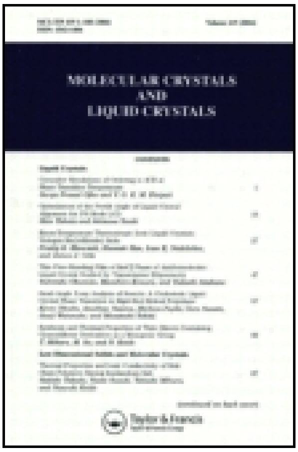

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Perimidmespirocyclohexadienones - a Novel Photo and Thermochromic System

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PERIMIDINESPIROCYCLOHEXADIENONES - a NOVEL PHOTO and THERMOCHROMIC SYSTEM

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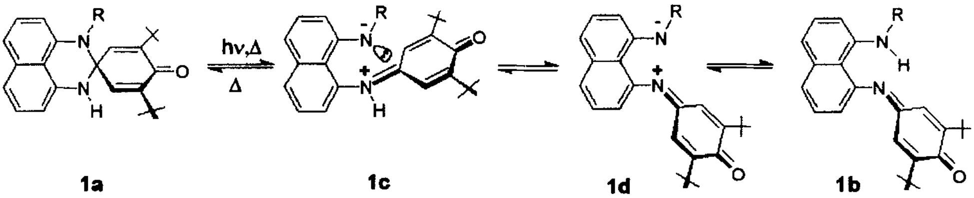
Abstract A new class of photochromic compounds, derivatives of 2,3-dihydro-2-spiro-4'-(2',6'-di-*tert*-butylcyclohexadienon-2',5'- one)perimidine is described and their photochromic and thermochromic rearrangements described.

INTRODUCTION

We have previously found out that 2,3-dihydro-2- spiro-4'-(2',6'-di-*tert*-butylcyclohexadienon-2',5'-one)perimidine (perimidinespirocyclohexadienone) **1** (R=H) and its N-methyl derivative are susceptible to photoinitiated and thermal rearrangements whose mechanism is given by Scheme 1. [1,2]



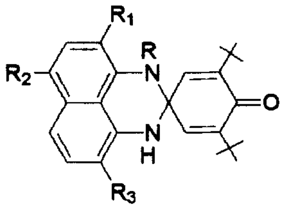
R = H, Me, Et, Pr, i-Bu, CH_2Ph

Scheme 1

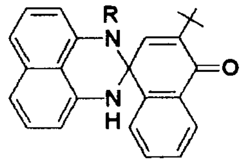
In the following studies the rearrangements featured by Scheme 1 were extended to various derivatives and heteroanalogues of **1**. This paper provides a concise survey and a progress report on the synthesis, structure, photochromic and thermochromic properties of perimidinespirocyclohexadienones **1**, congeneric compounds **2** - **5** and recently synthesized bis-spirocyclic derivatives **6**.

SYNTHESIS AND STRUCTURE

Coupling *o*-phenylenediamines with *p*-benzoquinones results in the formation of N-(o-aminoaryl)quinones which do not undergo cyclization into thermodynamically more stable ring-closed tautomers under heating or irradiation of their solutions. In contrast to this, 1,8-naphthylenediamines and 4,5-diaminoquinolines react with 2,6-di-*tert*-butylcyclohexadienone or 2-*tert*-butyl-1,4-naphtoquinone to afford corresponding spirocyclic compounds **1-3**, **5**.[1-3] The reaction readily occurs when refluxing propanol or toluene solutions of the components. Catalysis by strong proton acids, e.g. *p*-toluenesulfonic acid is required for the preparation of 2,3-dihydro-2-spiro[4(4H)-2-*tert*-butyl-1-naphthalenone]perimidines **2**, **3**. *Bis*-spirocyclic derivatives **6** were obtained when heating acenaphthylenediamine 2,6-di-*tert*-butylcyclohexadienone taken in 1:2 ratio at 120 °C for 4-5 hours. [4]



1



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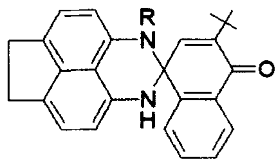

