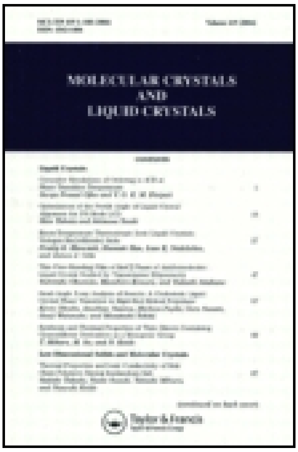

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New Photochromic bis-Spirocyclic Systems

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NEW PHOTOCHROMIC *bis*-SPIROCYCLIC SYSTEMS

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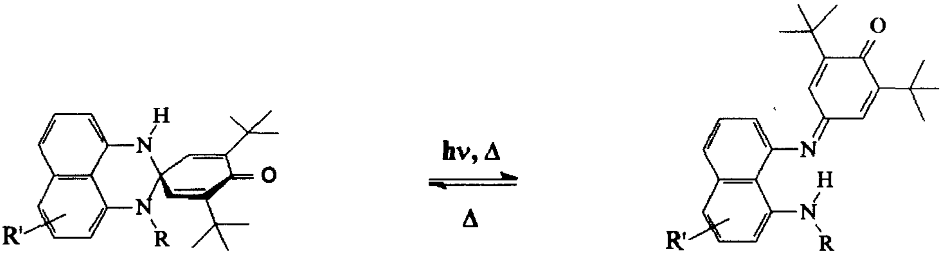
Abstract Novel photochromic *bis*-spirocyclic compounds, derivatives of di(4-cyclohexa-2,5-dien-1-one)benzimidazole **5a** and di(4-cyclohexa-2,5-dien-1-one) perimidine **8a** have been synthesized. Under UV-irradiation of their toluene solutions compounds **5a** (λ_{max} = 474 - 502 nm) undergo thermally irreversible rearrangement to the isomeric *bis*-quinoneimines **5b** (λ_{max} = 593 - 602 nm). When treated with trifluoroacetic acid in toluene **5a** and **8a** form monoprotonated cations **5aH**$^+$ and **8aH**$^+$ (λ_{max}=375 - 384 nm) which reveal photocromic properties. The photoisomers of the cations **5aH**$^+$ and **8aH**$^+$ possess long-wave absorption bands properties (λ_{max} = 766 - 810 nm). Quantum yields fall into the range of 0.13-0.17.

INTRODUCTION

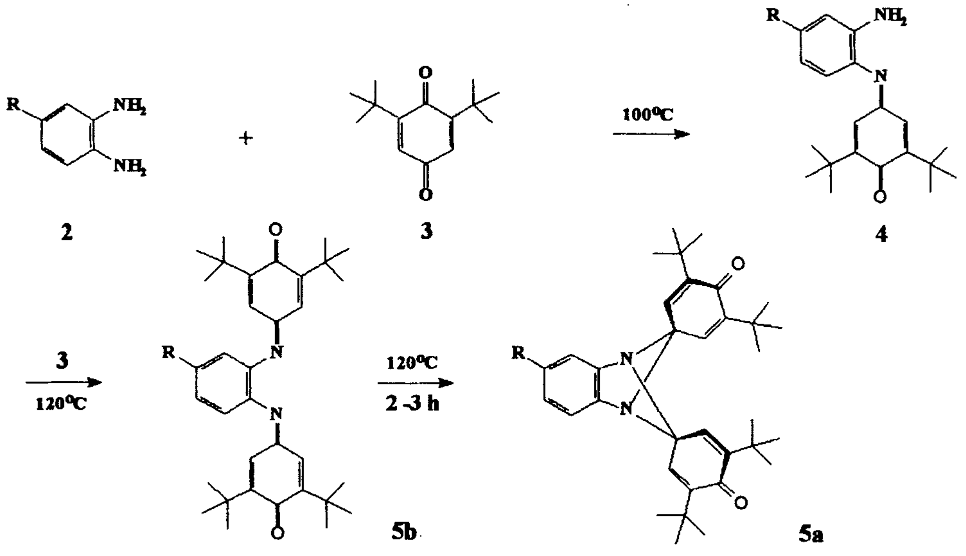
We have earlier reported on the synthesis and spectral study of a new photochromic system - perimidine spirocyclohexadienones.[1-3, 4]



