5) — C(10)	1.408	C(7) — C(6) — C(5)	121.47
		C(5) — C(6)	1.396	C(8) — C(9) — C(10)	120.49
C(6) — C(7)		1.378	C(6) — C(7) — C(8)	119.53	
C(7) — C(8)		1.379	C(9) — C(10) — C(5)	119.38	
C(8) — C(9)		1.382	N(1) — C(10) — C(5)	117.13	
C(9) — C(10)		1.394	C(10) — N(1) — C(2)	120.57	
C(10) — N(1)		1.407	N(1) — C(2) — C(3)	110.52	
Fluorene	C(1) — C(21)	1.526	C(21) — C(1) — C(2)	112.90	
	C(21) — C(22)	1.379	C(22) — C(21) — C(1)	128.85	
	C(22) — C(23)	1.395	C(21) — C(22) — C(23)	118.49	
	C(23) — C(24)	1.385	C(25) — C(24) — C(23)	12.14	
	C(24) — C(25)	1.372	C(25) — C(26) — C(21)	120.18	
	C(25) — C(26)	1.391	C(32) — C(1) — C(21)	101.73	
	C(26) — C(27)	1.471	C(26) — C(21) — C(1)	110.26	
	C(27) — C(28)	1.393	C(27) — C(32) — C(1)	110.45	
	C(28) — C(29)	1.385	C(32) — C(27) — C(26)	108.78	
	C(29) — C(30)	1.376	C(28) — C(27) — C(32)	119.68	
	C(30) — C(31)	1.381	C(29) — C(28) — C(27)	118.86	
	C(31) — C(32)	1.388	C(30) — C(29) — C(28)	121.15	
	C(32) — C(1)	1.523	C(29) — C(30) — C(31)	120.50	
	C(30) — C(31) — C(32)			118.99	
Esters	O(2) — C(33)	1.206	O(2) — C(33) — O(1)	126.05	
	O(1) — C(33)	1.320	O(1) — C(33) — C(11)	111.32	
	O(1) — C(34)	1.453	O(2) — C(33) — C(11)	122.59	
	C(11) — C(33)	1.502	C(33) — O(1) — C(34)	114.94	
	C(12) — C(35)	1.461	C(12) — C(11) — C(33)	124.94	
	C(35) — O(4)	1.210	C(11) — C(12) — C(35)	121.36	
	O(3) — C(35)	1.346	O(4) — C(35) — C(12)	124.44	
	O(3) — C(36)	1.450	O(3) — C(35) — C(12)	112.49	
			C(35) — O(3) — C(36)	114.81	
			O(4) — C(35) — O(3)	123.05	
9'-Styryl	C(4) — C(13)	1.483	C(5) — C(4) — C(13)	118.90	
	C(13) — C(14)	1.317	C(3) — C(4) — C(13)	121.34	
	C(14) — C(15)	1.474	C(14) — C(13) — C(4)	125.21	
	C(15) — C(16)	1.381	C(13) — C(14) — C(15)	125.67	
	C(16) — C(17)	1.381	C(16) — C(15) — C(14)	120.07	
	C(17) — C(18)	1.377	C(15) — C(16) — C(17)	120.88	
	C(18) — C(19)	1.367	C(18) — C(17) — C(16)	120.20	
	C(19) — C(20)	1.387	C(19) — C(18) — C(17)	120.24	
	C(15) — C(20)	1.401	C(18) — C(19) — C(20)	120.00	
			C(19) — C(20) — C(15)	120.150	
		C(20) — C(15) — C(14)	121.70		

showed the strongest colorability (highest ϵ) of all the DHIs (**5**) (Fig. 3). This is due to its strong electron-donating group.

Only the diphenyl system (**5c**) and the dicyano-DHI (**5w**) show longer lived green betaine forms (longer $\tau_{1/2}$, Fig. 4). Irradiation in CH_2Cl_2 solution at room temperature gave half-lives of 400 and 340 s, respectively. The ring-open form of the diphenyl-DHI **5c** absorbs at 770 nm, while the maximum of dicyano-DHI **5w** with

its strong electron-attracting cyano groups is shifted even to 710 nm. Dissolving **5c** and **5w** in methylenechloride and irradiating at 77 K (liquid nitrogen) gives the green color immediately. *Compound 5c could be stored at this temperature for several weeks.* Indefinite storage at this temperature is certainly possible, but was not verified experimentally.