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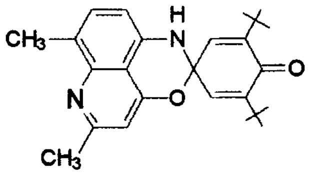

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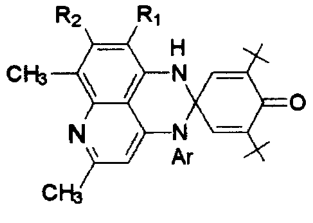

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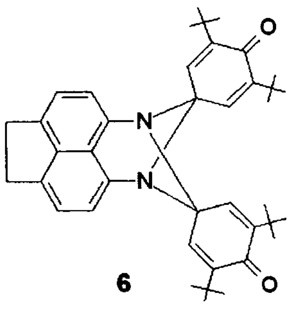

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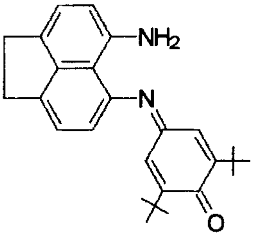
R = H, Alk, CH_2Ph; R_1, R_2, R_3 = H, Br, CH_3

The different courses of the reaction of quinones with aromatic *ortho-* and *peri-*diamines cannot be assigned to different terms for the thermodynamic control. As stems from the MNDO-PM3 calculations, the spirocyclic isomers represent energy preferable forms for any of the type **1** - **5** compounds. The cyclization step is, therefore, kinetically controlled, i. e. depends on energy requirements for the occurrence of **1b→1d→1c** interconversion. Structural variations strongly affect the result of the condensation reaction. For example, the reaction of 5,6-diaminoacenaphthene with 2,6-di-*tert*-butylcyclohexadienone gives rise to the ring-opened isomer **7**. Derivatives of ring-opened isomers of **1** and **2** can be also obtained by acylation or tosylation of these compounds. The ring-opened structure **8** of N-tosyl derivative of **1** was proven by an X-ray crystal study.[5]



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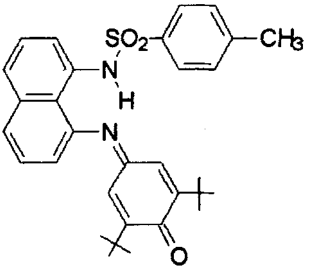


8

Molecular structures of perimidinespirocyclohexadienones **1** (R=Me, R_1, R_2, R_3=H) and **2** (R = H) were proven by an X-ray diffraction study.[2] A peculiar structural feature of this type spirocyclic compounds is significant folding of the six-membered diazaheterocyclic ring along the N(1)-N(2) axis. Same kind distortion has been recently revealed in molecules of structurally similar perimidinespiro-1,3-indandiones.[6]

SPECTRAL AND PHOTOCHROMIC PROPERTIES

As exemplified by Figure 1 , UV irradiation of solutions of perimidinespiro-cyclohexadienones **1** leads to their rapid coloration due to appearance of long-wave absorption bands ($\lambda_{max} \cong 600$ nm) assigned to the ring-opened isomers **1b**. Upon extinguishing UV-irradiation, the decoloration process which restores the initial spectrum occus slowly at room temperature. The compounds **1** possess sufficiently high fatigue resistance. Thus, under continous illumination of a polystyrene film of **1** (R=Et, R_1, R_2, R_3 = H) with the light of intensity 10^{15} photon/s at λ_{max} of **1a**, the period of time required for reduction of the absorbance in the long-wave absorption band of the colored isomer **1b** to half of the initial value lasts for more than 150 hours.

