

# Paper: Thermal Irreversible Organic Photochromes for Imaging Systems

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## Abstract

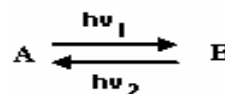
Development of the novel imaging systems requires application of new recording media in particular photochromic materials which provide the fast and reversible write-erasure of information in real time under laser irradiation. The thermal irreversible photochromic recording media providing unlimited life-time of recorded information are of prime interest for information technologies. These materials exhibit reversible transformation between two spectrally different forms under irradiation only. This paper is devoted to the analysis of own results in the study of photochromic and functional properties for more 100 synthesized photochromic compounds from three classes namely dihetarylethenes, fulgimides and phenoxy-derivatives of quinones. The dependences between properties and the compound structure have been revealed. The best photochromic compounds were used for preparation of photochromic polymer recording media. It was shown that readout of information may achieve by using a photoinduced change of optical density, fluorescence and refraction index. The received results demonstrate that the developed photochromic recording media may be used for increasing information capacity of optical disks for working bitwise and frequency-selective optical memory, photocontrolled devices for page forming and frequency switching, photographic masking, et al.

## Introduction

Photochromic substances and systems based on them reversibility changing own properties (transmission, optical density, luminescence, refractive index, at al.) under activating irradiation are called attention in the connection of the possibilities of their practical using.<sup>1-4</sup>

At the last time, the special interest due to the progress of laser technique takes on the photochromic materials as the recording media for devices of writing, storage and processing optical information. Urgency of this problem raised steeply as a result of the vigorous development of information technologies because of fast increasing volume of information and necessity of its using for the advancement of the society production forces..

The possibility for the decision of this problem was found possible merely after appearance of the thermal irreversible photochromic compounds<sup>5</sup> which unlike the majority of the well known photochromic compounds are characterized by the mutual transformations between two forms (A and B) under irradiation only:

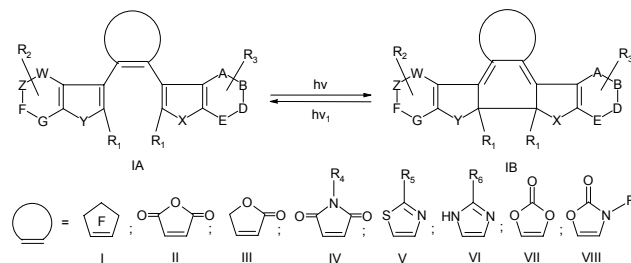


These compounds are not numerous and restricted to certain chemical classes of diarylethenes, fulgides and phenoxy-derivatives of quinines. Their properties and application in information technologies are discussed below.

## Photochromic Compounds and Their Properties

### Diarylethenes

Photochromism of diarylethenes (DAE) includes reversible photocyclization of the open form IA absorbing UV light to the cyclic form IB absorbing visible irradiation:



The synthesis and properties of photochromic compounds from this class are analyzed many times before.<sup>6-9</sup>

The comparative study of the spectral and kinetic characteristics for photochromic transformations of a number new thienyl - containing dihetarylethenes with the different five-member cyclic bridges (I-VIII) has been carried out by us.

It was found that all compounds are characterized by high thermal stability of both forms.

The spectral characteristics of studied dihetarylethenes in toluene depends on the nature of the bridges and the substituents  $R_1$ - $R_3$  (Fig. 1).

Open forms of all thienyl derivatives from I group absorb in the 285-320 nm range. The positions of the absorption maximum don't depend on the molecular structure practically. Compounds without substituents are characterized by maximum of the absorption bands for the cyclic B form at 535-540 nm. Introduction of the electron-acceptor groups in the thienyl cycles leads to the bathochromic

shift of the absorption maxima to 580-625 nm. The positions of these bands depend on a number and locations of carbonyl groups. The change of the electron-acceptor groups by electron-donor ones produces the hypsochromic spectral shift has high photocoloration efficiency. The volume substitutes decrease the value of photoinduced optical density. Compounds without carbonyl-groups are characterized by low photodegradation. Open forms of the benzothienyl derivatives have the absorption bands in more long-wave range as compared with the thienyl derivatives. Influence of the substituent nature is the same as for thienyl diarylethenes. The majority of compounds of this type are characterized by the acceptable value of photoinduced optical density.

