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Photochromism of dihydroindolizines Part VI: synthesis and photochromic behavior of a novel type of IR-absorbing photochromic compounds based on highly conjugated dihydroindolizines

Saleh Abdel Ahmed*[†,‡]
Chemistry Department, Faculty of Science, Assiut University, 71516 Assiut, Egypt

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ABSTRACT: Novel photochromic bis-styryl dihydroindolizines (DHIs) **5a-β** bearing different cycloalkanone ring sizes were prepared in 11–42% yield via nucleophilic addition of bis-styryl cycloalkanones **2a–k** to substituted spirocyclopropenes **1a–g**. The absorption maxima (λ_{max}) of the colored betaines **4a-β** (formed after UV-irradiation) were detected by millisecond flash photolysis, laser flash photolysis as well as FT-UV/VIS measurements. All betaines **4a-β** showed two absorption maxima, one in the visible region (500–575 nm) and another one in the IR-region (800–878 nm). The kinetics of the fast cyclizing process of betaines **4a-β** to DHIs **5a-β** were studied in dichloromethane solution by millisecond flash photolysis and were found to take place in the millisecond range (76–450 msec). The strong colorability of betaines **4a-β** may be attributed to the highly conjugated betaine structures as well as to the presence of the carbonyl chromophore. Interestingly, a remarkable photo-fatigue resistance of some studied betaines **4** showed t_{30}-values higher than the standard one. Large solvatochromic effects on the absorption maxima (λ_{max}) as well as a substantial increase of the half-lives ($t_{1/2}$) with solvent polarity of betaines **3a-β** were also observed. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: photochromism; Bis-styryl dihydroindolizines (DHIs); IR-sensitive materials; flash photolysis; solvatochromism

INTRODUCTION

Photochromism is defined as the reversible photocoloration of a single chemical species between two states having distinguishably different absorption spectra, which is brought about by the action of an electromagnetic radiation in at least one direction. Photochromism poses the same problems as other photochemical reactions, that is, the system generally represents a photoequilibrium and the photoproduct does not appear as a separate phase. However, it is distinguishable from general photochemical reactions by a characteristic feature: reversibility.[1]

Photochromic compounds are of great interest in industry. In deed, although they have been exploited in a wide range of applications that spans from manufacturing of optical lenses to color printing and optical recording, many other promising utilizations are as yet to be put in practice.[1] In 1952, Fisher and Hirshberg[2] first defined as photochromic a chemical species capable of undergoing, under the influence of an electromagnetic irradiation, a reversible isomerization to a new species with a different absorption spectrum. In the last decade, the design and synthesis of organic molecular materials, whose structure and macroscopic properties can be controlled by external triggers, has become a challenging topic of multidisciplinary research. This considerable research effort is justified by the potential applications of these materials in emerging opto-electronic and photonic technologies.[3] In this context, a photochromic system, working through an external light stimulus, can be the basic unit for a molecular switch.[3] Then, under appropriate light irradiation, intrinsic changes of the geometry and polarity of the chromophoric entity can lead to a topological change of an attached molecular system, modifying in turn the photophysical properties of the material under consideration.[4–10]

Since the discovery of the photochromic dihydroindolizines (DHIs) and tetrahydroindolizines (THIs) by Dürr in 1979,[11,12] they became a very interesting class of photochromic molecules and have been extensively studied and received particular attention owing to their remarkable photofatigue-resistance and wide broad photochromic properties.[13–39] Due to these important and interesting properties, they have already found their applications in optical technology,[33,35,36,39] ophthalmic

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*Correspondence to: S. A. Ahmed, Chemistry Department, Faculty of Science, Assiut University, 71516 Assiut, Egypt.
E-mail: saleh_63@hotmail.com

[†] Present address: Chemistry Department, Faculty of Science, Taiba University, Al-Madena Al-Mounnawara, 344, Saudi Arabia.

[‡] Dedicated to Prof. Dr. Heinz Dürr on the occasion of his 70th birthday.

lenses,[33,39] data storage,[27,33] photoswitches,[25,26,33,39] dental filling materials,[18,19,25,28] IR-sensitive photoswitchable materials,[14,18,19,38] and DNA markers.[29]

These interesting molecules undergo a photo-induced change of color in solutions and in polymer matrices when exposed to UV radiation or direct sunlight exposure. They return to the initial state when the illumination ceases, normally via a thermal pathway. The photochromic behavior of DHIs is based on a reversible pyrroline ring opening, induced by light, that converts a colorless form (usually named the 'closed form') to the colored form (betaine form). The thermal back reaction—the 1,5-electrocyclization—from the ring-open betaine to DHI shows rates extending from milliseconds to several weeks[14,19,33] depending on the substituents and structure of the involved molecule. This interesting wide range in the lifetime of the colored form leads these molecules to find many applications.[33,36,38]

In continuation of our previous work dealing with the synthesis and photochromic properties of DHIs,[14,15,18,19,24,27,32–39] in this manuscript, we wish to report the synthesis and photochromism of novel photochromic DHIs bearing highly conjugated bis-styryl cycloalkanone moieties, a system with interesting absorption in the IR-region and storage of the colored form for several weeks without any color fading.

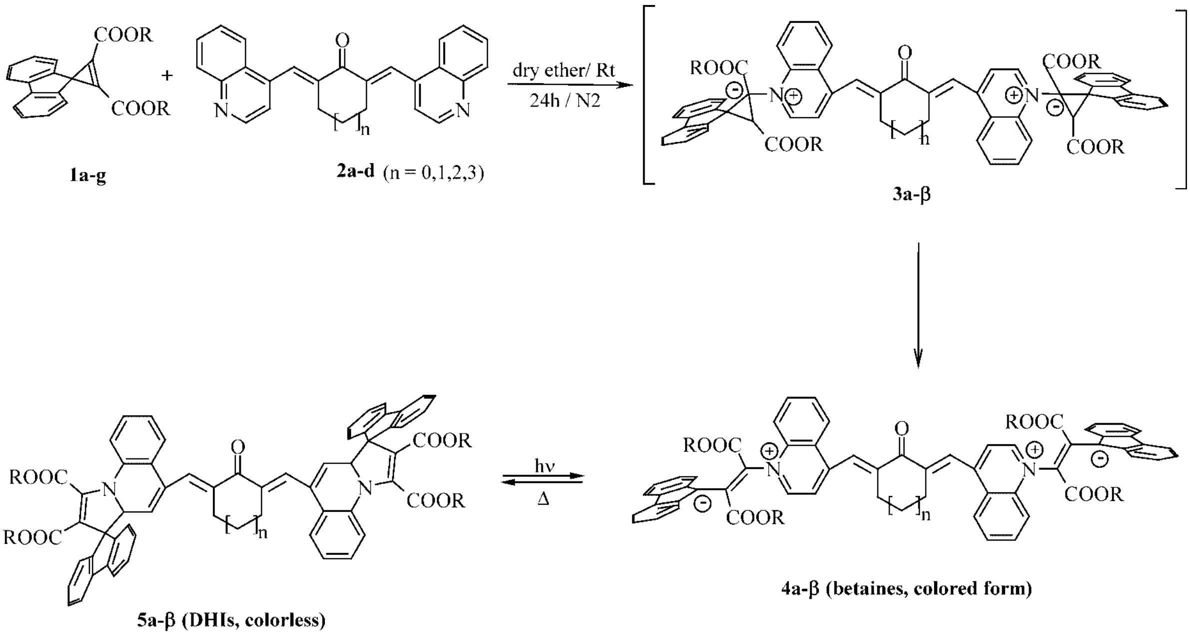
RESULTS AND DISCUSSION

Synthesis of novel bis-styryl dihydroindolizine cycloalkanones 4a-β system

Substituted fluorene spirocyclopropenes **1a–g** were obtained via the pyrazole route[11–13,32–39] by photolysis of the substituted fluorene pyrazoles using a 125 W high pressure mercury lamp in dry ether at room temperature. The obtained photolyzed products were used without further purification. The different 2,6-diquinolidenecycloalkanones precursors **2a–d** were prepared in low to moderate yields (20–50%) via zinc chloride catalyzed aldol condensation of quinoline-4-carboxaldehyde with cycloalkanones, namely, cyclopentanone, cyclohexanone, cycloheptanone, and cyclooctanone.[40–42] The reaction of the substituted fluorene spirocyclopropenes **1a–g** with 2,6-diquinolidenecycloalkanones **2a–d** in dry ether at ambient temperature for 24–66 h under dry nitrogen atmosphere in absence of light gave the fluorene-bis-styrylquinolinedihydroindolizines (DHIs) **5a-β** (Scheme 1) in poor to moderate yields (11–42%) (Table 1). Either increasing the reaction time or reactant ratio did not show any yield improvements.

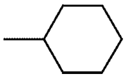
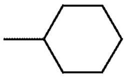
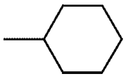
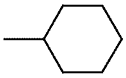
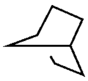
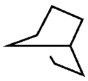
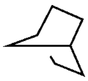
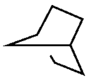
The formation of DHIs **5a-β** occurs through the nucleophilic addition of the nitrogen of the N-heterocyclic quinolines **2a–d** to the electron-deficient cyclopropenes **1a–g**, which undergo ring opening via a cyclopropyl-allyl conversion **3a-β** to the colored betaines **4a-β**. A subsequent ring-closure to DHI **5a-β** results in a fast 1,5-electrocyclization reaction (Scheme 1) which can be reversed upon exposure to light. Pure cycloalkanyl bis-styryl DHIs **5a-β** were obtained in all cases by twice column chromatography on silica using dichloromethane as the eluent (Table 1).