Very interesting is the strong effect of solvent polarity on the λ_{max} of betaines **4**. A solvent change from

Table 6. Spectroscopic data for styryl-DHI **5a–w**

5	$\lambda_{\max}(\text{DHI})$ (nm) ^a	$\lambda_{\max}(\text{betaine})$ (nm) ^b	$\lambda_{\max}(\text{betaine})$ (nm) ^c	$t_{1/2}$ (ms) ^a
a	365	475/810	465/770	219
b	332	475/850	421/470/795	315
c	365	368/770	366/720	400×10^3
d	366	478/810	467/770	143
e	333	477/850	473/795	161
f	353	475/845	470/800	127
g	355	473/540/745	465/527/730	66
h	366	470/810	460/765	116
i	368	471/810	463/765	53
j	369	473/825	462/770	55
k	365	473/820	463/775	70
l	364	473/820	463/780	109
m	351	485/840	470/820	98
n	354	485/845	470/815	86
o	374	— ^d	460/780	75
p	372	473/830	463/785	111
q	365	475/800	460/760	55
r	358	471/800	460/765	66
s	353	470/800	460/785	71
t	370	475/860	468/790	70
u	369	469/820	465/780	47
v	374	480/815	465/685	86
w	390	420/710	—	330×10^3

^a In CH₂Cl₂ at room temperature.^b In CH₂Cl₂ at –20°C.^c In EtOH at –20°C.^d Decomposition after irradiation in CH₂Cl₂.

dichlormethane to more polar ethanol causes hypsochromic shifts of about 10 nm in the visible region, and a noticeable shift of about 50–60 nm in the near-IR region. The biphotochromic system **5v**, having its maximum IR absorption at 820 nm in dichlormethane, even shows a hypsochromic shift of about 120 nm in ethanol (Fig. 3).

This solvatochromic effect is in agreement with previous observations on DHIs.^{10,18–20} For these unusually high shifts, $\pi \rightarrow \pi^*$ transitions in the visible region and charge-transfer transitions in the near-IR region can be concluded to occur.¹⁹

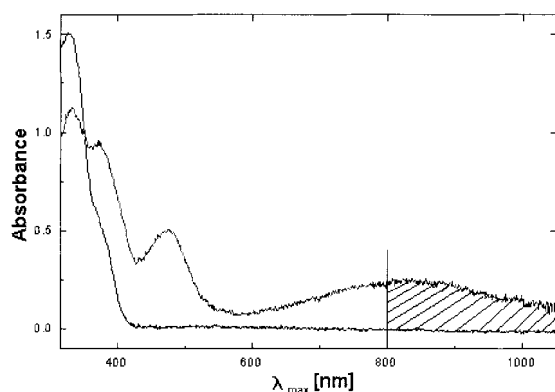


Figure 2. UV/VIS absorption of 9'-styryl-DHI **5t** in CH₂Cl₂ at 253 K, $c = 2 \times 10^{-4}$ mol l⁻¹

CONCLUSIONS

With the 9'-styrylphenylquinolinedihydroindolizines **5**, a new photochromic material based on DHI systems having absorption in the VIS/IR region has been prepared. The photochromism in **5** is based on a fast 1,5-electrocyclization of the colored betaines **4** in the millisecond range that could be recorded by flash photolysis. Longer living species were obtained by dicyano substitution in the ester region (**5w**) and diphenyl substitution (**5c**) in region A (Scheme 1). Their colored ring-open forms show $\tau_{1/2}$ of 400 and 340 s, respectively.

Absorption spectra of the fast cyclizing betaines **4** were obtained at low temperature (253 K). All compounds show two main absorption maxima, one in the visible and the other in the IR region. Almost all 9'-styrylphenylbetaines **4** have absorption maxima larger than 800 nm in methylene chloride. The *N,N*-dimethyl-substituted styrylphenyl betaine **4g** and the longer living dicyanobetaine **4w** and also the diphenyl system **4c** show hypsochromic shifts towards the visible region. Owing to their shifted absorption they exhibit blue-violet to greenish colors, unlike all other 9'-styrylbetaines **4** that exhibit orange-brownish colors after irradiation.

