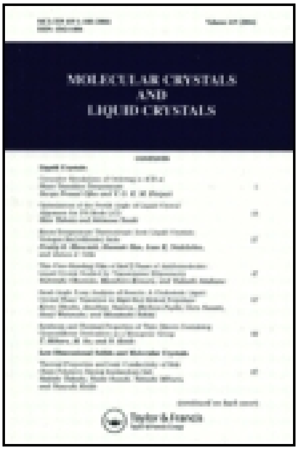

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Novel Fatigue-Resistant Spirooxazines

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NOVEL FATIGUE-RESISTANT SPIROOXAZINES

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Abstract Novel photochromic fatigue-resistant spirooxazines of the phenantrene and phenantroline series were synthesized and studied in solutions and PMMA films. The efficiency of photocoloration (η=0,36-0,95) is close to that of 6-NO$_2$-BIPS (η=1). Kinetics of the dark bleaching is of nonexponential type with $\tau_{1/2}$=2-7 s and 18-32 s (T=298 K) in solutions and PMMA respectively. The number of coloring-bleaching cycles n=210-1320 (PMMA) substantially overcomes that of 6-NO$_2$-BIPS (n=11).

INTRODUCTION

Spirooxazines are well-known as fatigue-resistant compounds[1]. To the effect of widening the range of objects of this class we have synthesized and studied new spirooxazines of phenanthrene (I)-(III) and phenanthroline (IV)-(VI) series.

EXPERIMENTAL

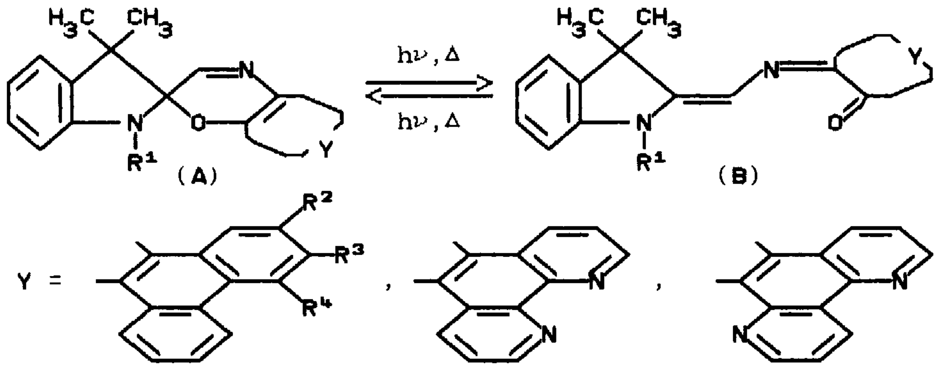
Absorption spectra were detected on a "Specord M 40" spectrophotometer (Germany), Photochemical reactions was initiated by irradiation with high pressure Hg-lamp (DRSH-250) and glass filters were employed. Kinetics of photocoloration and dark thermal bleaching in PMMA films was studied using "Hitachi Perkin-Elmer 139" spectrophotometer (Japan) adapted for these measurements.

Rate constant of the thermal bleaching is represented by the sum of at least two first order constants $k_B = k_B^1 + k_B^2$, $(k_B^1 \gg k_B^2)$.

Efficiency of photocoloration (η) was determined by the following way. The sum $k_A + k_B$ (where k_A is the rate constant of the direct photoreaction) is equal to the tangent of the slope of the photocoloration curve $D(\lambda^B_{max})/D_{eq}(\lambda^B_{max}) = f(t_{irrad})$ at the initial stage for studied spirooxazines and reference 6-NO_2-BIPS, where $D(\lambda^B_{max})$ and $D_{eq}(\lambda^B_{max})$ are optical densites in the maximum of the photoproduct absorption band at given time and in photostationary state respectively. The value of k_A was determined assuming $k_B = k_B^1$. Therefore, $\eta = k_A/k_A$(6-NO_2-BIPS) under estimated by us and authors[2] condition of photobleaching neglectively low at irradiation by UV light (365 nm). The number of coloring-bleaching cycles (n) in PMMA films was determined on the condition $D^B_{eq}(1)/D^B_{eq}(n) = 2$.

