A New Photochromic 8π-System Based on an Azaheptatriene-Tetrahydroazepinoisoquinoline Electrocyclization

Yongsheng Tan,[†] Thomas Hartmann,[†] Volker Huch,[†] Heinz Dürr,*[,†] Pierre Valat,[‡] Veronique Wintgens,[‡] and Jean Kossanyi[‡]

FB 11.2 Organische Chemie, Universität des Saarlandes, D-66041 Saarbrücken, Germany, and Laboratoire des matériaux moléculaires, CNRS, 2-8 Rue Henri Dunant, 94320 Thiais, France

ch12hd@rz.uni-sb.de

Received July 28, 2000

A new photochromic family of tetrahydroazepinoisoquinolines (THAI) **4a**−**i** has been prepared. It undergoes light-induced ring opening from spiro compounds **4** to betaines **3** that decolorize in a very fast cyclizing reaction. Depending on substitution of the precursors **1** and **6**, the photochromic styryltetrahydroindolizines (THI) **5k**−**q** are formed in a periselective way. The conformation and configuration of the new photochromic THAI **4** and THI **5** were investigated by NMR and the structure of both compounds was proven by X-ray analysis. The photochromic properties were studied by laser flash photolysis, which afforded the lifetime of the colored form **3** and **3′** in the micro- or nanosecond range.

Introduction

In the recent past photochromic materials steadily gained increasing interest since their commercial application in ophthalmological lenses.[1−3] These 6π-systems based on an electrocyclic ring-opening/ring-closure process are the most powerful and widespread basis for photochromic molecules.[1−5] Photochromes can be used also in many other domains such as actinometry[1−3] and information recording and storage,[1−4] in light switches,[2−4] in holography,[6,7] or in light switchable enzymes[8] to mention just a few applications. For ophthalmic lenses the spiroxazines and chromenes have become the most attractive candidates.[9,10] The colorization/decolorization cycles in these molecules are based on a 6π-six-atom electrocyclic ring-closure/ring-opening process.[1,9,10]

The related 4π-three-atom systems as the aziridines[1] are interesting photochromics but with limited applications, while the 6π-five-atom systems, the dihydroindolizines[1,4,11,12] have been shown to be very efficient and extensively adjustable photochromes, which cover a vast domain of half-lives of the colored form, spanning from 10^{-8} s to infinite. The latter also show extreme flexibility with regard to many photochromic properties.

However, reports on 8π-seven-atom photochromic systems (4*n*) are rare.[1,4] Only very few molecules have been reported, and the reversibility of the processes involved has not always been established.[13]

Extending our work on dihydroindolizines, we discovered recently a new photochromic system, the azaheptatrienes THAI **4** which constitute a new class of molecules with interesting properties.

In this paper, we report on the synthesis of a novel reversible photochromic system the aza-heptatriene **3**/tetrahydroazepinoisoquinoline (THAI) **4**, as well as on the aza-heptatriene **3**/tetrahydroisoquinoline (THI) **5**, both **4** and **5** formed in a pericyclic process. We further present the structure elucidation of **4** and **5** by X-ray analysis and the photophysical properties of systems **3** ⇔ **4** and **3** ⇔ **5**, respectively.

Results

Synthesis. The synthesis of tetrahydroazepinoisoquinoline (THAI **4a**−**i**) was envisaged from spirocyclopropene **1** and 1-(4-substituted-styryl)-3,4-dihydroisoquinolines **2** as precursors. By adding a styryl link to the 1-position of the quinoline base, an extended conjugated betaine **3** for the known THI[1,4,14] was expected to be formed.

The synthesis of precursor **2** was carried out according to Bischler−Napieralski[15] procedure by cyclization of

* To whom correspondence should be addressed.

[†] Universität des Saarlandes.

[‡] CNRS.

(1) Dürr, H. In *Photochromism − Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; p 210 ff. and p 510 ff.

(2) Guglielmetti, R. In *Photochromism − Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; p 314 ff.

(3) McArdle, C. B. *Applied photochromic polymer systems*; Chapman and Hall, New York, 1991.

(4) Dürr, H. In *Organic photochromic and thermochromic compounds Vol.1*; Crano, J. C., Guglielmetti, R. J., Eds.; Plenum Press: New York, 1998; 223 ff.

(5) Dürr, H. In *Organic Photochemistry and Photobiology*; Horspoole, W. M., Song, P.-S., Eds.; CRC Press: 1995; pp 1121−1140.

(6) Zelichanok, A.; Buchholz, F.; Fischer, E.; Katur, E.; Krongausz, V.; Ameser, H.; Bräuchle,C. *J. Photochem. Photobiol.* **1993**, *76*, 135.

(7) Dromikov, A. S.; Rentzepis, P. M. *Mol. Cryst. Liq. Crist.* **1994**, *246*, 379.

(8) Willner, I.; Rubin, S. *Angew. Chem.* **1996**, *108*, 419−439.

(9) Bertelson, R. C. In *Organic photochromic and thermochromic compounds Vol.1*; Crano, J. C., Guglielmetti, R. J., Eds.; Plenum Press: New York, 1998; pp 11−83.

(10) Maeda, S. In *Organic photochromic and thermochromic compounds Vol.1*; Crano, J. C., Guglielmetti, R. J., Eds.; Plenum Press: New York, 1998; pp 85−107.

(11) Weber, C.; Rustemeyer, F.; Dürr, H. *Adv. Mater.* **1998**, *10*(16), 1348−1351.

(12) Andreis, C.; Dürr, H.; Wintgens, V.; Valat, P.; Kossanyi, J. *Chem. Eur. J.* **1997**, *3*(4), 509.

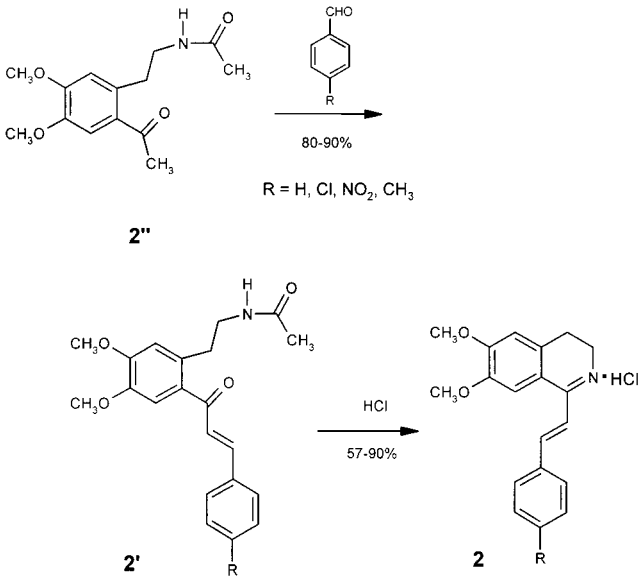
(13) Dürr, H. *Angew. Chem.* **1989**, *101*, 427−445; *Angew Chem., Int. Ed.* **1989**, *28*, 413−438.

(14) Dürr, H.; Gross, H. *Angew. Chem.* **1982**, *94*, 204.