The absorption of the betaine form **4** shows solvatochromism. In the case of **4** the maximum absorption of the 9'-styrylphenylquinolinebetaines leads to un-

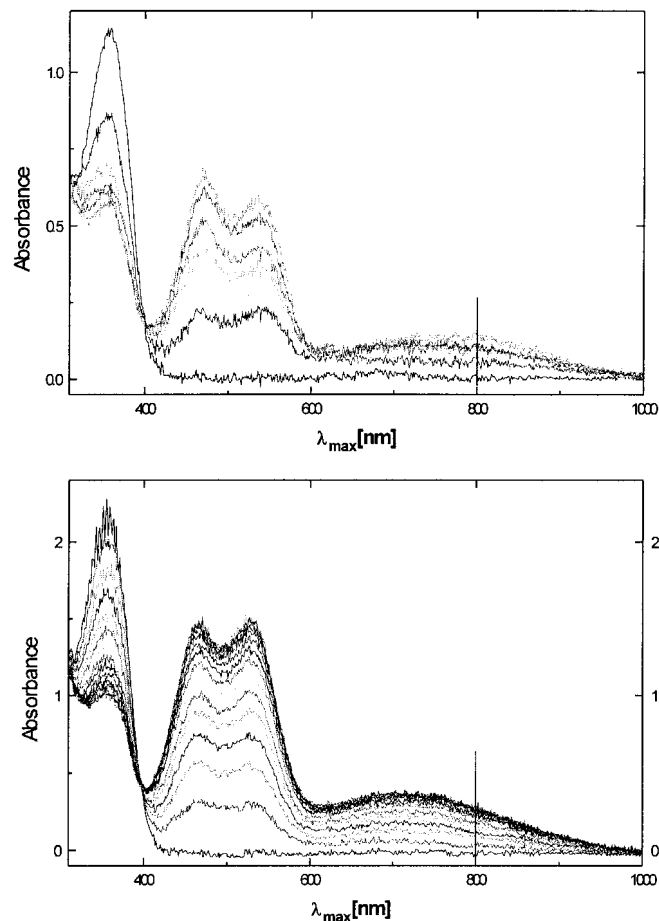


Figure 3. Thermal fading of 9'-styryl-DHI **5g** in CH_2Cl_2 and in ethanol at 253 K, $c = 2 \times 10^{-4} \text{ mol l}^{-1}$

usually high hypsochromic shifts on increasing the solvent polarity. This is in agreement with previous solvatochromic effects studied on DHIs. The betaines **4** can be used for IR-sensitive recording or storage materials at 77 K.

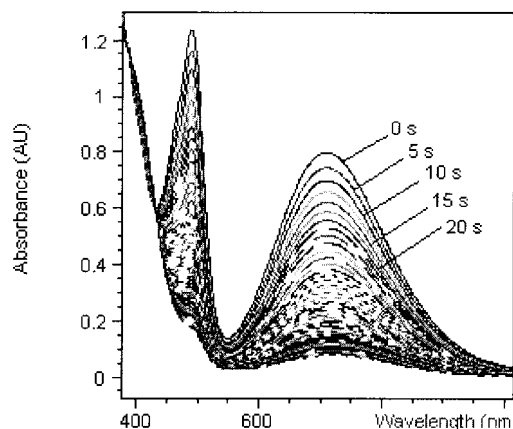


Figure 4. Thermal fading UV-Vis absorption (recorded every 5 s) of dicyano-9'-styrylquinolinebetaine **4w** (CH_2Cl_2 , $c = 4 \times 10^{-3} \text{ mol l}^{-1}$)

EXPERIMENTAL

All NMR spectra were collected at 500 MHz on a Bruker DRX 500 spectrometer in CDCl_3 using TMS as internal standard. Chemical shifts are reported in ppm (δ). Column chromatography was performed using silica gel (MN-60, 50–200 μm , 70–270 mesh). Solvents used were water free and dried according to standard procedures. IR spectra were measured on a Bio-Rad Excalibur series FTS 3000 instrument. Mass spectra were recorded on a Finnigan MAT Mat-90 mass spectrometer. Elemental analyses (C,H,N) were carried out on a LECO CHNS-932 analyzer. Melting-points are uncorrected and were measured on a Gallenkamp Smp-20 apparatus. UV spectra were recorded on an HP 6543 FT-UV/VIS computer spectrometer. Flash photolysis was carried out with a Photoflash (METZ 32 Z-1) 12 V (50 W) halogen lamp. X-ray structure analysis was carried out on a STOE IPDS diffractometer with SHELXS-97 programs.