The newly synthesized photochromic bis-styryl DHIs **5a-β** were characterized 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, mass and IR spectroscopy (see Experimental section). For example, it is worth commenting upon some typical features of the NMR spectra, illustrated by that of **5d** (Scheme 2). The ^{1}H–^{1}H-correlation of **5d** showed that



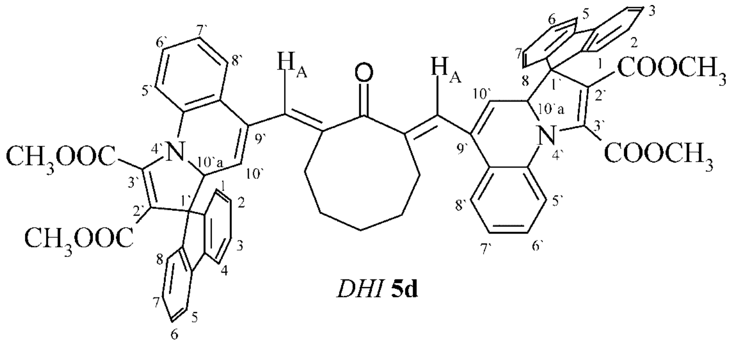
Scheme 1. Preparation outline of photochromic bis-fluorene styrylquinolines DHIs **5a-β** via the spirocyclopropene route

Table 1. Substituent pattern of the 28 DHI derivatives prepared (**5a-β**) and their melting points and reaction yields

DHIs 5	R	*n*	Reaction time (h)	Mp (°C)	Yield (%)
a	CH_3	0	24	172	42.4
b	CH_3	1	28	161	36.2
c	CH_3	2	44	154	30.9
d	CH_3	3	60	143	19.3
e	C_2H_5	0	30	163	30.4
f	C_2H_5	1	36	150	26.3
g	C_2H_5	2	40	136	24.6
h	C_2H_5	3	51	130	18.3
I	$CH(CH_3)_2$	0	40	150	30.8
j	$CH(CH_3)_2$	1	46	143	27.3
k	$CH(CH_3)_2$	2	53	130	20.9
l	$CH(CH_3)_2$	3	56	122	14.3
m	$C(CH_3)_3$	0	47	142	26.9
n	$C(CH_3)_3$	1	55	136	25.3
o	$C(CH_3)_3$	2	63	120	28.9
p	$C(CH_3)_3$	3	66	117	19.3
q	$CH_3(CH_2)_4$	0	46	120	19.3
r	$CH_3(CH_2)_4$	1	52	112	16.8
s	$CH_3(CH_2)_4$	2	58	103	11.0
t	$CH_3(CH_2)_4$	3	65	99	12.6
u		0	42	149	33.5
v		1	44	135	30.7
w		2	50	122	29.2
x		3	51	117	27.9
y		0	50	156	39.3
z		1	53	150	33.9
α		2	57	142	35.9
β		3	59	131	23.7

both 2′,3′-methyl ester groups experience no coupling with other protons and appear as two singlets at 3.18 and 4.26 ppm, respectively. The three protons $H_{10'a}$, $H_{10'}$, and H_A are the most characteristic. The chemical shifts for $H_{10'a}$ (5.52, dd, $J\ H_{10'}–H_{10'a} = 0.99$, $^5J\ H_{10'a}–H_A$, 4.6 Hz) and $H_{10'}$ (5.17, dd, $^4J\ H_{10'}–H_A$, 5.6, $J\ H_{10'}–H_{10'a}$, 0.99 Hz) are noticeable; the first is observed down field owing to the electronegative neighborhood of a nitrogen and a double bond as well as the anisotropic effect of the fluorene ring.[38] In contrast, the diamagnetic current of the aromatic nucleus induces a large high field shift for the $H_{10'}$ signal. Interestingly, the H_A proton appears as a doublet at 6.92 ppm ($^4J = 0.99$ Hz) due to the coupling with $H_{10'}$. Typical signals and couplings of cyclooctane methylene protons at 1.4, 2.3 ppm were recorded.

In addition, the chemical structure of **5d** was assigned by 2D-NMR spectroscopy. The $^1H–^1H$-correlation of **5d** was used to assign the protons of the quinoline rings as well as the H_A proton (region C) and in the $^1H,^1H$-COSY spectrum both 2′- and 3′-methyl ester groups showed no coupling with other protons and appeared as two singlets 3.18 and 4.26 ppm. The 10′-CH signal was shifted to high field and appeared as a double doublet at $\delta = 5.18$ ppm showing two coupling systems. The first is due to ^3J-coupling with the 10′a-CH, which appears as doublet at $\delta = 5.60$ ppm, the second is due to ^4J-coupling with the H_A which appears as a double doublet at $\delta = 6.92$ ppm. Further assignments of H_A, 10′CH and 10′a-CH were done by the aid of N*O*ESY spectrum of **5d**. Here we observed that 10′a-CH at $\delta = 5.60$ ppm is close in space to



2`-CH3	δ 3.18 (s)
3`-CH3	δ 4.26 (s)
10`-CH	δ 5.60 (dd)
10`a-CH	δ 5.18 (dd)
H$_A$-CH	δ 6.92 (d)

Scheme 2. ^{1}HNMR data for structure determination of DHI **5d**

both 10′-CH at $\delta = 5.17$ ppm and 1-CH of the fluorene moiety at $\delta = 7.64$ ppm. This system proves that 10′a-CH is in 10′a-position and not at 10′-position. Additionally, the connectivity between 10′-CH and 8-CH of the fluorene part at $\delta = 7.52$ ppm was observed. This vicinity of 10′-CH with 8-CH proved that the quinoline moiety is perpendicular to the fluorene skeleton as proved by a molecular modeling calculation[37] of **5d** (Fig. 1). It showed that the distance between both 10′a-CH, 10′-CH and 1-CH, 8-CH of the fluorene moiety is <3 Å. Probably 6′-CH and 3′-CH$_3$ of the ester group at $\delta = 4.26$ ppm are close in space to each other (Fig. 1).

Photophysical properties of new photochromic DHIs 5a-β and their corresponding betaines 4a-β in solution

Electronic spectra of the newly synthesized DHIs **5a-β** were measured in dichloromethane solution using a UV/Vis spectrophotometer with concentration of 1×10^{-5} mol/l at 23 °C. The intensities (log ε) of these bands were found to be between 3.88 and 4.25. The absorption of DHIs **5a-β** was observed in the UV-region and showed two absorption maxima, one lies between 331 and 352 nm and the other lies between 367 and 388 nm. These absorptions are depending on the type of the esters and the size of the cycloalkanone moieties. Due to the increase in the conjugated DHI skeleton and the presence of the chromophoric carbonyl group of the cycloalkanone moiety, a shift of around 20 nm was recorded compared with our previous work on 9-styryl DHI system.[38] As established previously,[1] these absorption bands can be assigned to the locally excited π–π^*-transition (LE) located in the butadienyl-vinyl-amine chromophore[1,32–39] of the DHIs **5** (Table 2).

Irradiation of DHI **5a-β** in CH$_2$Cl$_2$ solution with polychromatic light *at room temperature* did not led to any color change owing to the fast 1,5-electrocyclization of the betaines **4** back to DHIs **5**. On the other hand, after cooling to −20 °C (*FT-UV/VIS at 253 K)*, irradiation of **5a-β** afforded a brown colored solution with two