1a **1b**

The compounds **1a** were obtained by coupling equimolar amounts of corresponding 1,8-diaminonaphtalenes with 2,6-di-*tert*-butyl-1,4-benzoquinone through refluxing propanol or toluene solutions of the components. No spirocyclization occurred, however, when such diamines as o-phenylenediamines **2** or 5,6-diaminoacenaphthene **7** were introduced in this reaction under similar conditions, the ring-opened isomers, respectively **4** and **7** being the products. By heating **4** with an excessive amount of 2,6-

di-*tert*-butyl-1,4-benzoquinone or, simply, by meting o-phenylenediamines **2** with that quinone, taken in molar ratio 1:2, at 110-160° C for 4-7 hours, condensation on the second amino group became possible giving rise to the formation of both ring-opened **5b** and *bis*-spirocyclic isomers. The isomers differ in their color (dark-blue for **5b** and red for **5a**) and chromatographic properties. As seen form the thin-layer chromatogram (Al_2O_3), the primary products of the reaction of 1,2-phenylenediamine with 2,6-di-tert-butyl-1,4-benzoquinone are *bis*-quinoneimines **5b** which gradually and almost completely convert to 5a when allowed to stand at near-room temperature.

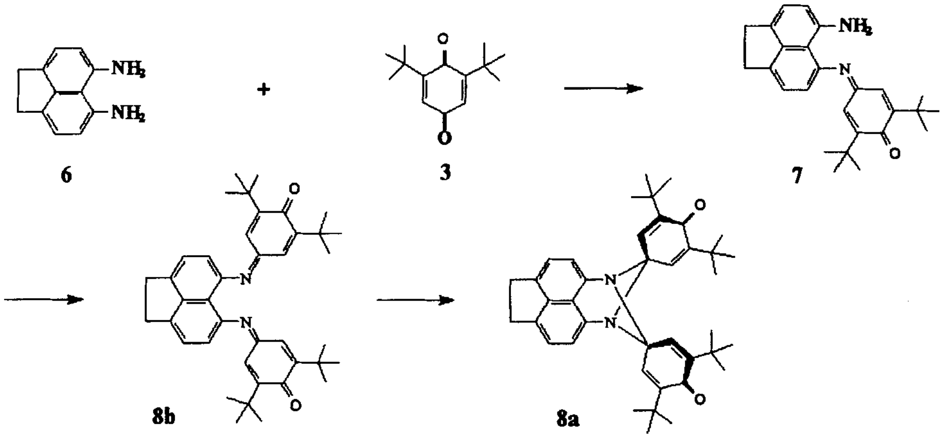


R = H, Me, OMe

In contrast to the *bis*-quinoneimines **5**, whose isolation in the pure state presents certain preparative difficulties, their ring-closed *bis*-spirocyclic isomers **5a** are stable well-crystallized compounds that were characterized analytically and by their IR-, UV-Vis, ^{1}H NMR and mass spectra.

In a similar way reaction of 5,6-diaminoacenaphtene **6** with quinone **3** affords the *bis*-spirocyclic compound **8a** through the intermediate formation of mono-, **7**, and *bis*-quinoneimine **8b**.

It was found out that in both series of the compounds the interconvertion of *bis*-spirocyclic and *bis*-quinoneimine isomers can be initiated by irradiation of their solutions. The present paper describes photochromic behavior of type 5 and 8 compounds.



EXPERIMENTAL

2,3- Benzo- 5,6- *bis*- [spiro- (4'- 2',6'-di-*tert*-butylcyclohexadienone)]-1,4-diazabicyclo [2.1.1]hexane, 5a (R=H).

A mixture of o-phenylenediamine (0.32 g, 3 mmol) and 2,6-di-*tert*-butyl-1,4-benzoquinone was heated at 130-140° C for 7 hours, then cooled to room temperature and dissolved in chloroform-hexane (3:2). The solution was passed through a column filled with Al_2O_3 and the dark-orange fraction collected. After removal of the solvent red needles of 5a (R=H). Were obtained (0.7 g, yield 46%). M.p. 87-89° C (from methanol). IR (nujol) : 1620 cm^{-1}, 1640 cm^{-1} (C=O). ^1H NMR (CD_2Cl_2, δ): 1.14 (s, t-Bu), 1.27 (s, t-Bu), 6.64, 6.94, J=2.6 Hz (q, quinonoid protons). Found: C, 79.93; H, 8.63; N, 5.30 $C_{34}H_{44}N_2O_2$ requires: C, 79.65; H, 8.65; N, 5.46.

