A Simple Access to Indolino-Azepines – A New Halochromic System for Information Recording

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Abstract: A new periselective reaction of an 8π-system is reported. This system is prepared by the reaction of spiro[2-cyclopropene-1,9′-fluorene]-2,3-dimethylcarboxylates 2 with 2-styryl-3H-indoles 1 to afford azepine derivatives 4. The addition of acids to 4 causes an important color change, thus generating a new halochromic system.

Key words: electrocyclization, halochromism, heterocycles, cyclo-reversion

Introduction

Electrocyclizations of polyenes are an easy and very general entry to cycloalkenes. The potential of these reactions has been shown for the heterocyclic series by Huisgen.1 In most cases the 6π-reaction proceeds in a stereoselective way. Employing an acyclic 8π-polyene anion or its heteroanalog can complicate the electrocyclic ring closure. Now two routes for the pericyclic process become available. Normally the longest π-system undergoes cyclization because terminal coefficients allow the largest energy gain;2 thus the reaction becomes periselective. These reactions are interesting for the development of new materials of commercial interest such as photochromic compounds based on electrocyclic reactions of spiropyranes, spiroazines, and chromenes.3 All these systems undergo a 1,6-electrocyclization. An exception is the dihydroindolizines (DHI) developed in our group, where the photochromism is due to a 1,5-electrocyclization.3–8

In this paper we describe 1) an access to new betaines 3, from 2-styryl-3H-indoles 1 and spirocyclopropenes 2, and their periselective 1,7-electrocyclization (8π-process) to the indolino-azepines 4, 2) the structure determination of indolino-azepines 4, 3) their static and time resolved spectra and 4) the reversible halochromic properties of these heterocycles 4, which may be of interest as copying or storage materials, being activated by acid or UV-light.

Results and Discussion

The reaction of spirofluorene-cyclopropene derivatives 2 with nitrogen containing heterocycles has been a powerful tool for the preparation of many photochromic dihydroindolizines (DHI).3–11 Based on this reaction, 2 and 2-styryl-3H-indoles 1 at room temperature should afford the betaines 3 as intermediates having an 8π-system, which might react by electrocyclization in two ways. One should lead to the indolino-azepines 4 and the other to the pyrrolizines 5 (9,9a-dihydro-1H-pyrrolo[1,2-a]indoles) (Scheme 1). Carrying out the reaction of 1 with 2 gave after workup a pale yellow solid, which could be further purified by column chromatography on silica gel. Elemental analysis and mass spectroscopy demonstrated clearly the formation of a 1:1 adduct of 1 and 2 possessing the molecular structure 4.

The 1H NMR spectra of all compounds 4a–f show two singlets at δ = 1.48–1.52 (3 H each), which belong to the geminal indoline-methyl groups. The signals at δ = 3.00 and 3.70 are attributed to the methoxy groups (2¢ and 3¢-position). A doublet at δ = 4.95 (2 J = 3.3 Hz) is due to the 6¢-H and the H-atoms in 5¢-position gave a broad signal at δ = 4.18–4.28. The 13C NMR shifts indicate that the final product is the indolino-azepine 4 and not the pyrrolizine 5, since the CS¢-carbons lead to signals at δ = 50.5. This value can only be assigned to an sp3 carbon such as in structure 4. For compound 4 both H-atoms are linked to an olefinic carbon, therefore 5 can be excluded. Finally, the structure of 4 was proven by the X-ray analysis of 4b (see Figure 1).12 A clear structure assignment for product 4b was possible. The N(1)–C(16) bond (141 pm) and C(26)–N(1) bond (139 pm) are shorter than the isolated C–N bond (147 pm), indicating an enamine moiety. The fluorene ring is almost perpendicular to the azepine ring and coplanar to phenyl.

In the case of 4f a second product 4f' was also isolated. The protonation of the 9¢-position of the fluorene unit results in the protonated betaine 3fH, which can be stabilized by the deprotonation of the phenolic hydroxyl group of the styryl moiety. This deprotonation leads to the stable merocyanine like structure 4f' (see Scheme 2).
Photophysical Properties

All compounds 4 show a weak fluorescence emission with very low fluorescence quantum yields, $\Phi_F$, of about $10^{-4}$ at room temperature that increases, when the temperature is lowered. Typical fluorescence maxima for the 7-ring indolines lie between $\lambda = 400$ and 445 nm (Figure 2). Phosphorescence emission is shifted bathochromically by about $\Delta\lambda = 90$ nm. Photophysical data of selected compounds are summarized in Table 1.