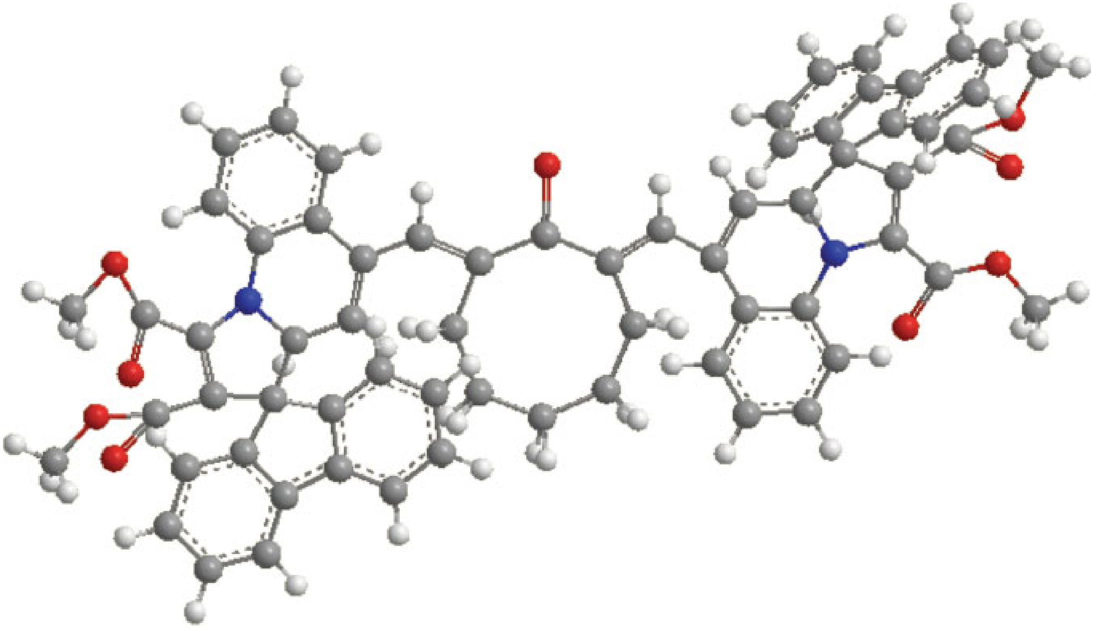


Figure 1. Representation of the optimized (MM2) structure of DHI **5d**

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

4/5	λ_{max}(DHI) (nm)	log (ε)	λ_{max}(betaine) (nm)	$k \times 10^{-3}$ (sec^{-1})	$t_{1/2}$ (msec)	Color of betaine
a	352;388	4.25	575;850	1.35	356	Orange-brown
b	349;386	4.15	550;875	1.77	397	Orange-brown
c	344;381	4.08	525;900	1.54	450	Brown
d	343;380	4.07	525;900	1.51	459	Brown
e	348;382	4.22	550;850	3.30	210	Orange-brown
f	243;378	4.17	525;825	2.92	237	Orange-brown
g	339;373	4.07	500;825	2.48	280	Orange-brown
h	339;372	4.04	500;800	2.44	284	Orange-brown
I	345;380	4.20	550;850	4.28	162	Orange-brown
j	342;377	4.14	525;825	3.48	199	Orange-brown
k	337;371	4.08	525;800	2.94	236	Orange-brown
l	337;370	4.07	525;800	2.88	241	Orange-brown
m	342;378	4.19	550;850	7.00	99	Brown
n	340;375	4.12	525;825	5.64	123	Orange-brown
o	336;372	4.03	525;800	4.18	166	Orange-brown
p	335;372	4.16	500;800	4.08	170	Orange-brown
q	340;377	4.10	500;800	2.04	340	Orange-brown
r	338;375	4.02	500;800	2.25	308	Orange-brown
s	336;373	4.00	525;825	2.50	277	Orange-brown
t	331;370	4.15	575;850	2.58	269	Brown
u	341;378	4.01	550;850	2.40	289	Brown
v	339;374	3.95	575;850	2.73	254	Brown
w	338;370	3.94	550;850	3.25	213	Brown
x	336;369	3.89	500;850	3.62	209	Brown
y	342;377	4.05	550;825	9.12	76	Brown
z	340;373	3.97	525;850	6.60	105	Brown
α	336;366	3.90	525;875	5.13	135	Brown
β	336;367	3.88	500;825	5.21	133	Orange-brown

absorption bands ranging (Table 2) between 500 and 575 nm and between 800 and 900 nm, respectively (Figures 2 and 3) with a tail extending beyond 1100 nm as recorded by *FT/UV-VIS* spectrophotometer. To examine more deeply the absorption maxima in the IR-region, both millisecond flash photolysis and laser flash photolysis measurements were done (Figures 4 and 5). For instance, the millisecond flash photolysis spectrum of betaine **4α** showed two maxima, one at 525 nm and the other in the IR-region at 875 nm (Figure 4). In addition,

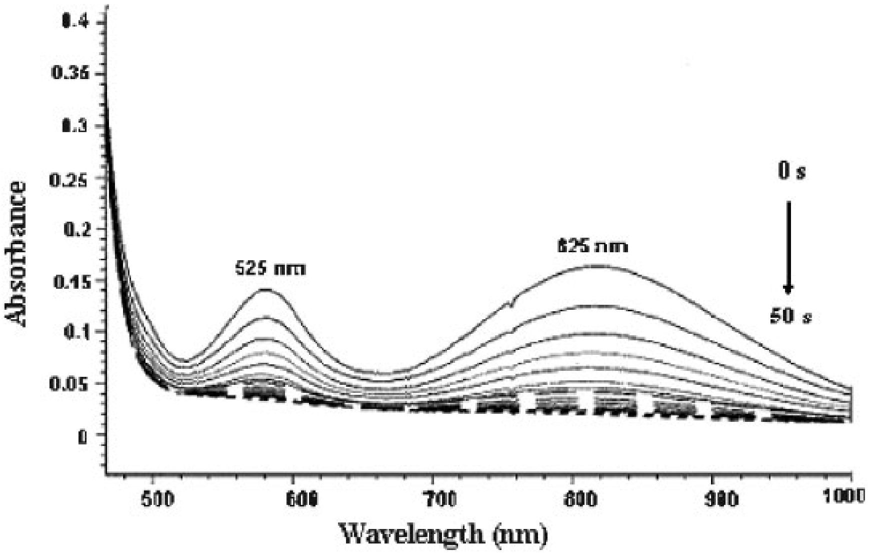


Figure 2. Kinetic FT-UV/VIS spectrum of the thermal fading of betaine **4s** to bis-DHI **5s** (cycle time = 2.5 sec, run time = 50 sec) in CH_2Cl_2 ($c = 1 \times 10^{-5}$ mol/l at 253 K)

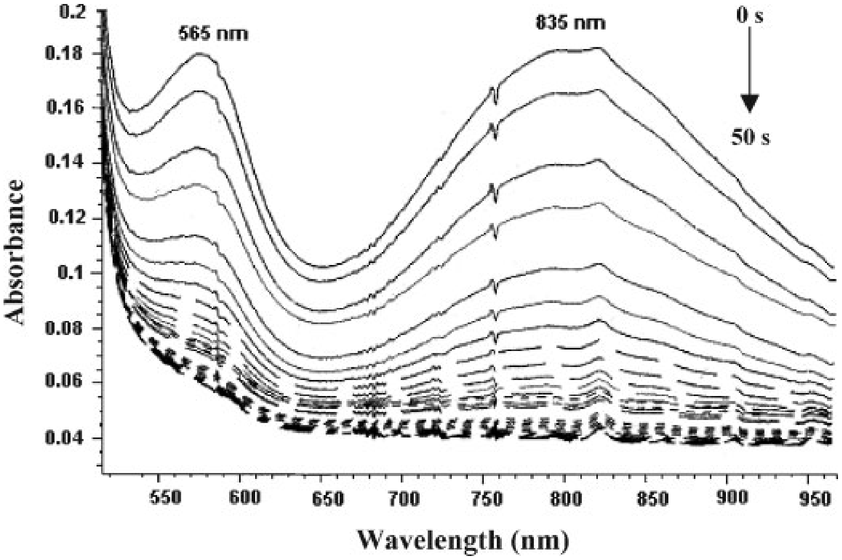


Figure 3. Kinetic FT-UV/VIS spectrum of the thermal fading of betaine **4y** to bis-DHI **5y** (cycle time = 1 sec, run time = 30 sec) in CH_2Cl_2 ($c = 1 \times 10^{-5}$ mol/l at 253 K)

the laser flash photolysis spectrum of betaine **4l** (Figure 5) revealed two maxima, one at 525 nm and the other in the IR-region at 800 nm. Irradiation of DHI **4a-β** in CH_2Cl_2 *at 77 K* (liquid nitrogen) afforded a very strong orange-brown to brown colored betaines **4a-β** which could be stored at this temperature for several weeks without any color decay. The strong colorability of betaines **4a-β** may be attributed to their highly conjugated structure as well as to the presence of the chromophoric carbonyl group.

Effect of Substituents on the λ_{max} of the bis-photochromic DHIs 5a-β.

(i) *Effect of the alkyl ester groups on the absorption maxima of the DHIs* **5a-β***(region B).* Generally,

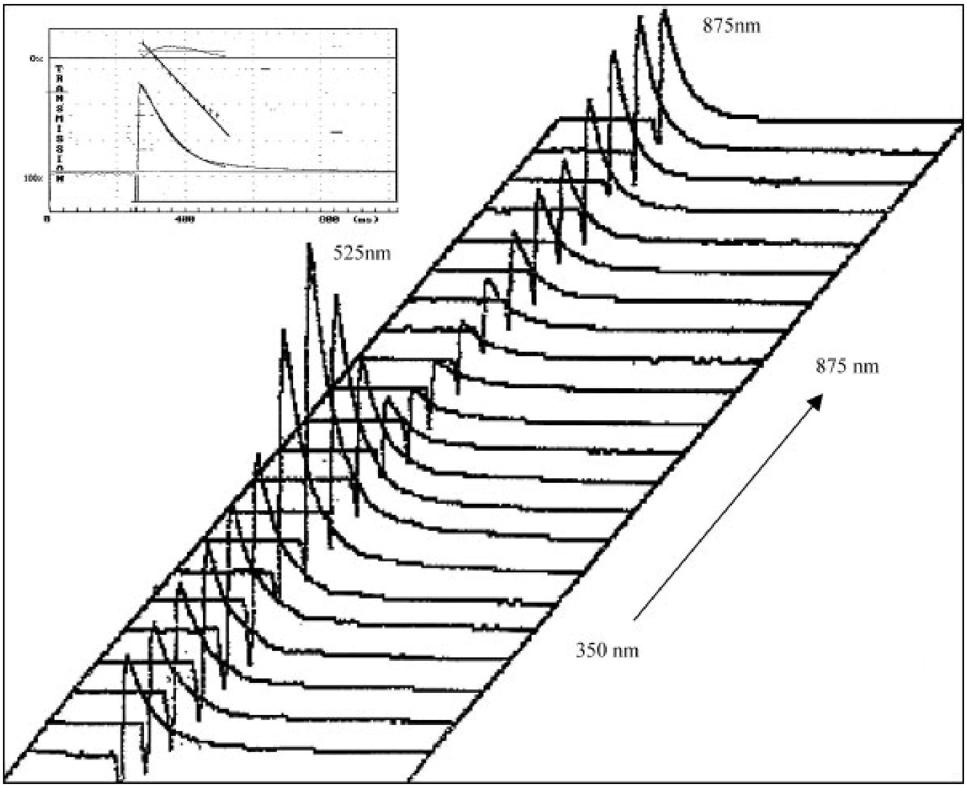


Figure 4. Absorbance decay curves and half-life determination of betaine **4α** at different wavelengths (350–900 nm every 25 nm). Insert shows the kinetic analysis of the curve at 525 nm ($t_{1/2} = 135$ msec with correlation coefficient = 0.9987)