(15) Bischler, A.; Napiralski, B. *Ber.* **1893**, *26*, 1903. Tietze, L. F.; Eicher, T. *Reaktionen und Synthesen*; Thieme: Stuttart, 1981; p 319.

10.1021/jo000807+ CCC: $20.00
Published on Web 02/01/2001

Scheme 1. Preparation of Dihydroisoquinoline Precursors 2



N-phenethylacetamide[16] that resulted in 1-methyl-6,7-dimethoxy-3,4-dihydroisoquinoline, which gave the corresponding acetophenone derivative **2″** after hydrolysis in diluted hydrochloric acid and addition of potassium carbonate.

Subsequent aldol condensation with benzaldehyde derivatives gave the α,*β*-unsaturated ketones **2′** (see Scheme 1), which cyclized in boiling diluted hydrochloric acid solution into 1-(4′-styryl)-3,4-dihydroisoquinoline[17] **2**. New *p*-nitro and *p*-methyl derivatives could be synthesized according to this method.

All 1-(4′-substituted-styryl)-3,4-dihydroisoquinolines **2** were quite unstable except the *p*-nitrostyryl-substituted compounds **2** (R = NO_2). Therefore, the former have been stabilized as HCl salts and were liberated from their hydrochlorides in situ with triethylamine.

Synthesis of Tetrahydroazepinoisoquinoline Esters (THAI). Reacting spirocyclopropene **1** with 1-styryl-phenyldihydroisoquinoline **2** at ambient temperature (dry diethyl ether) leads to the THAI **4** via the betaine intermediate **3′**. Compounds **4a**−**i** could be isolated in moderate to good yields (see Scheme 1, Table 1).

In this reaction the nitrogen of the N-heterocycle adds nucleophilically to the cyclopropene ring of **1**, which opens via a cyclopropyl−allyl conversion to intermediate A and leads in an electrocyclic reaction to the betaine form **3** and finally to the product **4**.

The NMR experiments carried out for the 7 ring THAIs **4** show a characteristic signal pattern. In all compounds four complex multiplets can be assigned to the methylene protons 11′, 12′ of the dihydroisoquinoline ring. They appear in the range from 2.6 to 4.5 ppm. Since these two methylene groups appear as two distinct triplets in the starting material **2**, it indicates that, in the THAI molecules **4**, they are no longer magnetically equivalent. This can be attributed to a distortion of the ring to a half-boat form (see also the crystal structure).

For styryl-substituted THI 5-rings two doublets are observed for each proton of the trans styryl group. They should be shifted to 6.0 and 6.5 ppm with coupling constants of about 16 Hz, whereas the signals found for THAI **4** appear around 4.3 ppm (5′-H) and 6.2 ppm (6′-H) and both show coupling constants of about 7.0 Hz. They result from the azepine allylic proton 5′ and the olefinic 6′ proton.

Thus, a five-membered ring THI structure can be excluded and the seven-membered ring structure of **4** is supported.

For the norbonylester THAI derivative **4i** a chiral center exists in the C_B position of the norbonyl group (see the Experimental Section); hence, two diastereomers are possible in the *R* and *S* configurations. The presence of two isomers for the norbonyl derivative is deduced from the ^{1}H NMR spectra, for example from the 7′ and 10′ protons, which appear as doublets (usually singlets) around 7.1 and 6.6 ppm, respectively.

The two configurations can also be verified from the ^{13}C NMR spectrum. The signal of the spiro carbon around 63.5 ppm is doubled just as the carbonyl carbon atoms that arise from the 2′ and 3′ positions. The two signals of the carbonyl methyl and ethylester derivatives at 167.5 and 167.9 ppm, respectively, split in two signals between 166.8 and 167.1 ppm.

All structures were characterized by mass spectroscopy, elemental analysis, and IR spectroscopy. The postulated structures **4a**−**i** are additionally based on homonuclear ^{1}H,^{1}H-COSY and ^{13}C,^{1}H-COSY experiments.

A table of the characteristic NMR data can be found in the Supporting Information for compounds **4a**−**i**.

Diastereoisomers of THAI **4h** and THI **5l**,**p**,**i** with *R* and *S* configurations are due to the unsymmetrically substituted fluorene rings. An isolation of these diastereomers was found impossible due to their light sensitivity. As the azepine ring and the pyrrole ring open to a transoid betaine form **3** the thermal back reaction to the closed form **4** yields always a mixture of diastereomers. The stereochemistry given for the phenyl group in position 5′ (Scheme 2) is clearly deduced from the X-ray structure of **4z**.

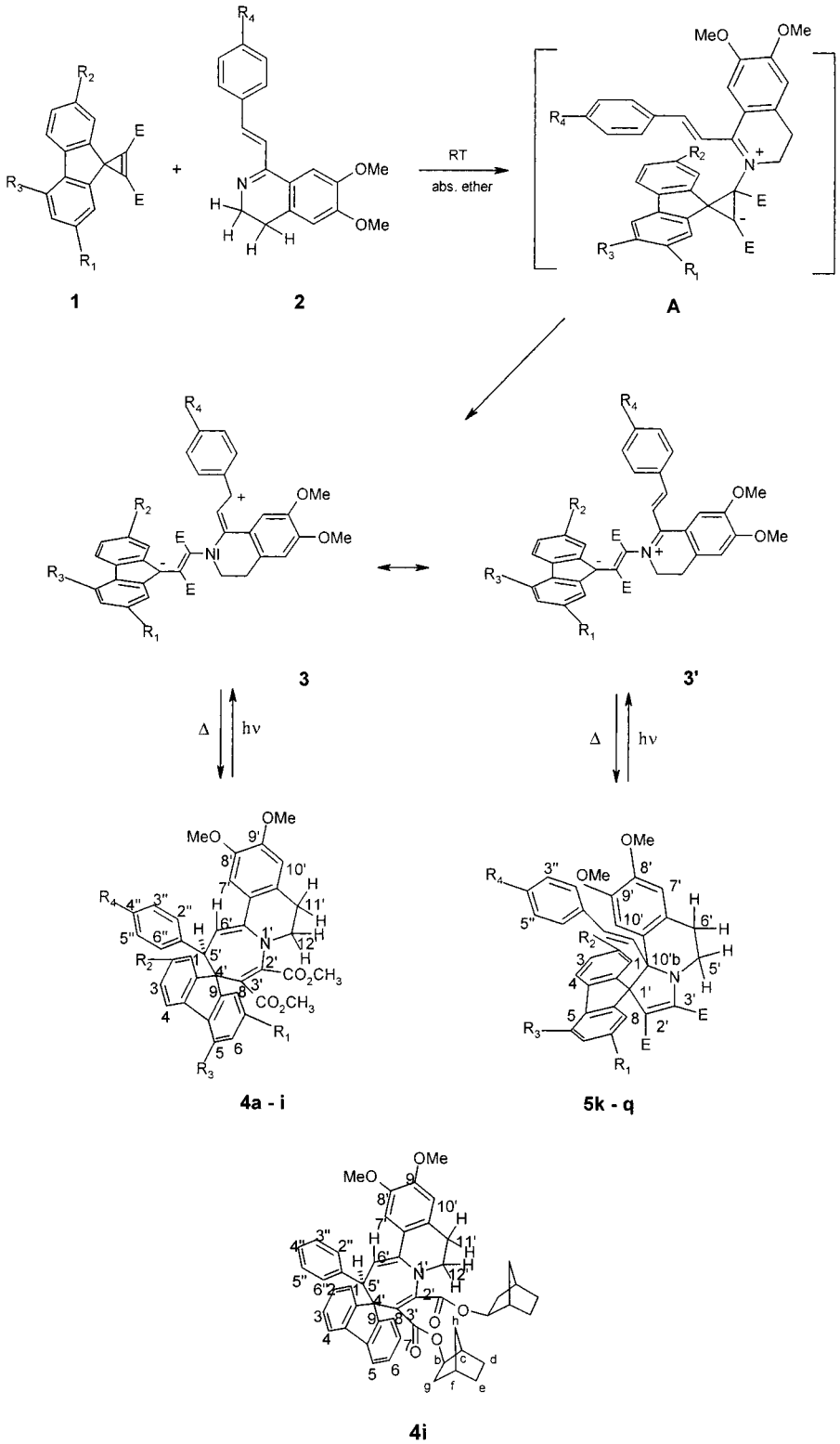
The diastereomeric ratio is about 1:1 in the mixtures for **4h** and THI **5l**,**p**,**i** as concluded from the NMR data. This is in contrast to previous findings, where the five-membered ring formation is normally diastereoselective.[1,4] The diastereoisomeric ratio of the THAI **4h**/THI **5l**,**p**,**i** are listed in the Supporting Information.