N,N'-*bis*-(2,6-di-*tert*-butyl-1,4-benzoquinonylidene-4)-*o*-phenylenediamine, 5b (R=H).

When the reaction above described was carried out at lower temperature (110-120° C) and the mixture of the initial components was heated for a shorter period of time (2 hours), it resulted in the formation of a greater relative amount of the isomer 5b, *bis*-spirocyclic isomer 5a being in this case a minor product. The compound 5b (R=H) was obtained in 31% yield as dark-blue crystals. M.p. 132-136° C (from octane). IR (nujol): 1620, 1635 cm^{-1} (C=O). Found C, 79.53; H, 8.78; N, 5.35. $C_{34}H_{44}N_2O_2$ requires: C, 79.65; H, 8.65; N, 5.46. To inhibit isomerization of 5b into 5a (R=H), which is rather fast at near-room temperature, the compound must be stored at the temperature lower than 4° C.

In a similar way the derivatives of **5a** (R=H) and **5b** (R=H) were prepared. **5a** (R=Me): M.p. 95-97° C (from methanol). **5b** (R=Me): M.p. 132-137° C (from octane).

5a (R=OMe). M.p. 78-80°C (from methanol). **5b** (R=OMe): M.p. 90-94°C (from octane).

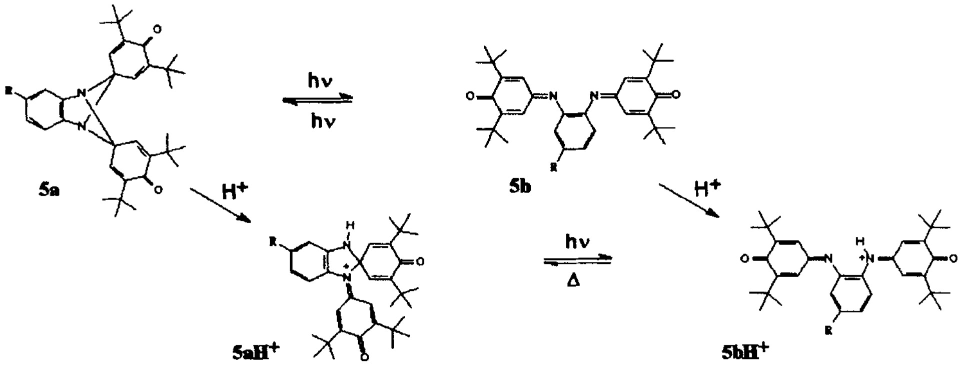
6,7-Di[spiro(4'-2'.6'-di-*tert*-butylcyclohexa-2',5'-dien-1-one)]acenaphtheno[5",5a", 6": 2,3,4]-1,5-diazabicyclo[3.1.1]heptane, **8a** was prepared in 26% yield as dark-red crystals. M.p. 214-216° C (from octane). IR (nujol): 1627 cm^{-1}, 1615 cm^{-1} (C=O).

^1H NMR (CD_2Cl_2, δ): 1.16 (s, t-Bu), 1.32 (s, t-Bu), 3.46 (s, CH_2), 6.88, 7.00 J = 2.6 Hz (q, quinonoid protons), 6.53 (s), 7.29 (s). Found: C, 81.62; H, 8.35; N, 4.57.$C_{40}H_{48}N_2O_2$ requires: C, 81.59; H, 8.22; N, 4.76.

Absorption and reflection spectra were recorded on a "Specord M 40" spectrophotometer. Photochemical transformations were initiated by irradiation with the light of a high-pressure mercury lamp (DRSH-250), glass filters being employed. Intensities of the irradiation were measured using "Aberochrome 540"actinometer.

RESULTS AND DISCUSSION

Bys-spirocyclics **5a** possess long-wave absorption in the spectral region of 474- 502 nm, whereas for the perimidine analogue **8a** λ_{max} is long-wave shifted to 535 nm.



Upon irradiation of solutions of **5a** and **8a** with the light in the λ_{max}, the isomerizations occur due to reversible heterolytic scissions of the carbon(spiro) - nitrogen bonds which lead to the formation of the deeply colored photoisomers **5b** and **8b** respectively.

The back reaction cannot be thermally initiated and proceeds only on irradiation of the solutions of photogenerated colored isomers with the light in their absorption maxima. Quantum yields of both direct and back reactions are low (less than 10^{-3}).