Preparation of dialkyl 9'-(substituted styryl and phenylbutadienyl)spiro(fluorene-9, 1'-pyrrolo [1,2-a]quinoline)-2,3-dicarboxylate (5a–v). *General procedure.* A solution of spirocyclopropene **2a, b** (306, 304 and 362 mg; 0.001 mol) in dry diethyl ether (50 ml) was added to a solution of substituted-4-styryl quinolines **3a–u** (0.001 mol) under a dry nitrogen atmosphere. The mixture was stirred at room temperature for 24–72 h in the dark (TLC controlled). The ether was evaporated under reduced pressure and the pure products were separated by column chromatography twice on silica gel using CH_2Cl_2 as eluent and recrystallized from diethyl ether–pentane (1:1) as white to yellow needles in 6–69% yield.

Diisopropyl- 9'-styrylspiro(fluorene-9, 1'-pyrrolo[1,2-a]quinoline)-2', 3'-dicarboxylate (5d). Reactants: 362 mg (0.001 mol) spirene **2b**, 231 mg (0.001 mol) 4-styrylquinoline **3a**, 50 ml diethyl ether; yield 369 mg (62%) as pale yellow crystals; m.p. 107°C. ^1H NMR (CDCl_3): $\delta = 7.71\text{--}7.74$ (t, 2H, $J = 6.2$ Hz, CH-arom.), 7.63–7.65 (d, 1H, $J = 7.1$ Hz, CH-arom.), 7.43–7.45 (d, 1H, $J = 7.1$ Hz, CH-arom.), 7.27–7.40 (m, 8H, CH-arom.), 7.16–7.23 (m, 4H, CH-arom.), 6.98–7.01 (m, 1H, CH-arom.), 6.80–6.84 (d, $J = 15.92$ Hz, 1H, CH-styryl), 6.46–6.51 (d, $J = 15.92$ Hz, 1H, CH-styryl), 5.52–5.53 (d, $J = 0.88$ Hz, 1H, 10'a-H), 5.38–5.47 (m, 1H, 3'-CH), 5.13–5.14 (d, $J = 0.88$ Hz, 1H, 10'-H), 4.48–4.56 (m, 1H, 2'-CH), 1.47–1.48 (d, $J = 6.2$ Hz, 3H, 3'-CH₃), 1.40–1.41 (d, $J = 6.2$ Hz, 3H, 3'-CH₃), 0.57–0.58 (d, $J = 6.2$ Hz, 3H, 2'-CH₃), 0.49–0.50 (d, $J = 6.2$ Hz, 3H, 2'-CH₃) ppm. ^{13}C NMR (CDCl_3): $\delta = 163.19$ (3'-CO), 163.10 (2'-CO), 149.16, 142.15, 140.98, 137.37, 136.56, 133.89, 132.79, 128.50, 128.79, 127.98, 127.86, 127.48, 126.67, 125.72, 125.68, 124.27, 123.05, 121.90, 121.80, 119.90, 119.67, 116.20, 71.27 (3'-CH), 69.42 (10'a-C), 66.35 (2'-CH), 63.29 (spiro-C), 21.95 (3'-CH₃), 21.87 (3'-CH₃), 21.50 (2'-CH₃), 21.34 (2'-CH₃) ppm. MS

(70 eV): m/z (%) = 593.31 (M^+ , calc. 593.73). IR (KBr): ν = 3021 (C—H, arom.), 2827–2979 (C—H, aliph.), 1731 (3'-C=O), 1692 (2'-C=O), 1598 (C=C), 1491, 1421, 1254, 1156, 1100, 991, 940, 834, 753, 623 cm^{-1} . Elemental analysis for $C_{40}H_{35}NO_4$ (M.W. = 593.72): calc. C, 80.92; H, 5.94; N, 2.36; found C, 80.97; H, 5.99; N, 2.35%.