Table 1. Substituent Pattern of THAI 4a−i and THI 5k−q, Melting Points, and Reaction Yields

compd	R_1	R_2	R_3	R_4	E	mp (°C)	yield (%)
4a	H	H	H	H	CO_2CH_3	148−149	65
4b	H	H	H	H	$CO_2C_2H_5$	167−169	71
4c	H	H	H	Cl	CO_2CH_3	138−140	50
4d	H	H	H	Cl	$CO_2C_2H_5$	168−170	60
4e	H	H	H	NO_2	CO_2CH_3	152−154	71
4f	H	H	H	NO_2	$CO_2C_2H_5$	150−152	60
4g	H	H	H	CH_3	CO_2CH_3	128−130	70
4h	H	H	CO_2CH_3	Cl	CO_2CH_3	140−142	57
4i	H	H	H	H	$CO_2C_7H_{11}$ (norbornyl)	129−131	53
5k	Cl	Cl	H	H	CO_2Et	196−198	29
5l	Cl	Cl	Cl	H	CO_2Me	211−213	36
5m	Br	Br	H	H	CO_2Me	213−215	66
5n	Br	Br	H	Cl	CO_2Me	231−232	75
5o	Br	Br	H	Cl	CO_2Et	204−206	46
5p	NO_2	H	H	H	CO_2Me	149−150	54
5q	NO_2	NO_2	H	H	CO_2Me	219−220	64

(16) Orito, K.; Matsuzaki, T.; Suginome, H. *Heterocycles* **1988**, *27*(10), 2403.
(17) Brossi, A.; Dolan, L. A.; Teitel, S. *Org. Synth.* **1977**, *56*, 3.

Scheme 2. Synthesis and Reaction Pathway of Ester THAI 4 and THI 5



Synthesis of Tetrahydroisoquinoline Esters (THI). The synthesis of the ester tetrahydroindolizines (THI, five rings) was carried out as described for the synthesis of the THAI esters **4** (seven rings). Only substitution in the 2,7-position of the fluorene ring afforded the formation of the styryl-substituted five-ring THI **5** periselectively (see Scheme 2, Table 2).

The structure of these new 1-styryl-tetrahydroindolizines (THI) was established by NMR, mass spectra, and IR.

The NMR analysis of the five-ring THI gave a quite different signal pattern in comparison to the seven-ring THAI. All ^{1}H NMR spectra of product THI **4r**−**z** show also four complex multiplets between 2.60 and 3.80 ppm for the methylene groups in positions 5′ and 6′, but they are shifted about 0.2−0.7 ppm to lower field. The signals in the olefinic part of the spectrum can be assigned to the 10′ und 7′-H of the isoquinoline phenyl ring.

The most characteristic signals are the two doublets in the THIs of the styryl double bond at 6.10 (**5l**)−6.30

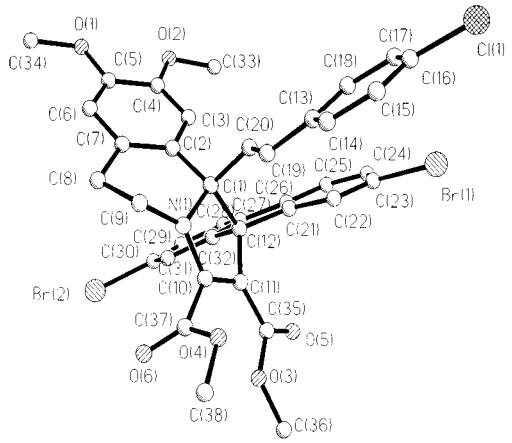


Figure 1. X-ray structure of **5n**.

Table 2. Substituent Pattern, Melting Points and Reaction Yields for THAI 4r−z

compd	R_1	R_2	R_3	R_4	mp (°C)	yield (%)
4r	H	H	H	H	180−182	25
4s	H	H	H	Cl	174−176	38
4t	H	H	H	CH_3	176−178	32
4u	Cl	Cl	H	H	186−188	28
4v	Cl	Cl	H	Cl	171−173	22
4w	Cl	Cl	H	CH_3	177−179	33
4x	Br	Br	H	H	203−205	40
4y	Br	Br	H	Cl	173−175	33
4z	Br	Br	H	CH_3	180−182	26

ppm (**5p**) and 6.44−6.49 ppm, respectively. They show coupling constants of $^3J = 15.5-16.0$ Hz, which correlate very well with the literature.[17] This is a major indication for the existence of the styryl-five ring (see Table 8 for THIs **5k**−**q** in the Supporting Information). In contrast to these findings, the THAI **4** show signals due to the olefinic 5'-H and 6'-H azepine bonds in the region 4.32 (**4w**)−4.41 ppm (**4r**) and 6.09−6.26 ppm (see Table 10 for THAIs **4r**−**z**, Supporting Information). Compounds **4h** and **5l**,**p**,**i** can exist as diastereomers (Tables 8 and 9, Supporting Information).

The final configuration and structure were additionally proven by homonuclear ^{1}H,^{1}H-COSY and ^{13}C,^{1}H-COSY experiments. The final structure proof of the 10′b-styryl-THI **5** was also obtained by an X-ray analysis, which has been performed on crystals of the 2,7 dibromofluorene methyl ester **5n** (Figure 1). The crystal structure corresponds very well with the conformation and configuration derived from NMR.

All three regions A, B, and C[1,13,18] of the THI can be clearly assigned. The five-ring ester groups are perpendicular to the fluorene embedded in the dihydroisoquinoline part. The bond lengths of the pyrrolidine ring show single bonds for C(11)−C(12), C(12)−C(1) with bond distances of 1.520 and 1.626 Å respectively, and 1.476 Å for C(1)−N(1).