The new light-induced indolino dihydroazepines 4 have been investigated further with regard to their photochromic properties. Compounds 4 contain a 6\pi-system, which on ring-opening can afford an 8\pi-system. A photoinduced ring-opening of 4 $\rightarrow$ 3 could however not be observed, neither by irradiation of the sample at 77 K nor by using laser flash photolysis which would permit the detection of short-living intermediates with very small half lives. Due to apparatus limitations of the ns-laser measurements, the kinetics of the photochromic ring closure process 3 $\rightarrow$ 4 have to be faster than 1–10 ns. Similar spiro-azepines, the dicyano substituted tetrahydro-azepinoisoquinolines (THAI) show reversible photochromic reactions in the \(\mu\)-\(\mu\) ns range. Nevertheless, the electrocyclic ring-opening could be proven by acidifying a solution of 4. This generates color changes, which are typical for 4b–f. Whereas 4a did not undergo a color change, 4b turned yellow, 4c violet, 4d,e blue, and 4f yellow on acidification. With ad-
tion of base (NH₃) the whole process is reversible (UV/Vis data are collected in Table 2).

1H NMR measurements have shown that in an acidified solution this negatively charged C-atom reacts with a proton to give the protonated merocyanine.

In general, the color of the pyrrolizines of type 5 results from a charge transfer between the negatively charged fluorene unit and the positively charged heterocycle.3 When the negatively charged center reacts with a proton, the charge transfer band is suppressed and the intense absorption band of the betaine in the visible region disappears.3 Earlier electron density calculations of a betaine of type 3 indicated that the positive charge resides at the N-atom and that the negative charge of the colored betaine form 3 is mainly localized on the C-9-atom of the fluorene unit.15 In the case of 3H the color of the compounds is caused by the merocyanine like moiety of 3H.16 The addition of an acid to a solution of 4 leads to a deeply colored salt, the protonated form 3H. Such an effect is called “halochromism”.17–19 An explanation for this halochromism of 4 is a thermal 1,7-cycloreversion from 4 → 3 and consecutive protonation of the betaine 3 to 3H. It is not clear if this sequence is acid-induced or only acid-catalyzed. The addition of the acid activates the moiety R of the styryl unit (see Scheme 1). The electronic behavior of the seven-membered ring is changed by conjugation of R with the azepine ring and a thermal 1,7-cycloreversion becomes possible. Compounds 4b–f can also be transformed to colored protonated betaines 3Hb–f. A light-induced process produces the proton by the following reaction: PhCH₂Br

![Figure 1](image1)

**Figure 1** X-ray structure of 4b. Selected bond-lengths [pm] and bond-angles [°]: N1–C16 141.2 (2), C16–C15 132.4 (2), C15–C14 150.6 (2), C14–C1 157.4 (2), C1–C27 153.8 (2), C27–C26 133.7 (2), C26–N1 139.3 (2), C26–N1 125.6 (1), N1–C16–C15 127.5 (1), C16–C15–C14 132.9 (1), C15–C14–C1 155.9 (1), C1–C1–C27 111.5 (1), C1–C27–C26 127.3 (1), C27–C26–N1 125.6 (1)

![Figure 2](image2)

**Figure 2** Excitation and emission spectra at low temperature (77K) of 4c in ethanol glass (c = 2×10⁻⁴ mol/L)

<table>
<thead>
<tr>
<th>Compd</th>
<th>τₜₚₑₚₑ (ns)</th>
<th>λₚₑₚₑ,77K (nm)</th>
<th>λₚₑₚₑ,77K (nm)</th>
<th>λₚₑₚₑ,77K (nm)</th>
<th>τₑ (ns)</th>
<th>Φₑ [10⁻⁴]</th>
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<tbody>
<tr>
<td>4a</td>
<td>&lt;1–10</td>
<td>346</td>
<td>465</td>
<td>555</td>
<td>&lt;0.25</td>
<td>16</td>
</tr>
<tr>
<td>4c</td>
<td>&lt;1–10</td>
<td>348</td>
<td>468</td>
<td>557</td>
<td>&lt;0.25</td>
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</tr>
</tbody>
</table>

**Scheme 2**

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The addition of 2-styryl-3H-indoles 1 to spiropencene 2 forms an intermediate 3 which undergo a 1,5- or 1,7-electrocyclisation. The exclusive formation of 4 from betaine 3 can be understood as a periselective 1,7-electrocyclisation.