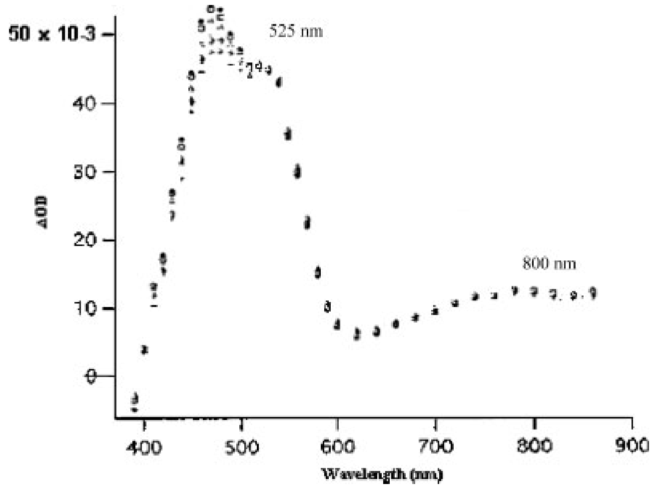


Figure 5. Transient absorption spectra of compound **4l** in dichloromethane solution excited at 340 nm with a ruby laser and analysed at different times (400, 2000, 4000, 8000, 14 000 msec) after the laser pulse at ambient temperature

changing the alkyl ester group has resulted in a very small influence on the λ_{max} of DHIs.[3,19] A hypsochromic shift in the absorption maxima of the bisphotochromic DHI **5a-β** from 3 to 8 nm was observed by changing the alkyl ester from methyl to *ter*-butyl group. The cyclohexyl and norbonyl alkyl ester groups DHIs **5u–x** and **5y-β** showed almost the same absorption maxima with a hypsochromic shift of about 10 nm compared with the substituted methyl ester groups DHI **5a–d** (Table 2). These small hypsochromic shifts did not lead to any color change of the DHIs in solution as well as in the solid state. These results were in good agreement with former studies on the styryl-DHI system.[32,38]

(ii) *Effect of the cycloalkanone ring size on the absorption maxima of DHI* **5a-β**. A small hypsochromic shift by about 5 nm in the first absorption maxima and 10 nm by increasing the DHIs cycloalkanone ring size was noticed. For example, DHI **5u** (bearing cyclopentanone) showed absorption maxima at 341 and 378 nm while DHI **5x** (bearing cyclooctanone) showed absorption maxima at 336 and 369 nm (Table 2). This noticeable bathochromic shift maybe due to the steric hindrance of the large size of the cycloalkanone with the DHI skeleton as well as the stabilization of the electron density on the carbonyl-oxygen chromophore. A non-pronounced difference of the absorption maxima of the DHIs bearing cycloheptanone and DHIs bearing cyclooctanone was recorded.

(iii) *Effect of alkyl ester groups on the absorption maxima of the colored betains* **4a-β** (region B). The change of the alkyl ester group in a fixed betaine system generally has no marked influence on the λ_{max} of the betaine form as well as on the color.[32–39] It was noticeable that there is a small hypsochromic

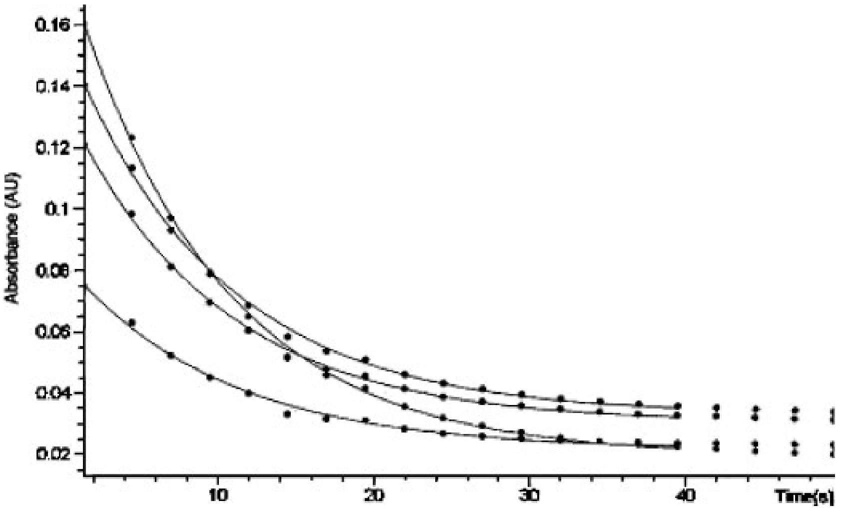


Figure 6. Absorbance-time relationship for the kinetic thermal fading of betaine **4s** at different wavelengths (450, 550, 650, and 750) for determination of the electrocyclization rate constant *k* at 253 K

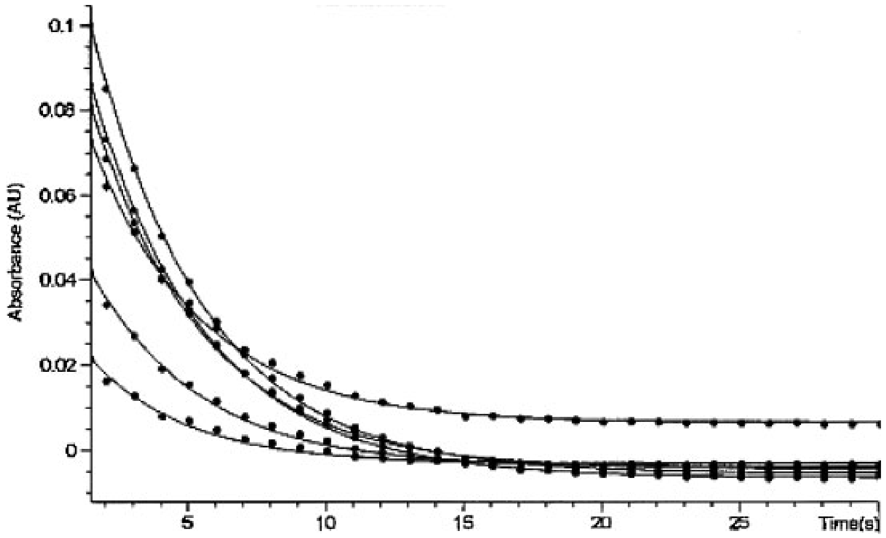


Figure 7. Absorbance-time relationship for the kinetic thermal fading of betaine **4y** at different wavelengths (450, 550, 600, 650, 700, and 750) for determination of the electrocyclization rate constant *k* at 253 K

shift by about 50 nm (as recorded by millisecond flash photolysis measurements) by changing the alkyl ester from methyl (**4a**) to pentyl groups. This was in agreement with the former results on the effect of ester groups on the absorption maxima of the colored betaines (Table 2) which showed that the bulky ester groups led to a hypsochromic shift. Also, a hypsochromic shift by 25 nm by changing the alkyl ester group from cyclohexyl to norbonyl groups. Generally, it has been considered that a bulky substituent sometimes causes strain to hamper charge delocalization, namely, planar structure formation resulted in hypsochromic shift.[37]

(iv) *Effect of the cycloalkanone ring size on the absorption maxima of DHI* **5a-β**. Interestingly, a bathochromic shift by 25–75 nm of the absorption band in the IR-region by increasing the cycloalkanone ring size was recorded. On the other hand, a hypsochromic shift by 25–50 nm of the absorption band in the UV-region was observed. This may be attributed to the enlargement of the ring size which has more-electron donating methylene groups, which led to increase the electron density on the carbonyl oxygen chromophore.[14,15] The absorption maxima of the DHIs bearing a cycloheptanone ring showed almost the same absorption maxima of the DHIs bearing cyclooctanone ring.

Kinetics of the 1,5-electrocyclization of betaines 4a-β to DHIs 5a-β

The kinetics of the fast reverse 1,5-electrocyclization of the colored betaines **4a-β** into the corresponding DHIs **5a-β** were detected using both FT-UV/VIS (Figs. 2,3,6,7), millisecond flash photolysis (Fig. 4) and laser flash photolysis measurements (Fig. 5). The decrease in absorption of the colored betaine with time was measured according to the measurement techniques. The cyclization rate constant (*k*) and the half-lives ($t_{1/2}$) are listed in Table 2.

(i) *Effect of alkyl ester groups on the half-lives of the colored betains* **4a-β**. Changing the alkyl group from methyl to ethyl and isopropyl or *ter*-butyl in the ester group leads to a decrease in the half-life time by a factor of 3.60. This may be due to the strong electron donation of the *ter*-butyl group compared with the methyl group. The norbornyl ester betaine **4y** showed a smaller $t_{1/2}$ by a factor of 4.68 than the betaine **4a**, in which the bulky norbornyl groups might be associated with larger electron-donating effects. These interesting results reflect well the tuning of the photophysical properties by changing the substitution in the DHI system, which may lead to tunable the DHI system for applications.