The C(12)−C(1) bond is unusually long, having 1.63 Å for a single bond, and hence is relatively weak; therefore, it is easily cleaved by UV light, leading to ring opening and to the formation of betaine **3**. The 1.360 Å for the C(10)−C(11) dihydropyrrole double bond in **5d** is also consistent with the NMR data.

(18) Dürr, H.; Kranz, C.; Schulz, C.; Kilburg, H.; Jönsson, H. P. *Proc. Indian Acad. Sci.* **1995**, *107*, 645−658.

The bond angles of the pyrrole ester moiety in the THI system show only slight distortion and exhibit, with minor deviations of about 3°−4° for C(10)−C(11)−C(12), C(1)−C(10)−C(11), and C(12)−C(1)−N(1), the same bond angles as a dihydropyrrole ring that was calculated by molecular mechanics. All further characteristics and important structural data are listed in the Supporting Information.

Synthesis of Dicyanotetrahydroazepinoisoquinolines (THAI). Cyano-substitued spiro-cyclopropenes, which could serve as precursors, are not stable[5] at room temperature; therefore, spiropyrazoles **6** are photolyzed in the presence of the 1-styryldihydroisoquinolines **2**.[13,14,18] The photolyses were carried out at room temperature with $\lambda > 290$ nm (125 W Philips HPK, Hg-lamp, Pyrex filter) in absolute diethyl ether. After some time, a turquoise blue color was obtained, which disappeared again when the reaction was finished.

Removal of the solvent and subsequent column chromatography of the reaction mixture on silica gel (in the dark) affords the pure dicyanotetrahydroazepinoisoquinolines **4r**−**z** in moderate yield (see Scheme 3). Irradiation of the spiro dicyanopyrazole **6** generated a vinylcarbene. The nitrogen of the isoquinoline attacks it as a nucleophile to form a ring open colored betaine **3**, that is able to undergo 1,7-electrocyclization to the desired products **4**. The structures of these new tetrahydroazepinoisoquinolines **4r**−**z** (THAI) have been established by NMR, mass spectra, elemental analysis, and IR. The ^{1}H NMR and ^{13}C NMR spectra of the dicyano-substituted THAI show the same characteristic pattern as their ester derivatives.

For **4z**, an X-ray analysis was carried out that led to the structure shown (see Figure 2).

The X-ray analysis of the 2,7-dibromofluorene THAI **4z** permits a definite and clear structural assignment. As given in Figure 2, the THAI molecule **4z** can be divided into three parts A, B, and C consisting of fluorene, dihydroazepine, and isoquinoline parts. In part B, the existence of the seven-membered ring is clearly evident.

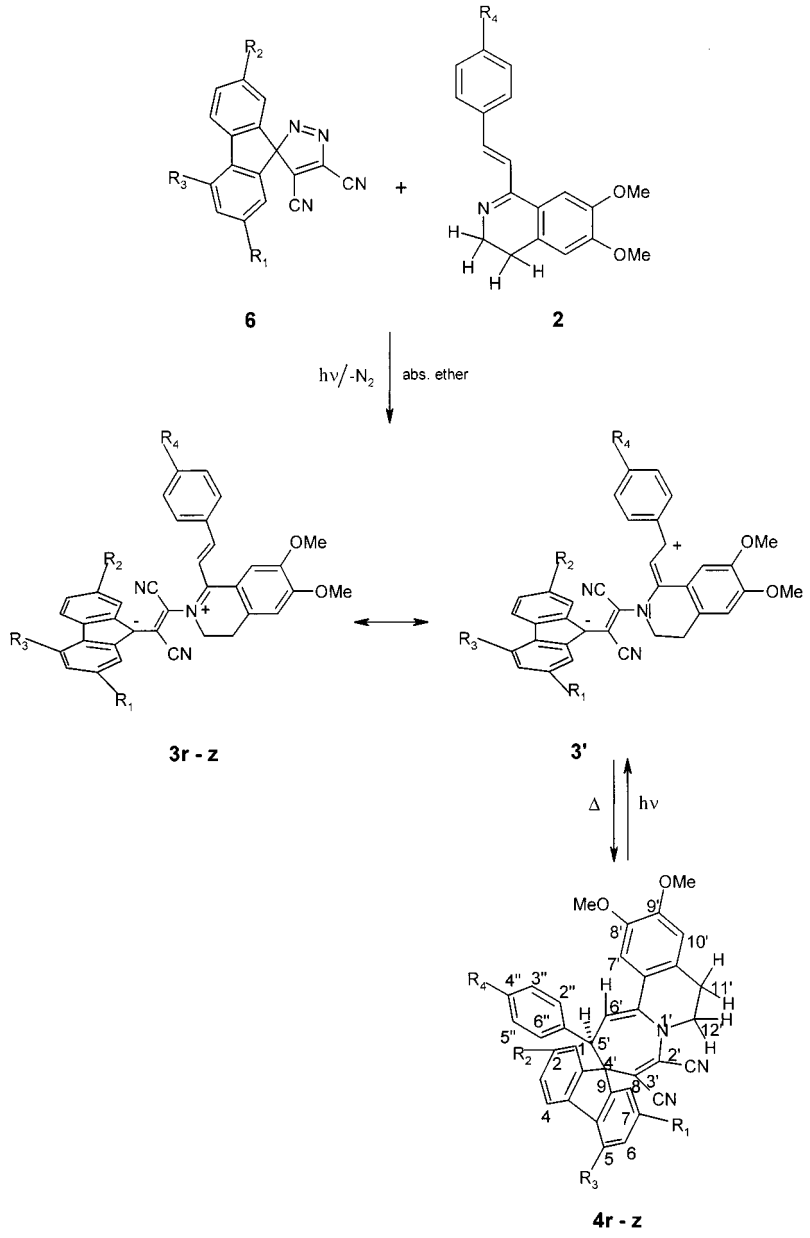
Bond distances, especially in the azepine ring, are of interest. All carbon atoms C(2)−C(5) in the 7 ring are incorporated as single bonds and have bond distances of 1.487−1.513 Å. The C(6)−N(1) shows a single bond, which is slightly shorter however with only 1.418 Å.

The C(1)−C(2)-bond and C(5)−C(6) bond with 1.316 and 1.295 Å respectively have double bond character in agreement with the NMR data. The short N(1)−C(1) bond with 1.365 Å results probably from a partially delocalized imine/ enamine structure.

From the bond angles it follows, that the dihydroazepine ring exists in a slightly distorted half tub conformation. While these bond angles of 122.5° C(4)−C(5)−C(6) and C(5)−C(6)−N(1) exhibit standard values, the angles of N(1)−C(1)−C(2) and C(1)−C(2)−C(3) with 130° are distorted by about 10°. Both the spiro-bonded carbon C(3) as well as carbon C(4) exhibit an sp^3 configuration with bond angles of 109.8° for C(2)−C(3)−C(4) and 111.1° for C(3)−C(4)−C(5).