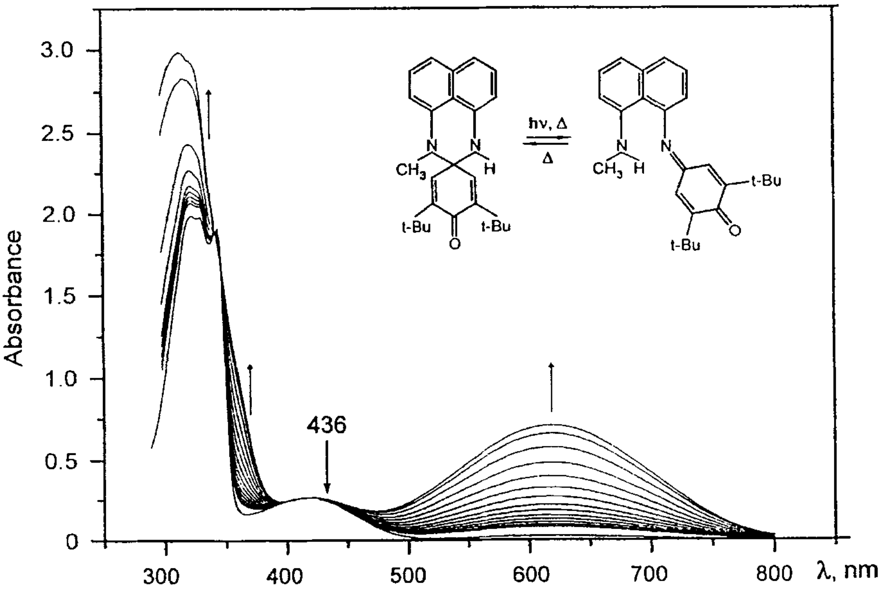


FIGURE 1. Evolution of the spectrum of **1a** (R=Me, R_1-R_3=H) during irradiation of its hexane solution (c=1·10^{-4} M, 295K) at the longest wavelength band with time interval 5 min.

The nature of the colored isomers, **1b**, of photochromic perimidinespirocyclohexadienones has been proven through comparison of their absorption spectra with those of ring-opened aceperimidinespirocyclohexadienone **7** (Table 1) and N-tosyl derivative **8**. Table 2 contains an excerpt of data on positions and intensities of the longest wavelength absorption bands of the ring opened photoisomers of perimidinespirocyclohexadienones and their analogues. Noteworthy is that, although the absorption maxima of these compounds lie in the range of 560-630 nm, the tails of the bands extend to 800-900 nm, i.e. near IR-region. Analogous spectral pattern is also characteristic of indoaniline dyes [7] whose structure and, therefore, the nature of the electronic transitons are similar to those of quinoneimines **1b**.

TABLE 1. Longwave absorption of the photoisomers of perimidinespirocyclohexadienones and their analogues (octane).

Compound	λ_{max}, nm	ε, L · M^{-1} cm^{-1}
1, R=H. R_1-R_3=H	584	5300
1, R=Et. R_1-R_3=H	626	4400
1, R=i-Bu. R_1-R_3=H	630	4200
2	571	4400
3	616	4600
4	580	4900
5 (Ar=$C_6H_4CH_3$-*p*)	560	7000
7	614	4700

The data on the quantum yields for the photocoloration reaction (determined with the use of "Aberochrome™ 540" actinometer) of the type **1a** compounds under excitation at 365 nm by the light of high-pressure Hg lamp and the lifetimes of the photoisomers **1b** are given in Table 2. A peculiar feature of the photochromic behavior of perimidinecyclohexadienones and their structural analogues is extremely slow thermal bleaching of colored quinoneimine photoisomers **1b**. Further retardation of thermal fading of **1b** is accomplished when strong bases, e.g. triethylamine are added to their solutions. [8]

TABLE 2. Quantum yields (Φ, mole · $einstein^{-1}$) of the photocoloration reaction **1a**→ **1b** (R_1-R_3=H) and lifetimes (τ_{24}, hours) of the photoisomers **1b**.