(ii) *Effect of cycloalkanone ring size on the half-lives of the colored betaines* **4a-β**. A pronounced increase in the half-lives of the colored betaines **4a–b** by increasing the cycloalkanone size was observed. For example, there is an increase of the $t_{1/2}$ of betaine **4m** (bearing cyclopentanone ring, $t_{1/2} = 99$ msec) by factor 1.72 compared with the $t_{1/2}$ of betaine **4p** (bearing cyclooctanone ring, $t_{1/2} = 170$ msec). A noticeable small increase in the $t_{1/2}$ of the betaines carrying the cyclooctanone ring by about 5 msec compared with those bearing cyclooctanone. These results are attributed to the steric effect of the bulky cycloalkanone ring which hinders the 1,5-electrocyclization process. All above mentioned influences are in agreement with our former studies on photochromic DHIs.[33–36]

Photo-Fatigue Resistance of Photochromic DHIs 5a-β and their Corresponding Betaines 5a-β at low temperature

In studying the quality of a photochromic system or in other terms, the thermal full reversibility of a specific photochromic molecule, the problem of carrying out a large number of colorization–decolorization cycles arises frequently. The gradual loss of the ability to change color by exposure to visible or ultraviolet light in this context has been termed fatigue.[1,16a] Gautron[43] has advanced a quantitative approach to measure the fatigue in photochromic systems.

By irradiation of degassed dichloromethane solutions of the bis-spirodihydroindolizines **5a-β** with polychromatic light ($\lambda = 200–400\,nm$) at 253 K (due to the fast thermal bleaching process), the orange-brown to brown colored betaines **4a-β** were produced. Upon continued irradiation they decomposed after some time. However, if oxygen is excluded, these systems are noticeably more stable. It is possible that in the presence of oxygen, the betaines **4a-β** act as sensitizers towards singlet oxygen.[1,38] The t_{30}-value which is the time of fading of the initial absorbance of the colored betaine from 100% at time = 0–30% of its initial absorbance in the photodegradation experiments was recorded.

From the photodegradation data represented in Table 3 and Figs. 8 and 9, it appears that, the betaine form of the dimethyl ester bis-styryl DHI **5a** ($t_{30} = 409$ min, Fig. 8)) is the most stable betaine studied, which is also more stable than the standard dicyano-pyridazine DHI ($t_{30} = 278$ min), by a factor of 1.47. This is due to the high electron attraction of the cyano groups in the reference compound. The betaines with *ter*-butyl, cyclohexyl, and norbornyl ester groups showed a lower stability than dimethyl substituted betaine **4a** probably due to the steric hindrance of the bulky ester groups.[22] Interestingly, by increasing the cycloalkanone ring size, a remarkable decrease in the photostability of the betaine forms was recorded. For example increasing the cycloalkanone ring size from cyclopentanone as in the case of betaine **4i** ($t_{30} = 395$ min.) to cycloheptanone ($t_{30} = 310$ min.) led to decrease the photostability by a factor of 1.27 but still has a t_{30}-value higher than that of the standard betaine by a factor 1.15. These results may be attributed to the highly pronounced steric hindrance of the large size cycloalkanone ring from cyclopentanone to cyclooctanone. The steric effect of the large size cycloalkanones showed a pronounced effect on the photodegradation of the colored betaines **4** which is the main goal of the present work.

Table 3. Photodegradation data of selected betaines **4** in dichloromethane ($c = 1 \times 10^{-5}$ mol/l) at −20 °C

4	$t_{1/2}$ (msec)	λ_{max} Betaine (nm)	t_{30}-betaine/DHI (min)	*F*
a	356	575;850	409	1.47
c	450	525;900	321	1.15
f	237	525;825	349	1.26
h	284	500;800	316	1.14
I	162	550;850	395	1.42
k	236	525;800	310	1.15
m	99	550;850	371	1.33
p	170	500;800	296	1.06
s	277	525;825	305	1.10
u	289	550;850	335	1.21
v	254	575;850	321	1.15
x	209	500;850	260	0.94
y	76	550;825	276	0.99
α	135	525;875	253	0.91
β	133	336;825	239	0.86
Standard	56.2	538	278	1.**0**

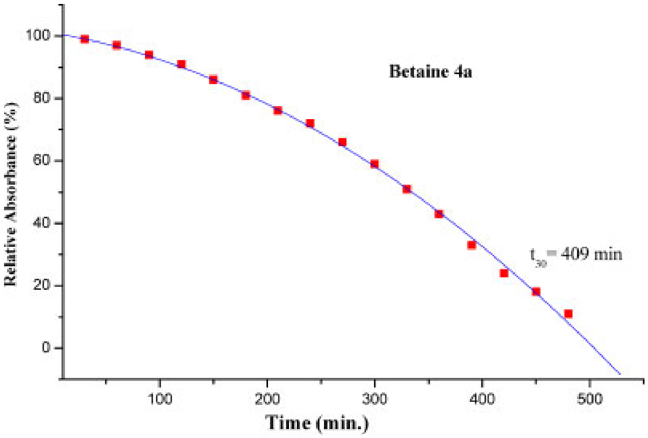


Figure 8. FT-UV/VIS curve analysis at 850 nm for betaine **4a** in CH_2Cl_2 at −20 °C ($c = 1 \times 10^{-5}$ mol/l)

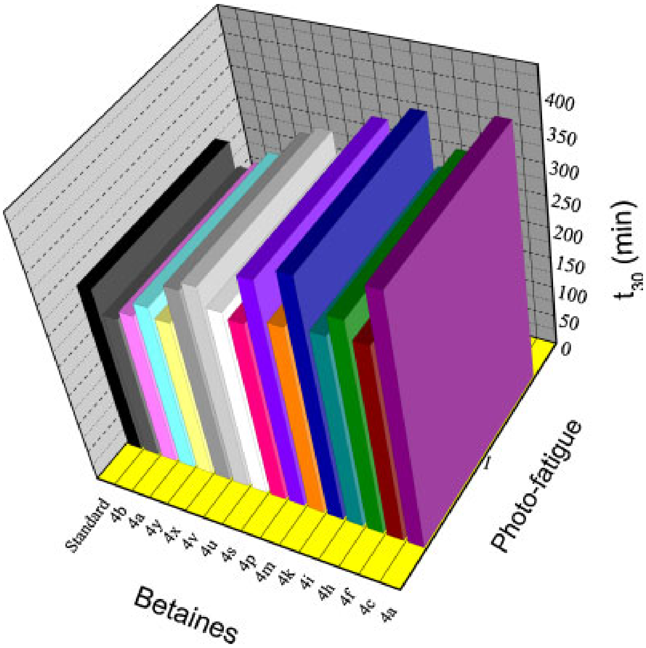


Figure 9. Balcony diagram showing the t_{30}-values of some selected betaines recorded from the photo-fatigue experiments ($c = 1 \times 10^{-5}$ mol/l)

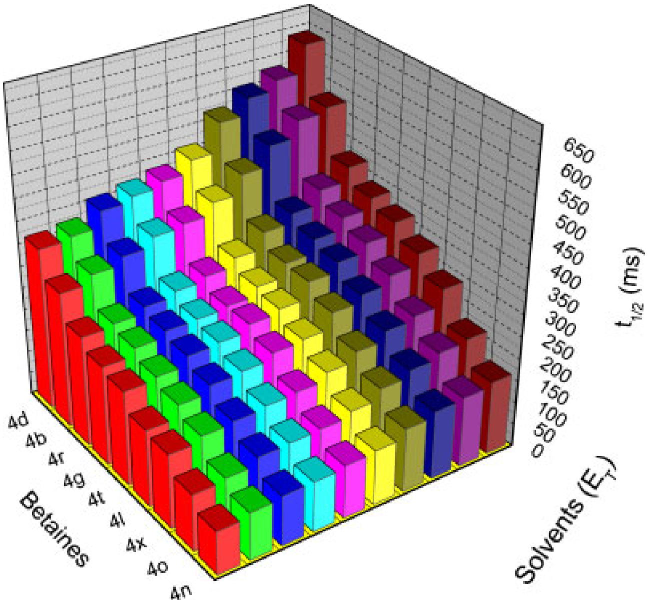


Figure 10. Balcony diagram showing the relationship between the half-lives ($t_{1/2}$) of betaines **3b,d,l,n,o,q,r,t,x** with differing solvent polarity ($c = 1 \times 10^{-5}$ mol/l) at 296 K

Solvatochromism

It has long been known that UV/vis/near-IR absorption spectra of chemical compounds may be influenced by the surrounding medium and that solvents can bring about a change in the position, intensity, and shape of absorption.[44] The term solvatochromism is, however, so well established in the literature that it would be difficult to convince the scientific community to change this term to perichromism, which is certainly a more general expression for the spectroscopic phenomena under consideration.

A strong effect of the solvent polarity on the λ_{max} and the half-lives of betaine **4a-β** were observed. Changing the solvent from dichloromethane to ethanol causes *hypsochromic* shifts of $\Delta\nu \cong +500\,\text{cm}^{-1}$ in the visible region, and markedly larger shifts of $\Delta\nu \cong +1100\,\text{cm}^{-1}$ in the near IR-region. This solvatochromic effect is in agreement with previous observations on DHIs.[18,19,38] These two solvatochromic shifts are ascribable to π–π^*-transitions in the visible region and charge transfer transitions in the near IR-region[32,34,45] (Table 4).