The bond angle of C(6)−N(1)−C(1) matches with 119.7° for a classical sp^2 carbon and, hence, indicates a partially delocalized polymethine system the C(2) cyano-group of the THI system. The cyano bond C(2)−C(18) is shortened by about 0.06 Å as compared to the C(1)−C(17) bond, and the C(18)−N(3) bond is 0.05 Å longer than the 1.12 Å C(17)−N(2) bond. Thus, the bond lengths indicate double

Scheme 3. Synthesis and Reaction Pathway of Dicyano THAI 4



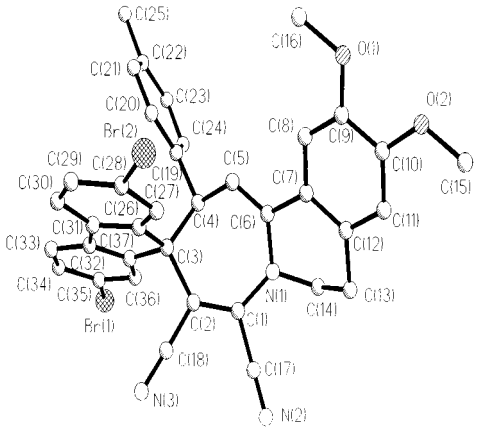


Figure 2. X-ray structure of **4z**.

bond tendencies for C(2)−C(18) and C(18)−N(3), which supports also the polymethine character.

The C(3)−C(4) bond with 1.504 Å is breaking in the photochromic process of the THAI **4z**. It is about 0.01 Å shorter than the longest bond (C(2)−C(3)) of the azepine system and even 0.12A shorter in comparison with the corresponding C(12)−C(1) bond, which is opening in five-membered ring THI **5n**.

From the differences in bond length of the THAI **4z** (C(3)−C(4)) and THI **5n** (C(12)−C(1)) systems, conclusions concerning the efficiency and the facility of the ring opening reaction may be drawn which correspond with quantum yield determinations. Further characteristic and important data of **4z** are listed in the Supporting Information.

Discussion

The nucleophilic addition of styryldihydroisoquinoline **2** to the spirocyclopropene **1**, via the betaine **3**, forms a conjugated azapentadienyl system. The ring-opened betaine **3** has basically two possibilities to close, either via the well-known 1,5-electrocyclization ($4n + 2\pi = 6$ electrons) to form tetrahydroindolizines (THI) **5k**−**q** or by including the conjugated styryl group to undergo a

Table 3. Spectroscopic Data of THAI 4 and THI 5 in CH_2Cl_2 ($c = 3 \times 10^{-4}$ mol/L) at Room Temperature

	UV/vis		fluorescence			transient lifetime	
compd	λ_{max} (nm)	log ϵ	$\lambda_{(exc)}$ (nm)	$\lambda_{(em)}$ (nm)	ϕ_{Fl} (10^{-4})	λ_{max} (nm)	τ^a (μs)
4a	311	4.10	339	431	35.4	−/−	<0.01
4b	311	3.95	340	430	15.4	−/−	<0.01
4c	310	4.06	341	445	10.5	−/−	<0.01
4d	311	4.01	340	445	11.4	−/−	<0.01
4e	310	4.04	338	431	6.5	−/−	<0.01
4f	310	4.08	338	430	7.5	−/−	<0.01
4g	311	3.99	337	425	49.1	−/−	<0.01
4h	311	3.93	341	439	59.3	−/−	<0.01
4i	314	3.98	336	422	15.7	−/−	<0.01
5k	327	4.10	400	456	19.6	490/720	0.37
5l	327	3.98	338	487	6.1		0.28
5m	328	3.98	335	491	9.1	490/720	0.21
5n	328	4.11	415	520	11.6		0.28
5o	329	4.09	333	495	7.5		0.22
5p	333	4.07	415	510	6.9	460/700	0.12
5q	337	4.04	415	495	7.8	480/740	0.66
4r	310	4.03	338	410	17.3	500/680	105
4s	314	3.95	336	405	4.4		95
4t	317	3.88	336	403	-/-		150
4u	310	4.10	334	389	2.5	500/680	260
4v	314	3.96	336	406	6.5		215
4w	315	3.97	336	402	5.3		230
4x	311	4.11	343	403	5.9		235
4y	314	3.89	338	420	1.9		260
4z	315	4.13	336	405	2.3		250

[a] For comparison $\tau_{1/2} = \ln 2 \times \tau$ (see ref 1).

1,7-electrocyclization to THAI **4** ($4n = 8$ electron process). For the THAI **4a**−**i** and **4r**−**z** exclusively a 1,7-electrocyclization was observed.

This corresponds very well with the theory for electrocyclic reactions where it is always the longest conjugated system which reacts, which leads here to the seven-membered ring (see in detail in ref 19). The THI **5** are formed in 1,5-electrocyclization, where only *part* of the *conjugated system* reacts. The formation of THAI **4** is therefore a *periselective reaction*.[19]

The 1,7-electrocyclization is, however, disfavored when acceptor groups are present such as both 2,7-halogenfluorenes and dicarboxylic ester as in the case of compounds **3**. Due to some steric hindrance but more likely to electronic effects the esters **3k**−**q** cyclize *periselectively* to five rings and thus form *the THI* ***5***.

The comparison to the dicyano-substituted betaines **3r**−**z** shows that the 2,7-fluorene substitution does not lead to **4r**−**z** by 1,5 cyclization. The strong electron withdrawing cyano groups seem to stabilize the positive charge on the styryl group providing in all cases **4** by a periselective 1,7-electrocyclization reaction. Here a resonance formula **3′** (positively charged in position 7) favors the 1,7-electrocyclization.

Photophysical Properties. Both the new THAI **4** and the THI **5** were investigated further with regard to photochromic properties. Irradiation of **4a**−**i**, **5k**−**q,** and **4r**−**z** in CH_2Cl_2 with a Xe lamp (Pyrex filter $\lambda > 290$ nm) at room temperature showed no color change. However, cooling the solutions to 77 K with subsequent irradiation gave in the cases of **4r**−**z** (CN) a turquoise blue color, which faded on warming to room temperature. This color is due to the colored betaine **3**.

(19) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley-Interscience: New York, 1990.

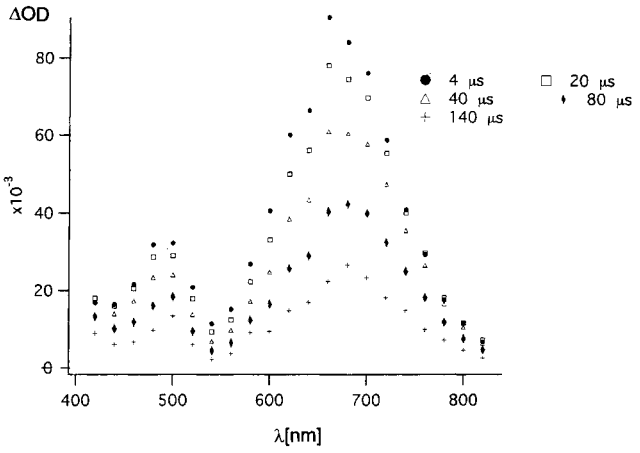
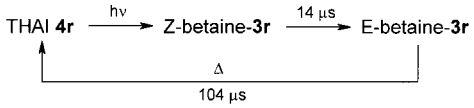


Figure 3. Transient absorption spectra of compound **4r** in dichloromethane solution excited at 347.5 nm with a ruby laser and analyzed at different times.