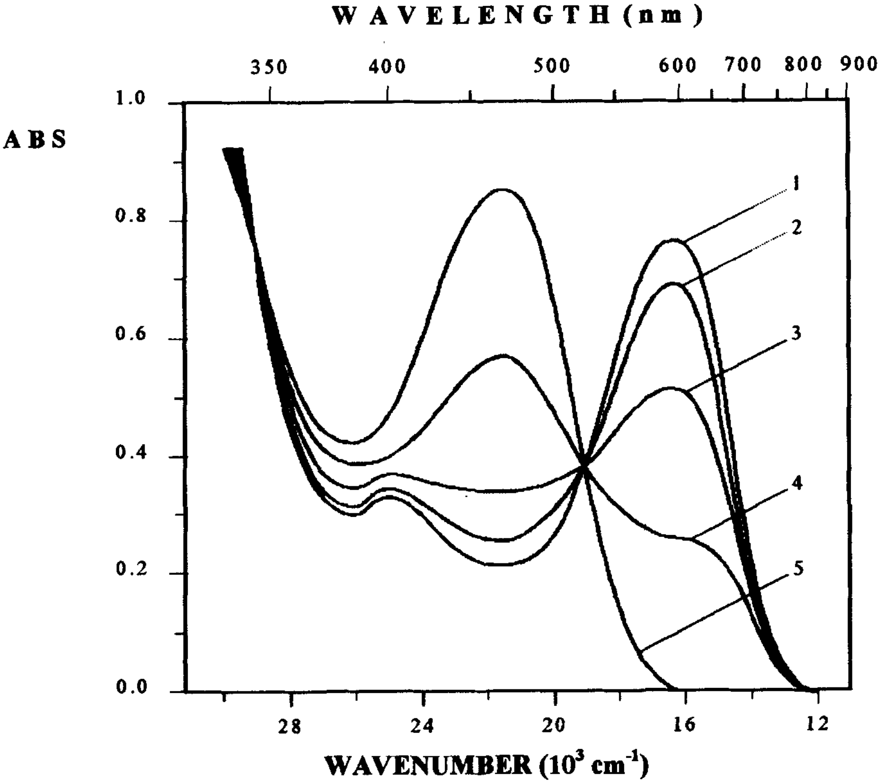


FIGURE 1. Absorption spectra of a toluene solution (c = 9.4×10^{-5} M) of **5b** (R=H) before irradiation (1) and after irradiation at 578 nm for 3600 s (2), 14400 s (3), 54000 s (4); 210000 s (5).

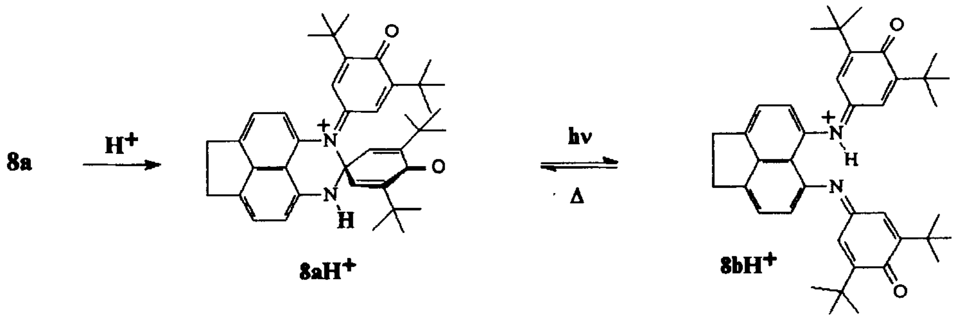
Same type reversible photoinitiated isomerizations occur also in crystal, as was shown by the study of the reflection spectra of compounds **5a**. Fig. 1 gives an example of spectral changes during the photoisomerizations. Data on spectral properties of the photoisomers of compounds **5** and **8** are listed in Table1.

TABLE 1. Photochromic characteristics of the bis-spyrocyclic compounds (**a**) and monoprotonated cations (**a**H^+) in toluene.