The effect of solvent polarity was also studied by using FT-UV/VIS technique to determine the half-life ($t_{1/2}$) of betaines **4a-β** in ten different solvents (Table 3). As expected, the half-lives increase with increasing solvent polarity (Fig. 10). 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 the solvent polarity due to the electrostatic interactions.[1,32–38]

SUMMARY AND CONCLUSION

The main motivation behind this work was to synthesize, develop and tune the photophysical properties of novel bis-photochromic DHIs based on 1,5-electrocylization bearing different sizes of cycloalkanone moieties at the 7′-position of the DHI skeleton. These novel photochromic compounds **5a-β** derived from bis-styrylquinolinedihydroindolizines (DHIs) showed an interesting absorption in the VIS/IR region. Irradiation of compounds **5a-β** led to colored betaines **4a-β** showing two main absorption maxima, one in the visible and the other in the IR-region, which were observed using *UV–VIS spectrometry at low temperature(253 K)*, millisecond flash photolysis at ambient temperature and laser flash photolysis. Tuning of the photophysical properties of DHIs **5a-β** and their colored betaines **4a-β** by changes in the ester groups as well as in the cycloalkanone ring size was clearly achieved. This series of substituted DHIs shows improved physical properties as compared with previous related compounds:[1b] longer half-lives and further bathochromic shifts in the IR region (more than $750\,\text{cm}^{-1}$). A noticeable increase of the t_{30}-values of some selected betaines **4a-β** by a factor ranging between

Table 4. Half-lives ($t_{1/2}$) of thermal 1,5-electrocyclization of selected betaines **4b,d,g,l,n,o,r,t,x** and $E_T(30)$ values of ten different solvents detected by millisecond flash photolysis experiments ($c = 1 \times 10^{-5}$ mol/l) at 23 °C

	Betaines $t_{1/2}$ (ms)									
Solvents	**4b**	**4d**	**4g**	**4l**	**4n**	**4o**	**4r**	**4t**	**4x**	$E_T(30)$
n-Pentane	306	366	224	173	97	127	248	213	166	32
Toluene	325	373	241	201	107	133	254	219	178	34
Dioxane	342	407	253	217	112	149	267	239	182	36
Tetrahydrofurane	364	419	255	222	113	152	279	244	188	37
Chloroform	371	431	260	236	119	154	289	259	191	39
Dichloromethane	397	459	280	241	123	166	308	269	209	41
Acetonitrile	439	522	310	276	143	189	344	306	229	46
2-Propanol	482	556	341	291	153	203	364	326	249	49
Ethanol	519	578	368	311	157	216	396	346	258	52
Methanol	529	638	391	337	165	221	427	371	294	56

1.10 and 1.47 compared with the betaine form of dicyanopridazine DHI used in former studies as standard ($t_{30} = 278$ min) was observed. The high photo-fatigue resistance of these betaines will help to find applications. An increase in the half-lives of selected betaines **3a-β** with increasing solvent polarity was observed. The steric effect of the large size cycloalkanones showed a pronounced effect on the photochromism of the colored betaines **4** such as absorption spectra, kinetics of 1,5-electrocyclization, photodegradation as well as solvatochromism, which is the main goal of the present work.

EXPERIMENTAL

The solvents used (Aldrich or Merck were spectroscopic grade) were dried, according to standard procedures,[46] over sodium or potassium metal (diethyl ether, toluene, THF, *n*-pentane, *n*-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 nitrogen atmosphere.

Spirocyclopropene derivatives were obtained via photolysis of the corresponding pyrazoles prepared according to reported procedures. Photolysis was carried out in the photochemical reactor of Schenck[47] made of Pyrex ($\lambda > 290$ nm). The source of irradiation was a high-pressure mercury lamp Philips HPK 125 W. 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 length × 2 cm diameter) on silica gel and CH_2Cl_2 as eluent. Melting points were measured on a Gallenkamp or a Büchi (Smp-20) melting point apparatus.

All NMR spectra were recorded 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. Mass spectra were recorded on a Mat-90, FINNIGAN MAT mass spectrometer. Elemental analysis (CHN) was carried out on a LECO CHNS-932-analyzer. UV-spectra were recorded on a FT-UV/ VIS HP 6543 computer-spectrometer. Millisecond flash photolysis was carried out with a 12 V (50 W) halogen lamp, Photoflash (METZ 32 Z-1). The laser flash photolysis experiments were carried out with frequency-double-pulsed ruby laser excitation and Nd:YAG-laser.[24,28,35,36,38] A detailed description of the experimental setup has been published.[24,28]

General procedure for preparation of DHIs **5a-β** and full spectroscopic and elemental analysis data of DHIs **5a–d** are listed below as reference compounds. A satisfactory typical NMR, IR, MS, and elemental analysis for the rest of the synthesized DHIs **5e-β** were recorded.

Preparation of bis-[dimethyl 9′-styryl-spiro[fluorene-9,1′-pyrrolo-[1,2-a] quinoline]-2,3-dicarboxylate]cycloalkanones 5a-β

General procedure. To a solution of spirocyclopropenes **1a–g** (0.001 mol) in dry diethyl ether (50 ml) was added a solution of 2,6-diquinolidenecycloalkanones **2a–d** (0.001 mol) in dry diethyl ether (10 ml) over 15 min under dry nitrogen atmosphere. The mixture was stirred at room temperature for about 24 h (TLC-controlled) in the absence of light. 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 **5a-β** as white to yellow needles in 11–42% yield.

*bis-[dimethyl 9′-styryl-spiro[fluorene-9,1′-pyrrolo-[1,2-a] quinoline]-2,3-dicarboxylate]cyclopentanone (***5a***)*. Reactants: 306 mg (0.001 mol) spirocyclopropene **1a**, 362 mg (0.001 mol) 2,6-diquinolidenecyclopentanone **2a**; yield 353 mg (42.4%) white crystals from ether; m.p. 172 °C. ^{1}HNMR ($CDCl_3$): $\delta = 7.75$–7.77 (m, 4H, CH-arom.), 7.56–7.58 (d, $J = 7.12$ Hz, 2H, CH-arom.), 7.47–7.49 (d, $J = 7.11$ Hz, 2H, CH-arom.), 7.35–7.42 (m, 2H, CH-arom.), 7.27–7.30 (m, 4H, CH-arom.), 7.17–7.22 (m, 6H, CH-arom.), 7.04–7.08 (dd, $J = 7.00$ Hz, 2H, CH-arom.), 6.90–6.99 (dt, $J = 7.55$, 2H, CH-arom.), 6.93–6.94 (d, 2H, H_A), 5.59–5.60 (dd, 2H, $H_{10'}$), 5.45 (dd, 2H, $H_{10'a}$), 4.29 (s, 6H, 3′-CH3), 3.19 (s, 3H, 2′-CH3), 2.68 (d, 4H, $2CH_2$-cyclopentanone), ppm. ^{13}CNMR ($CDCl_3$): $\delta =$ 163.23 (CO-cyclopentanone), 162.23 (3′-CO), 161.99 (2′-CO), 69.63 (10′a-C), 63.19 (spiro-C), 53.45 (3′-CH3), 51.01 (2′-CH3) ppm. MS (70 eV): m/z (%) = 975.00 [M^+] (12.30), 49.23 [B^+] (100). IR (KBr): $\nu = 3078$ (C—H, arom.), 2825–2993 (C—H, aliph.), 1736 (3′-C═O), 1687 (C═O-cyclopentanone), 1679 (2′-C═O), 1592 (C═C), 1499, 1263, 1219, 1153, 1100, 990, 736, 689 cm^{-1}. Elemental analysis for $C_{63}H_{46}N_2O_9$ (molecular weight = 975.01): calc. %: C, 77.60; H, 4.76; N, 2.87; found C, 77.61; H, 4.77; N, 2.90%.

*bis-[dimethyl 9′-styryl-spiro[fluorene-9,1′-pyrrolo-[1,2-a] quinoline]-2,3-dicarboxylate]cyclohexanone (***5b***)*. Reactants: 306 mg (0.001 mol) spiropcyclopropene **1a**, 376 mg (0.001 mol) 2,6-diquinolidenecyclohexanone **2a**; yield 358 mg (36.2%) white crystals from ether-CH_2Cl_2 (8:4); m.p. 161 °C. ^{1}HNMR ($CDCl_3$): $\delta = 7.78$–7.79 (m, 4H, CH-arom.), 7.57–7.59 (d, $J = 7.12$ Hz, 2H, CH-arom.), 7.46–7.47 (d, $J = 7.11$ Hz, 2H, CH-arom.), 7.35–7.40 (m, 2H, CH-arom.), 7.29–7.31 (m, 4H, CH-arom.), 7.19–7.24 (m, 6H, CH-arom.), 7.06–7.09 (dd, $J = 7.00$ Hz, 2H, CH-arom.), 6.92–6.96 (dt, $J = 7.55$, 2H, CH-arom.), 6.94–6.96 (d, 2H, H_A), 5.60–5.62 (dd, 2H, $H_{10'}$), 5.44–5.46 (dd, 2H, $H_{10'a}$), 4.32 (s, 6H, 3′-CH3), 3.21 (s, 3H, 2′-CH3), 2.69 (d, 4H, $2CH_2$-cyclohexanone), 1.99 (dt, 2H, CH_2-cyclohexanone) ppm. ^{13}CNMR ($CDCl_3$): $\delta = 163.00$ (CO-cyclohexanone), (162.26 (3′-CO), 162.00 (2′-CO), 69.67 (10′a-C), 63.22 (spiro-C), 53.49 (3′-CH3), 51.23 (2′-CH3) ppm. MS (70 eV): m/z

(%) = 990 [M^{+1}] (19.13), 39.92 [B^{+}] (100). IR (KBr): $\nu = 3093$ (C—H, arom.), 2885–2995 (C—H, aliph.), 1744 (3′-C═O), 1682 (C═O-cyclohexanone), 1687 (2′-C═O), 1586 (C═C), 1492, 1267, 1212, 1158, 1091, 967, 722, 684 cm^{-1}. Elemental analysis for $C_{64}H_{48}N_2O_9$ (molecular weight = 989.03): calc. C, 77.72; H, 4.89; N, 2.83; found C, 77.81; H, 4.92; N, 2.77%.