As the **3** → **4** cyclization is very fast, the UV/vis maxima of **3** could only be established clearly by laser flash photolysis measurements. The photophysical data obtained by time-resolved transient absorption spectroscopy are summarized in Table 3. Two maxima could be detected (measured by ns excitation Nd:YAG-laser flash photolysis[20]) in the transient absorption spectra of compounds **3r**−**z** (CN-substitution), which range between 500 and 680 nm. The maxima of these transients were about 40 nm bathochromically shifted for the ester THI's **5k**−**q** relative to the spectra obtained in the case of **4**.

A typical example is compound **4r**. The transient spectrum obtained in dichloromethane solution by excitation of compound **4r** at 347 nm with a ruby laser is depicted in Figure 3. As seen in Figure 3, the spectrum evolves with time. The change in the transient absorption is better visualized by examining the spectral change at different wavelengths. The shorter lifetime from the biexponential decay at 660 nm, that is 14 μs, can be found again in the growing-in of the transients at 410 and 780 nm (Figure 4). As this change occurs on the two sides of the transient absorption spectrum it is indicative of an overlap of two different species absorbing in the same region. These two species should correspond to the *Z* and *E* forms of the betaine, the latter (**3r**) being more stable.[12,21,22]



All lifetimes τ of the colored forms were established from decay curves of the transient absorption spectra.[12,21] The lifetimes τ of these betaines **3a**−**i** range between 100 and 260 μs for the CN-substituted compounds.[22] By comparison, the lifetime of the THI **5k**−**q** (five-membered rings), in the ns range, are shorter by about 3 orders of magnitude. The reversibility of the new THAI systems **3r**−**z** → **4r**−**z** as well as that of THI **3k**−**q** → **5k**−**q** has been clearly established by performing several coloration/decoloration cycles.

(20) Valat, P.; Tripathi, S.; Wintgens, V.; Kossanyi, J. *New J. Chem.* **1990**, *14*, 825.

(21) Bleisinger, H.; Scheidhauer, P.; Dürr, H.; Wintgens, V.; Valat, P.; Kossanyi, J. *J. Org. Chem.* **1998**, *63*(4), 990−1000.

(22) Detailed transient data will be discussed in a separate paper.

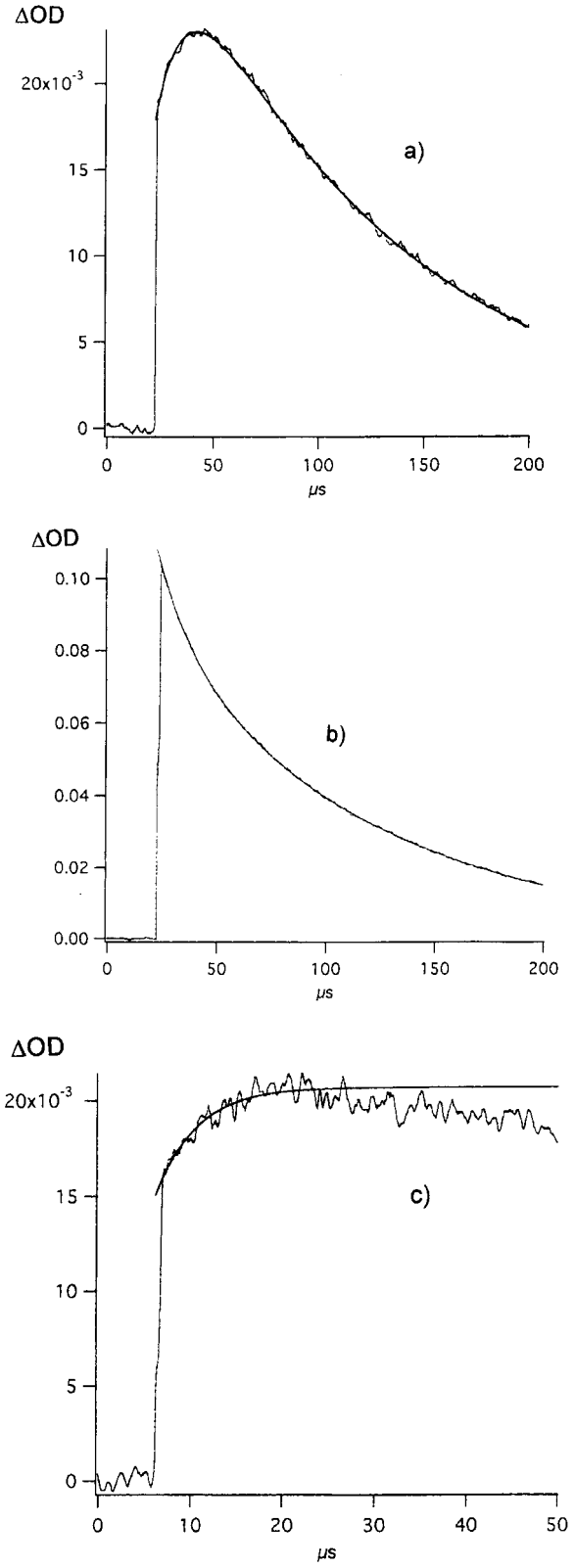


Figure 4. Oscilloscope trace of the growing-in and the decay of the transient absorption of compound **4r** in dichloromethane solution analyzed (a) at 410 nm, (b) at 660 nm, and (c) at 780 nm.

For compounds **4a**−**i** not showing photochromism with a laser flash, we assume that the electrocyclization is too fast owing to the fact, that the ring open betaine form of the ester THAI's **4a**−**i** can be blocked in a light induced azidochromic reaction. The decay τ of the excited esters THAI's **4a**−**i** could not be measured due to apparatus limitations,[20] since the kinetics of the photochromic processes appears to be faster than 1−10 ns.

All compounds **4** and **5** showed little fluorescence emission with fluorescence quantum yields ϕ_F ranging from $2 \cdot 10^{-4}$ for **4z** to $6 \cdot 10^{-3}$ for **4h** (Table 3). Typical fluorescence maxima of the 7-ring THAI lie between 400 and 445 nm. Going from diester (**4a**−**i**) to dicyano **(4r**−**z)** substitution caused hypsochromic shifts of the fluorescence spectra by about 30 nm. The THI **5k**−**q** emitted at higher wavelengths and showed maximum emission around 500 nm (Table 3).