Compound	**a** λ_{max}, nm (ε, 10^3 l $mol^{-1}cm^{-1}$)	**b** λ_{max}, nm (ε, 10^3 l $mol^{-1}cm^{-1}$)	**a**H^+ λ_{max}, nm (ε, 10^3 l $mol^{-1}cm^{-1}$)	**b**H^+ λ_{max}, nm (ε, 10^3 l $mol^{-1}cm^{-1}$)	Φ (**a**$H^+ \rightarrow$ **b**H^+)	τ (**b**H^+), s T=297K
5 (R=H)	474 (8,83)	593 (7,99)	375 (20,0)	803 (7,4)	0,17	900
5 (R=Me)	484 (8,52)	602 (7,81)	384 (21,1)	810 (7,3)	0,13	2400
5 (R=OMe)	502 (11,96)	597 (12,54)	377 (23,4)	766 (9,88)	0,16	1800
8	535 (9,15)	665 (19,6)	504 (12,02)	833		<1

An addition of trifluoroacetic acid to the solution of **5a** and **8a** leads to the formation of their cations, respectively **5a**H^+ and **8a**H^+ which represent another new photochromic system. Upon activation by UV-light the cations **5a**H^+ and **8a**H^+ undergo a rearrangement similar to that of perimidinespirocyclohexadienones **1** which leads to deeply colored protonated *bis*-quinoneimines **5b**H^+ and **8b**H^+ respectively. The structure of the latter cations was confirmed by the identity of their spectra with those observed on protonation of *bis*-quinoneimines **5b**, **8b**.

A peculiar feature of the photochromic behavior of the cations **5a**H^+ and **8a**H^+, as compared to that of their conjugated bases, is the fact that the back reaction readily occurs at room temperature as a thermal relaxation process.



The absorption of the colored photoisomers **5bH$^+$** and **8bH$^+$** is substantially long-wave shifted with respect to that of **5b** and **8b** and approaches the near-IR spectral region. Quantum yields of the photoisomerizations of **5aH$^+$** are almost of three order of value higher than those of the photoisomerizations of their conjugated bases.

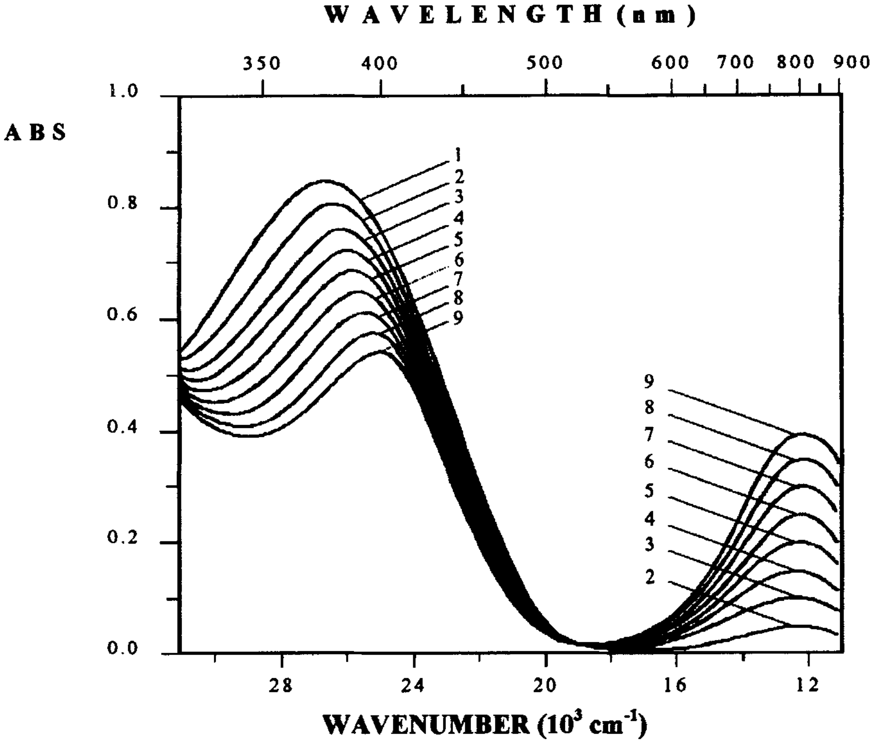


FIGURE 2. Absorption spectra of a toluene solution (c = 4.3×10^{-5} M with an addition of CF_3COOH) of **5aH$^+$** (R=H) before irradiation (1) and after irradiation at 365 nm for 10 s (2), 30 s (3), 60 s (4), 120 s (5), 240 s (6), 480 s (7), 960 s (8), 1920 s (9).

The data on spectral properties, quiantum yields and lifetimes of the colored photoisomers for the protonated *bis*-spirocyclic compounds are given in Table 1 and illustrated by Figure 2.

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