*bis-[dimethyl 9′-styryl-spiro[fluorene-9,1′-pyrrolo-[1,2-a] quinoline]-2,3-dicarboxylate]cycloheptanone (***5c***)*. Reactants: 306 mg (0.001 mol) spiropcyclopropene **1a**, 390 mg (0.001 mol) 2,6-diquinolidenecycloheptanone **2c**; yield 310 mg (30.9%) as white crystals from ether; m.p. 154 °C. ^{1}HNMR (CDCl$_3$): $\delta = 7.76$–7.78 (m, 4H, CH-arom.), 7.55–7.56 (d, $J = 7.12$ Hz, 2H, CH-arom.), 7.44–7.46 (d, $J = 7.11$ Hz, 2H, CH-arom.), 7.39–7.42 (m, 2H, CH-arom.), 7.26–7.28 (m, 4H, CH-arom.), 7.21–7.22 (m, 6H, CH-arom.), 7.11–7.14 (dd, $J = 7.00$ Hz, 2H, CH-arom.), 6.94–6.93 (dt, $J = 7.56$, 2H, CH-arom.), 6.93–6.96 (d, 2H, H$_A$), 5.63–5.65 (dd, 2H, H$_{10'}$), 5.44–5.45 (dd, 2H, H$_{10'a}$), 4.38 (s, 6H, 3′-CH3), 3.29 (s, 3H, 2′-CH3), 2.72 (d, 4H, 2CH$_2$-cycloheptanone), 1.98 (d, 4H, 2CH$_2$-cycloheptanone) ppm. ^{13}CNMR (CDCl$_3$): $\delta = 162.89$ (CO-cycloheptanone), (162.27 (3′-CO), 162.12 (2′-CO), 69.64 (10′a-C), 63.24 (spiro-C), 53.47 (3′-CH3), 51.27 (2′-CH3) ppm. MS (eV): *m/z* (%) = 1003 [M^{+}] (22.84), 43.99 [B^{+}] (100). IR (KBr): $\nu = 3085$ (C–H, arom.), 2884–2998 (C–H, aliph.), 1746 (3′-C═O), 1680 (C═O-cycloheptanone), 1690 (2′-C═O), 1584 (C═C), 1497, 1266, 1217, 1156, 1098, 967, 723, 686 cm^{-1}. Elemental analysis for $C_{65}H_{50}N_2O_9$ (molecular weight = 1003.06): calc. C, 77.83; H, 5.02; N, 2.79; found C, 77.96; H, 4.98; N, 2.81.

*bis-[dimethyl 9′-styryl-spiro[fluorene-9,1′-pyrrolo-[1,2-a] quinoline]-2,3-dicarboxylate]cyclooctanone(***5d***)*. Reactants: 306 mg (0.001 mol) spirocyclopropene **1a**, 196 mg (0.001 mol) 2,6-diquinolidenecyclooctanone **2d**; yield 194 mg (19.3%) as white crystals from ether; m.p. 143 °C. ^{1}HNMR (CDCl$_3$): ^{1}HNMR (CDCl$_3$): $\delta = 7.79$–7.81 (m, 4H, CH-arom.), 7.54–7.55 (d, $J = 7.12$ Hz, 2H, CH-arom.), 7.46–7.48 (d, $J = 7.11$ Hz, 2H, CH-arom.), 7.41–7.43 (m, 2H, CH-arom.), 7.28–7.29 (m, 4H, CH-arom.), 7.22–7.27 (m, 6H, CH-arom.), 7.11–7.15 (dd, $J = 7.00$ Hz, 2H, CH-arom.), 6.95–6.96 (dt, $J = 7.56$, 2H, CH-arom.), 6.91–6.93 (d, 2H, H$_A$), 5.60–5.61 (dd, 2H, H$_{10'}$), 5.17–5.19 (dd, 2H, H$_{10'a}$), 4.26 (s, 6H, 3′-CH3), 3.18 (s, 3H, 2′-CH3), 2.72 (d, 4H, 2CH$_2$-cyclooctanone), 1.98 (d, 6H, 2CH$_2$-cyclooctanone) ppm. ^{13}CNMR (CDCl$_3$): $\delta = 162.84$ (CO-cyclooctanone), 162.24 (3′-CO), 162.11 (2′-CO), 69.62 (10′a-C), 63.21 (spiro-C), 53.43 (3′-CH3), 51.26 (2′-CH3) ppm. MS (eV): *m/z* (%) = 1018 [M^{+1}] (16.89), 32.01 [B^{+}] (100). IR (KBr): $\nu = 3072$ (CH-arom.), 2865–2993 (C—H, aliph.), 1742 (3′-C═O), 1679 (C═O-cyclooctanone), 1673 (2′-C═O), 1582 (C═C), 1489, 1264, 1222, 1151, 1093, 967, 720, 681 cm^{-1}. Elemental analysis for $C_{66}H_{52}N_2O_9$ (molecular weight = 1017.09): calc. C, 78.06; H, 5.15; N, 2.75; found C, 77.99; H, 5.02; N, 2.69%.

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REFERENCES

1. (a) Dürr H. In *Photochromism-Molecules and Systems*, Dürr H, Bouas-Laurent H (eds). Elsevier: Amsterdam, 1990; (b) Dürr H. In *Organic Photochromic and Thermochromic Compounds*, (vol. 1), Crano JC, Guglielmetti RJ (eds). Plenum Press: New York, 1999; 223–266; (c) Crano JC, Guglielmetti RJ (eds). *Photochromic and Thermochromic Compounds*, vol. I and II, 1999; Kluwer Academic Publishers, Plenum Press, New York; (d) Brown GH. *Photochromism*, Wiley-Interscience: New York, 1971.
2. Fisher E, Hirshberg Y. *J. Chem. Soc.* 1952; **1**: 4522.
3. Ashwell GJ. *Molecular Electronics*, 1992; John Wiley & Sons Inc.: New York.
4. (a) Irie M. *Chem. Rev.* 2000; **100**: 1685–1716; (b) Berkovic G, Krongauz V, Weiss V. *Chem. Rev.* 2000; **100**: 1741–1753; (c) Kawata S, Kawata Y. *Chem. Rev.* 2000; **100**: 1777–1788.
5. (a) Gilat SL, Kawai SH, Lehn JM. *J. Chem. Soc., Chem. Commun.* 1993; 1439–1442; (b) Saika T, Irie M, Shimidzu T. *J. Chem. Soc., Chem. Commun.* 1994; 2123–2124; (c) Gilat SL, Kawai SH, Lehn JM. *Chem. Eur. J.* 1995; **1**: 275–284; (d) Tsivgoulis GM, Lehn JM. *Angew. Chem. Int. Ed. Engl.* 1995; **34**: 1119–1122; (e) Kawai SH, Gilat SL, Ponsinet R, Lehn JM. *Chem. Eur. J.* 1995; **1**: 285–293; (f) Tsivgoulis GM, Lehn JM. *Chem. Eur. J.* 1996; **2**: 1399–1406; (g) Irie M. *Bull. Chem. Soc., Jpn.* 1998; **71**: 985–996.
6. (a) Takeshita M, Irie M. *Tetrahedron Lett.* 1999; **40**: 1345–1348; (b) Kawai SH, Gilat SL, Lehn JM. *Eur. J. Org. Chem.* 1999; 2359–2366; (c) Yamagushi T, Inagawa T, Nakazumi H, Irie S, Irie M, *Chem. Mater.* 2000; **12**: 869–871; (d) Lucas LN, Van Esch J, Kellogg RM, Feringa BL. *Chem. Commun.* 2001; 759–760; (e) Kawai T, Sasaki T, Irie M. *Chem. Commun.* 2001; 711–712.
7. Feringa BL (ed.). *Molecular Switches*. Wiley-VCH: Darmstadt, 2001.
8. (a) Feringa BL, Van Delden RA, Koumura N, Geertsema EM. *Chem. Rev.* 2000; **100**: 1789; (b) Yamada T, Muto K, Kobataka S, Irie M. *J. Org. Chem.* 2001; **66**: 6164–6168; (c) Irie M. *Supramol. Sci.* 1996; **3**: 87–89.
9. (a) Ahmed SA, Sallenave X, Fages F, Mieden-Gundert G, Muller WM, Muller U, Vogtle F, Pozzo JL. *Langmuir* 2002; **18**(19): 7096–7101; (b) Sallenave X, Delbaere S, Vermeersch G, Ahmed SA, Pozzo JL. *Tetrahedron Lett.* 2005; **46**(18): 3257–3259; (c) Sanguinet L, Ahmed SA, Pozzo JL, Rodriguez V, Adamietz F. *J. Nonlinear Opt. Phys. Mater.* 2004; **13**(3–4): 423–426; (d) Sallenave X, Delbaere S, Ahmed SA, Vermeersch G, Pozzo JL. *Int. J. Photoenergy.* 2004; **6**(4): 169–173.
10. (a) Ahmed SA, Tanaka M, Ando H, Tawa K, Kimura K. *Tetrahedron.* 2004; **60**(28): 6029–6036; (b) Ahmed SA, Tanaka M, Ando H, Iwamoto H, Kimura K. *Tetrahedron.* 2004; **60**(14): 3211–3220; (c) Ahmed SA, Tanaka M, Ando H, Iwamoto H, Kimura K. *Tetrahedron.* 2003; **59**(23): 4135–4142, 2003; (d) Ahmed SA, Tanaka M, Ando H, Iwamoto H, Kimura K. *Eur. J. Org. Chem.* 2003; **13**: 2437–2442.
11. Hauck G, Dürr H. *Angew Chem.* 1979; **91**: 1010; *Int. Ed.* 1979; **18**: 945.
12. (a) Dürr H, Hauck G. *Deutsche Offenlegungs-Schrift.* Pat. 1979; 29 06 193. (b) Dürr H, Gross H, Hauck G. *Deutsche Offenlegungs Schrift.* 1983; **116**: 856–861.