1,2-Bis[diisopropoxycarbonyl-1'H, 10'a-H-spiro(fluorene-9, 1'-pyrrolo-[1,2-a]quinolin-9-yl)ethene (5u). Reactants: 362 mg (0.001 mol) spirocyclopropene **1b**, 282 mg (0.001 mol) 1,2-(bisquinolin-4-yl)ethene **3r**, 50 ml diethyl ether; yield 230 mg (23%) as yellow-brown crystals; m.p. 154 °C. ^1H NMR (CDCl_3): δ = 7.68–7.71 (dd, J = 3.44, 5.44 Hz, 4H, CH-arom.), 7.58–7.61 (t, J = 6.88 Hz, 2H, CH-arom.), 7.31–7.40 (m, 8H, CH-arom.), 7.13–7.18 (m, 6H, CH-arom.), 7.06–7.08 (d, J = 7.40 Hz, 2H, CH-arom.), 6.91–6.96 (m, 2H, CH-arom.), 6.19–6.21 (d, J = 5.40 Hz, 1H, CH-styryl), 6.13–6.15 (d, J = 5.40 Hz, 1H, CH-styryl), 5.44–5.45 (d, J = 1.96 Hz, 2H, 10'a-H), 5.36–5.44 (m, 2H, 3'-CH), 4.95–4.97 (d, J = 1.36 Hz, 2H, 10'-H), 4.48–4.54 (m, 1H, 2'-CH), 1.44–1.45 (d, J = 6.40 Hz, 6H, 3'-CH₃), 1.36–1.38 (d, J = 6.40 Hz, 6H, 2'-CH₃), 0.56–0.57 (d, J = 6.40 Hz, 6H, 2'-CH₃) ppm. ^{13}C NMR (CDCl_3): δ = 163.01 (3'-CO), 162.85 (2'-CO), 148.82, 148.66, 144.64, 141.73, 140.62, 128.36, 128.06, 127.81, 127.55, 127.29, 127.04, 125.19, 12.95, 122.73, 119.63, 119.36, 115.83, 109.59, 70.98 (3'-CH), 68.97 (10'a-C), 68.90 (2'-CH), 66.06 (spiro-C), 21.55 (3'-CH₃), 21.47 (3'-CH₃), 21.12 (2'-CH₃) 20.96 (2'-CH₃) ppm. MS (70 eV): m/z (%) = 1007.20 (M^+ , calc. 1007.20). IR (KBr): ν = 3063 (C—H, arom.), 2836–2979 (C—H, aliph.), 1738 (3'-C=O), 1691 (2'-C=O), 1596 (C=C), 1491, 1419, 1372, 1299, 1254, 1209, 1156, 1032, 829, 841, 752, 681 cm^{-1} . Elemental analysis for $C_{66}H_{58}N_2O_8$ (M.W. = 1007.20): calc. C, 78.70; H, 5.80; N, 2.78; found C, 78.77; H, 5.91; N, 2.81%.

Preparation of 1,4-bis[2-(diisopropoxycarbonyl-1'H, 10'a-H-spiro(fluorene-9, 1'-pyrrolo-[1,2-a]quinolin-9-yl)ethenyl)benzene (5v). Reactants: 362 mg (0.001 mol) spirene **1b**, 384 mg (0.001 mol) 1,4-bis[2-(quinolin-4-yl)ethenyl]benzene **3s**, 50 ml diethyl ether; yield 66 mg (6%) as yellow-brown crystals, m.p. 122 °C. ^1H NMR (CDCl_3): δ = 7.70–7.71 (d, J = 7.52, 6H, CH-arom.), 7.59–7.61 (t, J = 7.52 Hz, 4H, CH-arom.), 7.43–7.45 (d, J = 7.52 Hz, 4H, CH-arom.), 7.31–7.37 (m, 9H, 2H, CH-styryl + 7H, CH-arom.), 7.17–7.22 (m, 2H, CH-styryl + 5H, CH-arom.), 7.14–7.15 (d, 3J = 0.88 Hz, 2H, CH-arom.), 7.14–7.15 (d, J = 0.88 Hz, 2H, CH-arom.), 6.96–6.99 (m, 2H, CH-arom.), 5.50–5.51 (d, J = 1.32 Hz, 2H, 10'a-H), 5.37–5.42 (m, 2H, 3'-CH), 4.95–4.97 (d, J = 1.32 Hz, 2H, 10'-H), 4.46–4.54 (m, 1H, 2'-CH), 1.45–1.46 (d, J = 6.64 Hz, 6H, 3'-CH₃), 1.38–1.39 (d, J = 6.64 Hz, 6H, 2'-CH₃), 0.55–0.57 (d, J = 6.64 Hz,