RESULTS AND DISCUSSION

Absorption spectra of the compounds (I)-(VI) contain the long-wavelength bands with maxima in the region of 280 - 370 nm, the vibronic structure appearing as a shoulder at 375-415 nm.



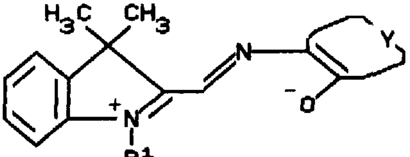
(I) - (III) (IV), (V) (VI)

I $R^1=CH_3$, $R^2=NO_2$, $R^3=R^4=H$; **II** $R^1=CH_3$, $R^2=R^4=H$, $R^3=NO_2$; **III** $R^1=CH_3$, $R^2=R^3=H, R^4=NO_2$; **IV** $R^1=CH_3$; **V** $R^1=C_3H_7$; **VI** $R^1=CH_3$

Whereas the position of the long-wavelength absorption bands is not affected by the solvent polarity, it strongly influences the vibronic structure of these bands. From comparison with the electron absorption spectra of spironaphtooxazines[1] it follows that the long-wavelength absorption band in (I)-(VI) are redshifted ($\Delta\lambda$=20-40 nm).

All the spirooxazines (I)-(VI) display photochromic properties due to formation upon irradiation of the merocyanine isomers absorbing in the region of 570-625 nm both in solutions and polimeric films. Batochromic shift of the long-wavelength absorption bands of the colored form is observed upon increase of solvent polarity.

After interruption of radiation, dark bleaching is observed as a result of the thermal recyclization $(B)\rightarrow(A)$ with decay time $\tau_{1/2}$= 1,8-6,6 s at 295K in solutions (hexane, isopropanol). With increase of solvent polarity, the decay time of compounds (II), (VI) grows in accordance with substantial contribution of the zwitterionic resonance forms (IIC), (IID), (VIC).



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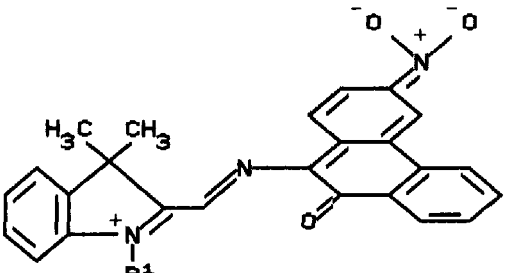

(D)

The efficiencies of the photocoloration of all spirooxazines under study are comparable to that of the reference 6-NO_2-BIPS (η=0,36-0,95). In PMMA films the highest efficiency is exhibited by spirooxazines (II) (0,95) and (VI) (0,74).

Kinetics of dark thermobleaching processes having decay time $\tau_{1/2}$=30-70 s in PMMA (T=295 K) is nonexponential and can be described by at least two exponents with k_B^1=(2,8-3,5)$10^{-2}s^{-1}$ and k_B^2=(2,4-2,9)$10^{-3}s^{-1}$.

The number of coloring-bleaching cycles for the compounds (I)-(VI) in PMMA is in the range of n=210-1320 exceeding that of 6-NO_2-BIPS (n=11) by one or two order of magnitude. The spirooxazines (II) (n=490) and (VI) (n=210) are characterized by the lowest fatigue-resistance. As it is pointed above the zwitterionic structures can play essential role in forming of the colored product for the compounds (II) and (VI) Therefore the irreversible reactions leading to relatively high degradation of the latter may be associated with the zwitterionic character of the structure of the photocolored form for which high reactivity is expected[1].

CONCLUSIONS

Studied spirooxazines of the phenanthrene and phenanthroline series are novel fatigue-resistant photochromic compounds having high efficiency of photocoloration comparable to that of the reference compound 6-NO_2-BIPS. Unlicke of the latter, spirooxazines under study exibit low efficience of photodegradation. Efficiency of photocoloration, bathochromic shifts and decay time in polar solvents as well as the efficiency of photodegradation increase strongly by growth of contribution of the zwitterion resonance form in the colored structure.

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