The addition of an acid to a solution of 4 triggers halochromism and allows the acid-induced 1,7-cycloreversion of 4, resulting in the betaine 3, which is protonated to 3H. The protonated form 3H exhibits an intensive color in the visible range caused by the merocyanine part of 3H, thus constituting a new halochromic system. This halochromic color formation can also occur in a light-induced fashion in 4 + PhCH2Br/pyrrolidine matrices, thus allowing an information recording or display material.

Melting points are uncorrected. 1H NMR spectra were recorded in CDCl3 or DMSO with TMS as internal standard on a Bruker DRX 500 spectrometer. The mass spectra were obtained with a Varian MAT-311 spectrometer (70 eV). UV/Vis spectra were taken on a Unikon 860 UV/VIS spectrophotometer. The CH2Cl2 used for UV/Vis spectroscopy was spectrograde and used without further purification. For acidification, HCl having a concentration of ca 2 × 10−2 mol/L was used.

Singlet lifetimes were measured by excitation with a frequency-tripled pulsed YAG laser (B.M. Industries) of 30 ps fwhm. The signal output from a photodiode was fed into a Tektronix 7912AD digitized oscilloscope and the data, were stored in an Apple II+ microcomputer. Average decays could be analyzed directly by the microcomputer. Low temperature measurements were carried out at 77 K in ethanol glass, for excitation, fluorescence, and phosphorescence. A liquid-nitrogen cooled Dewar was used with a chopper for phosphorescence emission or without the chopper for excitation and fluorescence.

Flash photolysis experiments were carried out with a frequency-doubled pulsed ruby laser (347.5 nm; 20 ns fwhm) from JK Laser Co. The usual crossed beam system was used, the analyzing light being a pulsed Xenon lamp from Applied Photophysics. A detailed description of the experimental setup has been given already.13

X-ray data were obtained by C. Krüger, Max-Planck-Institute Mülheim/Ruhr.

Azepines 4a–f and the Merocyanine 4f, General Procedure

A solution of 1a–f (1 mmol) in anhyd Et2O was added to a solution of spiropencene 2 (1 mmol) in Et2O (50 mL). The solution was stirred at r.t. in the dark until a precipitate had formed (DC). The crude product was purified by column chromatography (silica gel/CH2Cl2) and recrystallized from CH2Cl2–MeOH.

2',3',5'-Di(methoxycarbonyl)-7',7'-dimethyl-5'-phenylspiropfluorene-9,4'-(1-aza-2,6-cycloheptadieno)[1,7-α]indoline (4a)

Yield: 0.35 g (63%); mp 235–236 °C.

1H NMR (CDCl3): δ = 7.45–7.15 (m, 10 H, ArH), 7.08 (m, 2 H, ArH), 6.88 (t, J = 7.6 Hz, 1 H, ArH), 6.75 (t, J = 7.6 Hz, 1 H, ArH), 6.70 (d, J = 8.0 Hz, 1 H, ArH), 6.35 (d, J = 7.1 Hz, 2 H, ArH), 4.98 (d, J = 3.3 Hz, 1 H, 6'-H), 4.32 (br s, 1 H, 5'-H), 3.70 (s, 3 H, CO2CH3), 3.06 (s, 3 H, CO2CH3), 1.53 (s, 3 H, CH3), 1.49 (s, 3 H, CH3).

13C NMR (CDCl3): δ = 168.1 (C=O), 165.4 (C=O), 149.4–103.7 (ArC and olefin. C), 60.4 (spi-ro-9,4'-C), 52.7 (CO2CH3), 51.4

Table 2 UV/Vis-Spectral Data of 4a–f in CH2Cl2 and CH2Cl2/HCl after Irradiation

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<thead>
<tr>
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<th>λmax (ε) nm</th>
<th>λ2max (ε) nm</th>
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<tr>
<td>(CH2Cl2)</td>
<td>(CH2Cl2/HCl)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>263 (26300)</td>
<td>339 (7250)</td>
<td>–</td>
</tr>
<tr>
<td>b</td>
<td>263 (29500)</td>
<td>339 (7100)</td>
<td>482</td>
</tr>
<tr>
<td>c</td>
<td>266 (39600)</td>
<td>339 (7150)</td>
<td>587</td>
</tr>
<tr>
<td>d</td>
<td>256 (35500)</td>
<td>363 (29590)</td>
<td>638a</td>
</tr>
<tr>
<td>e</td>
<td>266 (41900)</td>
<td>393 (35900)</td>
<td>650a</td>
</tr>
<tr>
<td>f</td>
<td>258 (28950)</td>
<td>339 (7200)</td>
<td>498 (37700)</td>
</tr>
<tr>
<td>f'</td>
<td>–</td>
<td>505 (32000)</td>
<td>495 (38300)b</td>
</tr>
</tbody>
</table>