R	Octane		Acetonitrile		Polystyrene	
	Φ	τ_{24}	Φ	τ_{24}	Φ	τ_{24}
Me	0.24	0.19	0.06	0.10	0.12	1.9
Et	0.42	0.47	0.06	0.25	0.19	8.9
Pr	0.38	0.82	0.05	0.63	0.13	9.3
CH_2Ph	0.26	34.5	0.06	28.2	0.08	36.2

The compounds **1-5** exhibit photochromism not only in solution, but also in polymeric (polystyrene, PMMA) films and in thin solid vacuum-deposited films. The latter were deposited on fused quartz or KBr substrates by evaporation of perimidinespirocyclohexadienones and their analogues under the pressure of 10^{-5} Torr at 250-400 °C with the rate of 3-30 Å/s. When exposed to UV-light, they showed thermally reversible spectral changes similar to those portrayed by Figure 1. Interestingly, that in solid polystyrene films, the back reaction of conversion of the photocolored isomer to its initial spirocyclic form can be achieved only through irradiation at the λ_{max} of the colored isomer. Therefore, in polystyrene the compounds **1** work as optically switchable triggers.

THERMOCHROMISM

Upon dissolution of spirocyclic compounds **1** - **5** in nonpolar solvents, e. g. hydrocarbons or CCl_4, an equilibrium is gradually established with the quinoneimine type **1b** isomeric forms, whose appearance is detected by the characteristic long-wavelength absorption bands (Table 1). Position of the equilibrium between type **1a** and **1b** forms depends strongly on the origin of the solvent (proton donor and polar solvents shift the equilibrium to spirocyclic structures) and temperature of the solution. The slowness of the interconversion of the isomers is determined mostly by inclusion of the Z - E configurational isomerization step (Scheme 1), that is associated with the high-energy barrier processes of internal rotation about the $C{=}N^+$ bond in **1c** or planar inversion of the dicoordinate nitrogen atom in the quinoneimines **1b**. The time during which the thermal equilibrium is established is particularly long for the type **5** quinazoline compounds. Thermodynamic and activation parameters of thermal equilibria of a number of perimidinespirocyclohexadienones have been determined by use of dynamic ^{1}H NMR spectroscopy technique. Table 3 contains the data obtained for some of these compounds.

TABLE 3. Equilibrium constants and free energy barriers for the interconversion of spirocyclic (type **1a**) and quinoneimine (type **1b**) forms of compounds **5** (Ar = H).

Compound	K_{293}=[quinoneimine/spirocycl]	$\Delta G^{\#}$, kcal/mol
$R_1 = R_2 = H$	0.37	22.5 (423K)
$R_1 = H$, $R_2 = Me$	0.64	24.0 (453K)
$R_1 = Me$, $R_2 = H$	0.06	-

PHOTOCHROMIC PROPERTIES OF *bis*-SPIROCYCLIC DERIVATIVES

By heating **7** with an equimolar amount of 2,6-di-*tert*-butylcyclo-hexadienone or by coupling 5,6-diaminoacenaphthene with this quinone, taken in molar ratio 2:1

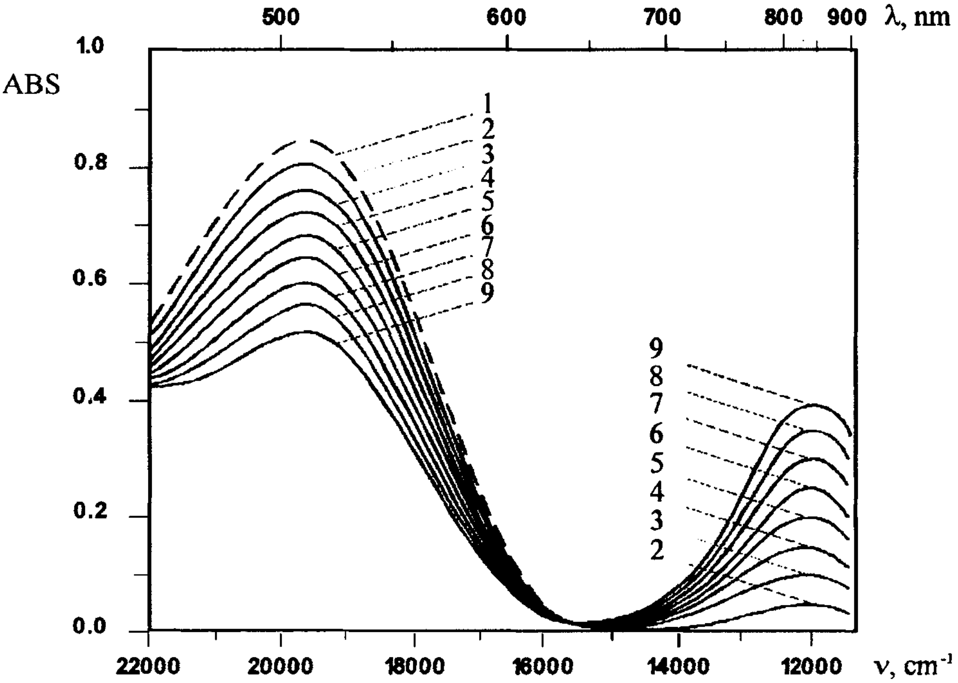
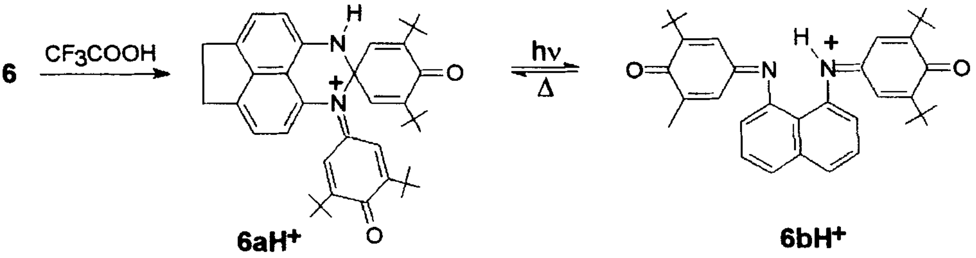