13. (a) Dürr H, Schommer C, Münzmay T. *Angew. Chem*. 1986; **25**: 565–567; *Int. Ed*. 1986; **25**: 572–574; (b) Dürr H, Thome A, Kilburg H, Bossmann S, Blasius E, Janzen K, Kranz C. *J. Phys. Org. Chem*. 1992; **5**: 689–698; (c) Dürr H. *Chimica*. 1994; 514–515; (d) Dürr H, Amlung M, Rustemeyer F, Tan YS. *Deutsche Offenlegungs-Schrift Pat*. 1998; 198 349 408.
14. (a) Fromm R, Ahmed SA, Hartmann Th, Huch V, Abdel-Wahab AA, Dürr H. *Eur. J. Org. Chem*. 2001; **21**: 4077–4080; (b) Weber C, Rustemeyer F, Dürr H. *Adv. Mater*. 1998; **10**: 1348; (c) Andreis C, Dürr H, Wintgens V, Valat P, Kossanyi J. *Chem. Eur. J*. 1997; **3**: 509–516.
15. (a) Ahmed SA, Abdel-Wahab AA, Dürr H. *CRC Handbook of Organic Photochemistry and Photobiology* (2nd edn). Horspool WM, Lenci F (eds). CRC press: New York, 2004, Chapter 96, 1–25; (b) Seto J. In *Infrared Absorbing Dyes*, Matsuoka M (ed). Plenum Press: New York, 1990; 71–88.
16. (a) Bouas-Laurent H, Dürr H. *Pure Appl. Chem*. 2001; **73**: 639–665; (b) Dürr H. *Angew. Chem*. 1989; **101**: 427–445; *Int. Ed. Engl*. 1989; **28**: 413–438; (c) Dürr H. *Wiss. Zeitschr. TH Leuna-Merseburg*. 1984; **26**: 664–671; (d) Dürr H, Gross H, Zils KD. *Deutsche Offenlegungs-Schrift Pat*. 1983; 32 20 275 A 1.
17. (a) Dürr H, Jönsson HP, Scheidhauer P, Münzmay T, Spang P. *Deutsche Offenlegungs-Schrift Pat*. 1985; 35 21 432; (b) Dürr H, Janzen KP, Thome A, Braun B. *Deutsche Offenlegungs Schrift Pat*. 1988; 35 21 432 5; (c) Dürr H, Gross H, Zils KD, Hauck G, Hermann H. *Chem. Ber*. 1983; **116**: 3915–3925; (d) Düerr H, Spang P. *Deutsche Offenlegungs-Schrift Pat*. 1984; 32 20 25 71.
18. Ahmed SA, Weber C, Hozien ZA, Hassan KhM, Abdel-Wahab AA, Dürr H. *Unpublished results*.
19. Ahmed SA. *Ph.D Thesis*, Saarland-Assiut universities, 2000.
20. Burtscher P, Dürr H, Rheinberger V, Salz U. *German Pat*. 1995; DE 19 52 00 1 60.
21. Dürr H, Gross H, Zils KD. *Deutsche Offenlegungs-Schrift Pat*. 1983; 32 20 275 A 1.
22. Dürr H, Jeonsson HP, Scheidhauer P, Münzmay T, Spang P. *Deutsche Offenlegungs-Schrift Pat*. 1985; 35 214 325.
23. Dürr H, Janzen KP, Thome A, Braun B. *Deutsche Offenlegungs Schrift Pat*. 1988; 35 21 432 5.
24. Tan YS, Hartmann Th, Huch V, Dürr H, Kossanyi K. *J. Org. Chem*. 2001; **66**: 1130.
25. Weber C, Rustemeyer F, Dürr H. *Adv. Mater*. 1998; **10**: 1348.
26. Dürr H, Amlung M, Rustemeyer F, Tan YS. *Deutsche Offenlegunges-Schrift Pat*. 1998; 198 349 408.
27. Hartmann H, Ahmed SA, Tan YS, Dürr H, Renn A, Wild U. *Under Publication*; 2006.
28. Burtscher P, Dürr H, Rheinberger V, Salz U. *Fa. IVOCLAR German Pat*. 1995; 195200160. Chapter 1.
29. Gogritchiani E, Hartmann Th, Palm B, Samsoniya Sh, Dürr H. *J Photochem. Photobiol. B*, 2002; **67**: 18.
30. Andreis C, Dürr H, Wintgens V, Valat P, Kossanyi J. *Chem. Eur. J*. 1997; **3**: 509.
31. Bleisinger H, Scheidhauer P, Dürr H, Wintgens V, Valat P, Kossanyi J. *J. Org. Chem*. 1998; **63**: 990.
32. Ahmed SA, Hartmann Th, Huch V, Dürr H, Abdel-Wahab AA. *J. Phys. Org. Chem*. 2000; **13**(9): 539–548.
33. Tan YS, Ahmed SA, Dürr H, Huch V, Abdel-Wahab AA. *Chem. Comm*. 2001; **14**: 1246–1247.
34. Ahmed SA. *Mol. Cryst. & Liq. Cryst*. 2005; **430**: 295–300.
35. Ahmed SA, Dürr H. *Mol. Cryst & Liq. Cryst*. 2005; **431**: 275–280 (or 575–580).
36. Ahmed SA. *Monatshefte für Chemie*. 2004; **135**(9): 1173–1188.
37. Ahmed SA, Abdel-Wahab AA, Dürr H. *J. Photochem. Photobiol*. 2003; **154**(2–3): 131–144.
38. Ahmed SA. *J. Phy. Org. Chem*. 2002; **15**(7): 392–402.
39. Fromm R, Ahmed SA, Hatmann Th, Huch V, Abdel-Wahab AA, Dürr H. *Eur. J Org. Chem*. 2001; **21**: 4077–4080.
40. (a) Bergman C. *J. Org. Chem*. 1947; **12**: 363–367; (b) Geoffrey G, Spiros P. *Aust. J. Chem*. 1989; **42**: 279–285; (c) Radhakrishnan K, Srinivasam C. *Indian J. Chem. Sect. A*. 1995; **34**: 712–715.
41. (a) Kaplan H, Lindwall HG. *J. Am. Chem. Soc*. 1943; **65**: 927–928; (b) Tipson RS. *J. Am. Chem. Soc*. 1945; **67**: 507; (c) Hamer FM. *J. Chem. Soc*. 1923; **123**: 246; (d) Gilman H, Karmas G. *J. Am. Chem. Soc*. 1945; **67**: 342.
42. Hesse M, Meier H, Zeeh B. *Spektroskopische Methoden in der Organischen Chemie*. Georg Thieme Verlag, Stuttgart: New York, 1995; 185–186.
43. Gautron R. *Bull. Soc. Chim. France*. 1968; 3190.
44. (a) Schulz C, Dürr H. In *Photochromism-Molecules and Systems*, Dürr H, Bouas-Laurent H (eds). Elsevier: Amsterdam, 1990; 193–209; (b) Reichardt C. In *Solvent Effects in Organic Chemistry*. Verlag Chemie: Weinheim, 1979; (c) Reichardt C.*Chem. Soc. Rev*. 1992; 147–153 and all references therein; (d) Reichardt C. *Angew. Chem*. 1979; **91**: 119; Reichardt C, Echner M, Schäfer G.*J. Phys. Org. Chem*. 2001; **14**: 737–751.
45. Guglielmetti RJ. In *Photochromism-Molecules and Systems*, Dürr H, Bouas-Laurent H (eds). Elsevier: Amsterdam, 1990; 333–336.
46. (a) Perrin DD, Armarego WLF. *Purification of Laboratory Chemicals* (3rd edn). Pergamon Press: Oxford, 1988; (b) Becker HGO, Beckert R, Domschke G, Fanghänel E, Habicher WD, Metz P, Pavel D, Schwetlich K. *Organikum-Organisch-chemisches Grundpraktikum* (21st edn). Wiley-VCH: Weinheim, 2001; Chapt. F, 741–762.
47. Schönberg A. *Prðparative Organische Photochemie*. Springer Verlag: Berlin 1958; Chapt. 1.