6H, 2'-CH₃), 0.47–0.48 (d, J = 6.64 Hz, 6H, 2'-CH₃) ppm. MS (70 eV): m/z (%) = 1109.00 [M^+ , calc. 1109.33]. IR (KBr): ν = 3063 (C—H, arom.), 2823–2980 (C—H, aliph.), 1738 (3'-C=O), 1689 (2'-C=O), 1594 (C=C), 1491, 1419, 1372, 1254, 1292, 1209, 1155, 825, 749, 688 cm^{-1} . Elemental analysis for $C_{74}H_{64}N_2O_8$ (M.W. = 1109.33): calc. C, 80.12; H, 5.81; N, 2.53; found C, 80.14; H, 5.80; N, 2.49%.

9'-Styryl-spiro(fluorene-9, 1'-pyrrolo[1,2-a]quinoline)-2', 3'-dicarbonitrile (5w). To a suspension of 4-styrylquinoline **3a** (231 mg, 0.001 mol) in absolute diethyl ether after stirring at room temperature, an equimolar solution of fluorenespiroindolepyrazole **2c** (268 mg, 0.001 mol) in diethyl ether (500 ml) was added. After flushing the reaction mixture for 15 min with dry nitrogen, the solution was photolysed through a Pyrex filter with an HPK 125 W high-pressure mercury lamp. After 1.5 h of photolysis, the development of nitrogen ceased and the reaction was complete (TLC control). The ether was removed and the residue purified by column chromatography (SiO_2) with CH_2Cl_2 to afford **5w**. The product was recrystallized from diethyl ether to yield pale yellow crystals (112 mg, 24.5% yield; m.p. 193 °C).

^1H NMR (CDCl_3): δ = 7.70–7.73 (m, 2H, CH-arom.), 7.58–7.60 (d, J = 7.08 Hz, 1H, CH-arom.), 7.43–7.45 (d, J = 7.08 Hz, 1H, CH-arom.), 7.30–7.40 (m, 4H, CH-arom.), 7.25–7.28 (m, 3H, CH-arom.), 7.14–7.25 (m, 3H, CH-arom.), 7.05–7.08 (dd, J = 7.96 Hz 1H, CH-arom.), 6.97–7.01 (dt, J = 7.52, 1H, CH-arom.), 6.74–6.78 (d, J = 15.92 Hz, 1H, CH-styryl), 6.39–6.42 (d, J = 15.92 Hz, 1H, CH-styryl), 5.47 (s, 1H, 10'a-H), 5.03–5.04 (d, J = 1.32 Hz, 1H, 10'-H) ppm. ^{13}C NMR (CDCl_3): δ = 149.08, 148.56, 144.19, 141.85, 140.63, 137.04, 136.23, 134.10, 132.59, 129.14, 128.86, 128.65, 128.34, 128.18, 128.07, 127.55, 126.12, 125.92, 125.41, 124.96, 124.11, 123.40, 121.63, 120.21, 119.28, 115.60, 109.45, 69.82 (10'a-C), 63.16 (spiro-C) ppm. IR (KBr): ν = 3061 (C—H, arom.), 2812–2979 (C—H, aliph.), 2180 (3'-CN), 2165 (2'-CN), 1595 (C=C), 1490, 1253, 1209, 1154, 1099, 1002, 965, 725, 692 cm^{-1} . Elemental analysis for $C_{34}H_{21}N_2$ (M.W. = 457.55): calc. C, 89.25; H, 4.63; N, 6.12; found C, 89.28; H, 4.61; N, 6.14%.

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