Conclusions

The azaheptatriene-dihydroazepines (THAI) **4** constitute a new class of very fast cyclizing photochromic molecules. The photochromism is based on an electrocyclic ring opening/ ring closure reaction of a seven-membered ring (8π). The conformation and configuration of **4** and **5** were determined by NMR. Definite structures of **4z** and **5n** were elucidated by X-ray analysis to show a half-boat form for the 7 ring of **4z** and an almost planar geometry for the five-membered ring of **5n**. The process of the ring closure **3** → **4** and its reverse is an 8π-seven-atom electrocyclization. In the presence of electron-attracting substituents as in **5k**−**q** (ester) only five-membered ring THIs are obtained in a 6π-five-atom process. The transformation of betaines **3** to the THAI **4** is thus a periselective $4n$ process. This is one of the very few 8π-systems for which a reversible light-induced process is clearly established.

Experimental Section

All NMR spectra were collected on a 500 MHz spectrometer in $CDCl_3$ using TMS as internal standard. Chemical shifts are reported in ppm (δ). Column chromatography was performed using silica gel (50−200 μm /70−270 mesh). Solvents used were water free and dried according to standard procedures. IR spectra were measured as powder in KBr. Melting points are uncorrected. Flash photolysis experiments were carried out with a frequency-double-pulsed ruby laser (347.5 nm, 20 ns fwmh). The usual crossed beam system was used, the analyzing being a conventional pulsed Xenon lamp. A detailed description of the experimental setup has been given already.[20]

General Procedure for the Preparation of Diester 1-Aza-2,6-cyclohexadieno[1,7]isoquinolines (4a−**i, 5k**−**q).** To a suspension of 2-styryldihydroisoquinoline HCl salt **2** (1.0 mmol) in absolute ether was added an equimolar solution of triethylamine/ether (1.0 mmol). After 10 min of stirring at room temperature, an equimolar ether solution of spirocyclopropene **1** (0.306 g, 1.0 mmol) was given to the mixture. After further stirring for 24 h (TLC control) in the dark at room temperature, the solvent was removed under reduced pressure. The residue was taken up in CH_2Cl_2 and separated by column chromatography (on SiO_2) with eluent mixtures of [CH_2Cl_2/EtOAc, 9:2] to afford compound **4**. The product was recrystallized from diethyl ether to yield white, colorless crystals.

11′,12′-H-2′,3′-Dimethoxycarbonyl-8′,9′-dimethoxy-5′-phenylspiro[fluorene-9,4′-(1-aza-2,6-cycloheptadieno)-[1,7-a]isoquinoline] (4a). Standard Procedure. Preparation: 0.306 mg (1.0 mmol) of methylester-spirocyclopropene **1**, 0.33 g (1.0 mmol) of 1-styryl dihydroisoquinoline **2**, 101 mg (1.0 mmol) of triethylamine, 50 mL of diethyl ether. Reaction time: 72 h. Yield: 389 mg (65%) colorless crystals. IR ν (cm^{-1}): 3062−3003 (C−H, arom.), 2952, 2835 (C−H, aliph.), 1733 (C=O), 1714 (C=O), 1607 (C=C), 1577, 1511, 1452, 1261, 1233, 1207, 1046, 858, 755. ^{1}H NMR δ: 2.69 (dt, 1H, ^2J = 15.9 Hz, ^3J = 3.1 Hz), 2.80 (s, 3H), 3.43 (m, 1H), 3.74 (m, 1H), 3.88 (s, 3H), 3.89 (m, 1H), 3.90 (s, 3H), 3.96 (s, 3H), 4.40 (d, 1H, ^3J =

7.5 Hz), 6.20 (d, 2H, ^3J = 7.5 Hz), 6.23 (d, 1H, ^3J = 7.52 H), 6.62 (s, 1H), 6.74 (t, ^3J = 7.52 Hz, 2H), 6.85 (t, 1H, ^3J = 7.5 Hz), 7.02 (t, 1H, ^3J = 7.5 Hz), 7.10 (s, 1H), 7.17 (t, 1H, ^3J = 7.5 Hz), 7.22 (d, 1H, ^3J = 7.5 Hz), 7.30 (t, 1H, ^3J = 7.5 Hz), 7.35 (t, 1H, ^3J = 7.5 Hz), 7.42 (d, 1H, ^3J = 7.5 Hz), 7.44 (d, 1H, ^3J = 7.1 Hz), 7.60 (d, 1H, ^3J = 7.1 Hz). ^{13}C NMR δ: 29.34, 48.11, 50.41, 51.28, 52.67, 55.81, 56.27, 63.17, 106.38, 106.87 (q), 111.11, 116.68, 118.76, 122.51, 123.24, 124.77, 125.78, 126.07, 126.24, 126.50, 126.58, 126.76, 126.90, 128.46, 138.56 (q), 139.14 (q), 139.28 (q), 142.60 (q), 147.86 (q), 149.38 (q), 149.47 (q), 150.98 (q), 151.87 (q), 167.54, 167.86. MS (for $C_{38}H_{33}NO_6$): 600.1 (13.2) ($M^+ + 1$), (calcd 599.69 g/mol).

11′,12′-H-2′,3′-Dinorbornylester-8′,9′-dimethoxy-5′-phenylspiro[fluorene-9,4′-(1-aza-2,6-cycloheptadieno)[1,7-a]-isoquinoline] (4i). Standard Procedure. Preparation: 0.33 g (1.0 mmol) of 1-styryl-6,7-dimethoxy-3,4-dihydroisoquinoline (HCl salt) **2**, 0.466 g (1.0 mmol) of norbornylester-spirocyclopropene **1**, 101 mg (1.0 mmol) of triethylamine. Reaction time: 72 h. Yield: 0.402 g (53%) colorless crystals. IR ν (cm^{-1}): 3060−3000 (C−H, arom.), 2955, 2871 (C−H, aliph), 1726 (C=O), 1686 (C=O), 1609 (C=C), 1550, 1512, 1451, 1420, 1360, 1255, 1141, 1022, 850, 747. ^{1}H NMR δ: 0.43−0.91 (m, 4H), 1.07−1.28 (m, 7H), 1.48−1.80 (m, 7H), 2.34 (s, 1H), 2.55−2.69 (m, 2H), 3.48 (m, 1H), 3.68 (m, 1H), 3.88 (s, 3H), 3.89 (s, 3H), 3.92 (d, 1H), 3.99 (m, 1H), 4.38 (d, 1H. ^3J = 4.9 Hz), 4.91 (d, 1H, ^3J = 4.4 Hz), 6.17 (d; 2H, ^3J = 7.5 Hz), 6.22 (d; 1H, ^3J = 7.1 Hz), 6.62 (d; 1H), 6.72 (t; 2H, ^3J = 7.5 Hz), 6.84 (t; 1H, ^3J = 7.5 Hz), 6.98−7.02 (m; 1H), 7.09 (d; 1H), 7.13−7.18 (m; 2H), 7.27−7.33 (m; 2H), 7.37−7.44 (m; 2H), 7.59−7.62 (m; 1H). ^{13}C NMR δ: 24.13, 24.19, 24.36, 27.89, 28.29, 28.35, 29.65, 34.42, 34.47, 34.79, 35.46, 35.54,38.00, 38.38, 38.43, 38.52, 38.75, 40.34, 40.54, 40.97, 41.09, 41.32 (21 aliph-C in norbornyl group of isomeric A and B), 47.76, 51.66, 55.94, 56.37, 63.51, 63.62, 76.79, 79.42, 106.03 and 106.12, 106.41 (q) 111.23, 116.63, 116.72, 118.85, 119.03, 122.84, 122.90,123.42, 124.95, 125.01, 125.82, 126.13, 126.34, 126.54, 126.71, 126.86, 127.09, 128.73, 138.70 (q), 139.45 (q), 139.59 (q), 139.71 (q) 142.83 (q), 147.91 (q), 149.44 (q), 150.37 (q), 150.43 (q), 151.70 (q), 152.45 (q), 166.83, 166.92, 167.07. MS (for $C_{50}H_{49}NO_6$): 760 (24.2) [M^+ +1], (calcd 759.95 g/mol).