Figure 2. Changes in the absorption spectrum of **6aH**$^+$ under irradiation of its toluene solution (c=$9 \cdot 10^{-5}$ M, 16μL of CF_3COOH is added to 1mL of the solution) under irradiation with filtered light of a Hg lamp (365 nm): 1 - before irradiation, 2-9 - after irradiation for correspondingly 30, 90, 210, 450, 930, 1890, 3810 and 7410 s.

with respect to diamine, at 120 °C for 5 hours, 6,7-*bis*-[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 6 has been obtained.[4]

Irradiation of a toluene solution of 6 with the light in its λ_{max} (535 nm) results in a reversible photocoloration with the formation of the colored bis-quinoneimine isomer (λ_{max} = 665 nm). Photochromic transformation is also characteristic of a protonated form of the compound 6. The photochemical reaction described by Scheme 2 is thermally reversible. Its spectral parameters are illustrated by Fig. 2.



Scheme 2

ACKNOWLEDGEMENT

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REFERENCES

1. V. N. Komissarov, V.A. Kharlanov, L. Yu. Ukhin, and V. I. Minkin, Doklady Akad. Nauk SSSR, 301, 902 (1988).
2. S. M. Aldoshin, M. A. Novozhilova, L. O. Atovmyan, V. N. Komissarov, V.A. Kharlanov, L. Yu. Ukhin, and V. I. Minkin, Izv. Akad. Nauk SSSR (ser. khim.), 1991, 702.
3. V. N. Komissarov, V. N. Gruzdeva, V. A. Kharlanov, V. A. Kogan, and V. I. Minkin, Zh. Org. Khim., 29, 2030 (1993).
4. A. V. Metelitsa, V. N. Komissarov, M. I. Knyazhansky, and V. I. Minkin, Mol. Cryst. Liq. Cryst., this issue.
5. S. M. Aldoshin, M. A. Novozhilova, L. O. Atovmyan, V. N. Komissarov, L. Yu. Ukhin, and V. A. Kharlanov, Izv. Akad. Nauk SSSR (ser. khim.), 1991. 1802.
6. P. Maslak, A. Chopra, C. R. Moylan, R. Wortmann, S. Lebus, A. R. Rheingold, and G. P. A. Yap, J. Am. Chem. Soc., 118, 1471 (1996).
7. J. Fabian, H. Nakazumi, and M. Matsuoka, Chem. Rev., 92, 1197 (1992).
8. V. A. Kharlanov, M. I. Knyazhansky, and V. E. Kuznetsov, Zh. Org. Khim., 28, 1093 (1992).