Table 3 Transmission ΔT% and Spectral Data of UV-Photography-Layers from 4d,e

<table>
<thead>
<tr>
<th>Layer</th>
<th>λmax (of colored form)</th>
<th>T% (without irradiation)</th>
<th>T% (with irradiation)</th>
<th>ΔT%</th>
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</thead>
<tbody>
<tr>
<td>4c</td>
<td>593</td>
<td>85.1</td>
<td>56.7</td>
<td>28.4</td>
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<tr>
<td>4d</td>
<td>637</td>
<td>78.3</td>
<td>7.7</td>
<td>70.6</td>
</tr>
<tr>
<td>4e</td>
<td>632</td>
<td>84.8</td>
<td>69.2</td>
<td>15.6</td>
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</tbody>
</table>

Compound 4d with a ΔT% of 70.6 is a very promising material, which may be used as an information recording or storage system. The images found are fully stable at room temperature. They can be erased by treatment with NH3.

**Conclusion**

The addition of 2-styryl-3H-indoles 1 to spiropencene 2 forms an intermediate 3 which undergo a 1,5- or 1,7-electrocyclisation. The exclusive formation of 4 from betaine 3 can be understood as a periselective 1,7-electrocyclisation.
(CO\textsubscript{2}CH\textsubscript{3}), 51.0 (5'-CH), 45.2 (7'-q-C), 30.3 (7'-CH\textsubscript{3}), 29.0 (7'-CH\textsubscript{3}).

MS: m/z = 553.6 (M* , 100 %).

Anal. Calcd for C\textsubscript{37}H\textsubscript{31}NO\textsubscript{5} (569.6): C, 78.01; H, 5.49; N, 2.46.
Found: C, 77.98; H, 5.54; N, 2.10.

2',3'-Dimethoxycarbonyl)-7',7'-dimethyl-5'-[4-(4-methoxyphenyl)spirofluorene-9,4'-[1-aza-2,6-cycloheptadieno][1,7]-\textbeta-jindoline (4b)
Yield: 0.40 g (60%); mp 210–211 °C.

1\textsuperscript{H} NMR (CDCl\textsubscript{3}): δ = 7.43–7.39 (m, 3 H, ArH), 7.27–7.13 (m, 6 H, ArH), 7.06 (m, 2 H, ArH), 6.69 (d, J = 7.9 Hz, 1 H, ArH), 6.50 (m, 2 H, ArH), 4.95 (d, J = 3.3 Hz, 1 H, 6'-H), 4.24 (br s, 1 H, 5'-H), 3.70 (s, 3 H, CO\textsubscript{2}CH\textsubscript{3}), 3.58 (s, 3 H, OCH\textsubscript{3}), 3.05 (s, 3 H, CO\textsubscript{2}CH\textsubscript{3}), 1.52 (s, 3 H, CH\textsubscript{3}), 1.48 (s, 3 H, CH\textsubscript{3}).

13\textsuperscript{C} NMR (CDCl\textsubscript{3}): δ = 168.2 (C=O), 165.4 (C=O), 157.7–104.0 (ArC and olef. C), 60.5 (spiro-9,4'-C), 54.9 (OCH\textsubscript{3}), 52.7 (CO\textsubscript{2}CH\textsubscript{3}), 51.4 (CO\textsubscript{2}CH\textsubscript{3}), 50.3 (5'-CH), 45.1 (7'-q-C), 30.2 (7'-CH\textsubscript{3}), 29.0 (7'-CH\textsubscript{3}).

MS: m/z = 583.6 (M* , 100%).

Anal. Calcd for C\textsubscript{37}H\textsubscript{31}NO\textsubscript{5} (569.6): C, 78.19; H, 5.70; N, 2.40.
Found: C, 77.83; H, 5.85; N, 2.69.