1′,5′,6′-H-8′,9′-Dimethoxy-10b′-styryl-2′,3′-dimethoxycarbonylspiro[2,7]dibromfluorene-9,1′-pyrrolo[2,1-*a*]-isoquinoline (5m). Standard Procedure. Preparation: 0.464 g (1.0 mmol) of 2,7-dibromospirocyclopropene, 0.330 g (1.0 mmol) of HCl salt of 1-styryl-6,7-dimethoxy-3,4-dihydroisoquinoline, 0.110 g (1.0 mmol) of triethylamine. Reaction time: 72 h. Yield:210 mg (55.5%).IR ν (cm^{-1}): 3075−3000 (C−H, arom.), 2990, 2840 (C−H, aliph.), 1747 (C=O), 1686 (C=O), 1580, 1476, 1256, 1061, 967, 862, 770 cm^{-1}. ^{1}H NMR δ: 2.72 (dd; 1H, ^2J = 15.9 Hz, J = 2.7 Hz), 3.11 (m; 1H), 3.30 (s; 3H), 3.35 (s; 3H), 3.47 (m; 1H), 3.71 (m; 1H), 3.75 (s; 3H), 4.08 (s; 3H), 5.56 (s; 1H), 6.15 (d; 1H, ^3J = 15.9 Hz), 6.46 (s; 1H), 6.47 (d; 1H, ^3J = 15.9 Hz), 7.10 (d; 1H, ^4J = 1.8 Hz, 7.21 (dd; 1H, ^3J = 8.0 Hz, ^4J = 1.8 Hz), 7.27 (dd; 1H, ^3J = 8.0 Hz, ^4J = 1.8 Hz), 7.30−7.43 (m; 5H), 7.50−7.55 (m; 2H), 7.73 (d; 1H, ^4J = 1.8 Hz. ^{13}C NMR δ: 29.71, 40.51, 50.59; 53.25, 55.33, 55.71, 68.62, 74.98, 101.21(q), 108.25, 110.97, 120.21, 120.62, 121.16, 125.38, 126.91, 127.29, 128.01, 128.59, 128.85, 129.66, 131.16 (q), 131.25 (q), 135.90 (q), 137.66 (q), 140.03 (q), 147.08 (q), 147.22 (q), 147.83 (q), 149.30 (q), 152.54 (q), 163.08, 163.57 (C=O). MS ($C_{38}H_{31}NO_6Br_2$): 758.5 (56.8), [M^+ + 1], calcd (757.48 g/mol).

General Procedure for the Preparation of Dicyano-1-aza-2,6-cyclohexadieno[1,7]isoquinolines (4r−z). To a suspension of 2-styryldihydroisoquinoline (HCl salt) **2** (0.33 g, 1.0 mmol) in absolute ether was added an equimolar solution of triethylamine/ether (0.101 g 1.0 mmol). After 10 min of stirring at room temperature, an equimolar solution of dicycano spiro-pyrrazole **5** (0.268 g 1.0 mmol) in ether (500 mL) was added. After the reaction mixture was flushed for 15 min with dry nitrogen, the solution was photolyzed (Pyrex filter, 125 W HPK mercury high-pressure lamp). After 2 h nitrogen development ceased and the reaction was complete (TLC control). The ether was removed and the residue purified by column chromatography (SiO_2) with eluent mixtures of [CH_2Cl_2/ EtOAc, 9:2] to afford compound **4**. The product was recrystallized from ether to yield colorless to slightly yellow crystals **4j**−**r**.

11′,12′-H-2′,3′-Dicyano-8′,9′-dimethoxy-5′-(4*R*-phenyl)-spiro[fluorene-9,4′-(1-aza-2,6-cycloheptadieno)[1,7-a]isoquinoline] (4r) Standard Procedure. Preparation: 0.33 g (1.0 mmol) of HCl salt of 1-styryl-3,4-dihydroisoquinoline **3a**, 0.268 g (1.0 mmol) of 4′,5′-dicyanespiro[9*H*-fluoren-9,3′-[3*H*]-pyrazole], 0.101 g (1.0 mmol) of triethylamine. Reaction time: 1 h. Yield: 0.133 g (25%) colorless crystals. IR ν (cm^{-1}): 3065, 3045, (C−H, arom.), 2939, 2837 (C−H, aliph), 2219 (C≡N), 2199 (C≡N), 1670, 1620 (C=C), 1558, 1515, 1450, 1275, 1252, 1210, 1024, 856, 743 cm^{-1}. ^{1}H NMR δ: 2.84 (dt, 1H, ^2J = 15.4 Hz, ^3J = 3.6 Hz), 3.39−3.47 (m, 1H), 3.84−3.88 (m and s, 4H), 3.93 (s; 3H), 4.41 (d; 1H, ^3J = 7.1 Hz), 4.47 (dt; 1H, ^2J = 12.8 Hz, ^3J = 4.0 Hz), 6.26 (d; 1H, ^3J = 7.1 Hz), 6.36 (d; 2H, ^3J = 7.1 Hz), 6.70 (s; 1H), 6.80 (t; 2H, ^3J = 7.1 Hz), 6.93 (t; 1H, ^3J = 7.1 Hz), 7.07 (s; 1H), 7.19 (t; 1H, ^3J = 7.5 Hz), 7.28 (t; 1H, ^3J = 7.5 Hz), 7.35 (d; 1H, ^3J = 7.5 Hz), 7.36 (t; 1H, ^3J = 7.5 Hz), 7.49 (d; ^3J = 7.5 Hz, 1H), 7.53 (d; 1H, ^3J = 7.5 Hz), 7.54 (d; 1H, ^3J = 7.5 Hz). ^{13}C NMR δ: 28.73, 50.22, 50.42, 56.05, 56.52, 62.73, 104.41 (q), 106.81, 110.59, 111.49, 113.71, 115.76, 117.32, 119.98, 122.20, 124.46, 126.10, 126.74, 127.17, 127.32, 127.64, 128.18, 128.62, 128.82, 130.84, 138.01 (q), 139.65 (q), 140.14 (q), 142.89 (q), 146.79 (q), 147.74 (q), 148.58 (q), 150.31 (q). Anal. Calcd for $C_{36}H_{27}N_3O_2$ (533.64): C, 81.03; H, 5.10; N, 7.87. Found: C, 80.78; H, 4.87; N, 7.72.

Acknowledgment. Financial help from the "DFG" and the "Fonds der chemischen Industrie" is acknowledged.

JO000807+