2',3'-[Dimethoxycarbonyl]-7',7'-dimethyl-5'-[4-(dimethylamino)phenyl]spirofluorene-9,4'-[1-aza-2,6-cycloheptadieno][1,7]-\textbeta-jindoline (4c)
Yield: 0.48 g (60%); mp 248–249 °C.

1\textsuperscript{H} NMR (CDCl\textsubscript{3}): δ = 7.45–7.36 (m, 3 H, ArH), 7.26–7.12 (m, 6 H, ArH), 7.03 (m, 2 H, ArH), 6.68 (d, J = 7.9 Hz, 1 H, ArH), 6.26 (m, 2 H, ArH), 6.16 (d, J = 6.9 Hz, 2 H, ArH), 4.99 (d, J = 3.3 Hz, 1 H, 6'-H), 4.18 (br s, 1 H, 5'-H), 3.67 (s, 3 H, CO\textsubscript{2}CH\textsubscript{3}), 3.04 (s, 3 H, CO\textsubscript{2}CH\textsubscript{3}), 2.72 [s, 6 H, N(CH\textsubscript{3})\textsubscript{2}], 1.51 (s, 3 H, CH\textsubscript{3}), 1.47 (s, 3 H, CH\textsubscript{3}).

13\textsuperscript{C} NMR (CDCl\textsubscript{3}): δ = 168.3 (C=O), 165.4 (C=O), 149.4–104.5 (ArC and olef. C), 60.6 (spiro-9,4'-C), 52.4 (CO\textsubscript{2}CH\textsubscript{3}), 51.3 (CO\textsubscript{2}CH\textsubscript{3}), 50.2 (5'-CH), 45.1 (7'-q-C), 40.4 (NCH\textsubscript{3}), 30.1 (7'-CH\textsubscript{3}), 29.2 (7'-CH\textsubscript{3}).

MS: m/z = 596.5 (M* , 33%).

Anal. Calcd for C\textsubscript{37}H\textsubscript{31}NO\textsubscript{5} (569.6): C, 78.50; H, 6.08; N, 4.49.
Found: C, 78.28; H, 6.09; N, 5.03.

2',3'-[Dimethoxycarbonyl]-7',7'-dimethyl-5'-[4-(3,5-diphenyl-1-phenylamino)phenyl]spirofluorene-9,4'-[1-aza-2,6-cycloheptadieno][1,7]-\textbeta-jindoline (4d)
Yield: 0.40 g (52%); mp 207–210 °C.

1\textsuperscript{H} NMR (CDCl\textsubscript{3}): δ = 7.61 (m, 2 H, ArH), 7.40–7.02 (m, 18 H, ArH), 5.70 (d, J = 7.9 Hz, 1 H, ArH), 6.47 (m, 2 H, ArH), 6.23 (m, 2 H, ArH), 5.28 (m, 1 H, pyraz.-H), 4.95 (d, J = 3.4 Hz, 1 H, 6'-H), 4.18 (br s, 1 H, 5'-H), 3.69 (s, 3 H, CO\textsubscript{2}CH\textsubscript{3}), 3.68 (m, 1 H, pyraz.-H), 3.03 (s, 3 H, CO\textsubscript{2}CH\textsubscript{3}), 3.00 (m, 1 H, pyraz.-H), 1.50 (s, 3 H, CH\textsubscript{3}), 1.46 (s, 3 H, CH\textsubscript{3}).

13\textsuperscript{C} NMR (CDCl\textsubscript{3}): δ = 168.1 (C=O), 165.5 (C=O), 149.7–103.3 (ArC and olef. C), 64.2 (pyraz.-C), 60.3 (spiro-9,4'-C), 52.8 (CO\textsubscript{2}CH\textsubscript{3}), 51.4 (CO\textsubscript{2}CH\textsubscript{3}), 50.5 (5'-CH), 45.1 (7'-q-C), 43.3 (pyraz.-C), 30.4 (7'-CH\textsubscript{3}), 28.9 (7'-CH\textsubscript{3}).

MS: m/z = 774.8 (M*).

Anal. Calcd for C\textsubscript{50}H\textsubscript{43}NO\textsubscript{3} (773.9): C, 80.70; H, 5.60; N, 5.43.
Found: C, 80.27; H, 5.75; N, 5.25.

Acknowledgement
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References


(12) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge CB2 1EW, UK as supplementary publication under the number CCDC 117323.