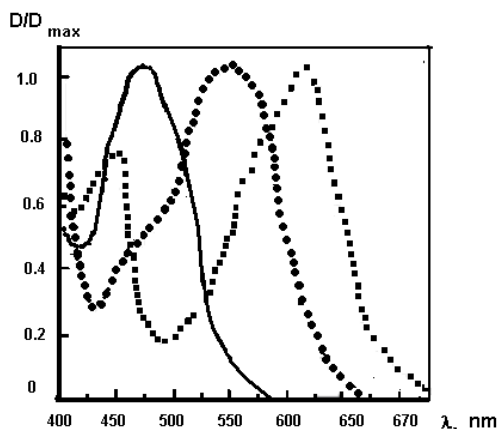


Figure 1. Absorption spectra of the cyclic forms for several dihetarylethenes of the different structure in toluene

The certain compounds from the I group manifest photoinduced fluorescence (Fig. 2).

The absorption maximum for the derivatives of maleic anhydride II may be changed from 510 up to 625 nm according to the nature of the R substituent. The photodegradation process depends critically on the structure the thienyl fragment.

Spectral and kinetic characteristics for lactones of the III group depend on the structure of the substituents in the bridge and thienyl fragments. Usually the compounds are characterized by the short wave absorption band of the cyclic form with the maximum at 515 nm. Introduction of the carbonyl group into the thienyl fragment leads to increasing light-sensitivity and decreasing fatigue. The electron-donor substituents in the bridge fragment induce the bathochromic spectral shift of the absorption band for the open A and cyclic B forms and, as a rule, decreasing photodegradation efficiency. The nature of the substituent into a phenyl group has the minor effect on the spectral – kinetic characteristics. Introduction of amino – groups into the bridge fragment leads to the fast photodegradation of the lactone derivatives.

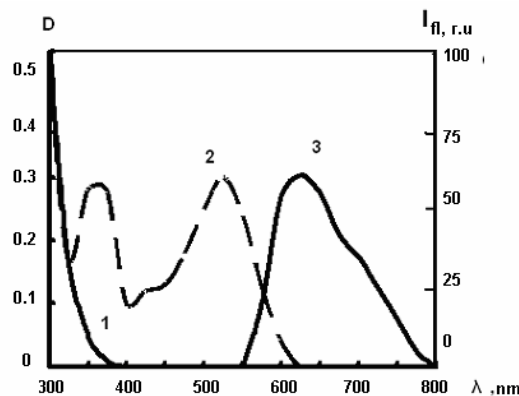


Figure 2. Absorption spectra (1,2) and fluorescence of diarylethene from the I group in toluene before (1) and after (2,3) UV irradiation

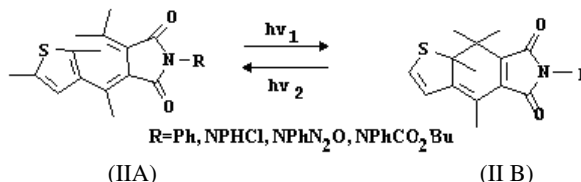
The maleimide derivatives from the IV group exhibit two absorption bands of the cyclic form at  $\lambda_{max}=420$  and  $595$  nm. Increasing electron-donor capacity of the substituents in the bridge fragment increases the light-sensitivity of the photochromic system. The certain compounds from this group have no photochromic transformations because of the structure of the substituents.

The most short – wavelength absorption maxima of the B form are observed for the derivatives of azoles from the V and VI groups ( $\lambda_{max}<520$  nm) and cyclic ethers from the VII and VIII groups. The compounds from the VI group are characterized by fast photodegradation. Introduction electron-donor substituents into molecules from the VII group shifts the absorption maximum of the cyclic form to the long – wave spectral region as compared with unsubstituted compound. The electron-acceptor groups lead to the loss of the photochromic properties. The same effect is observed for the photochromic compounds from the VIII group. The benzothienyl derivative from the VIII group is characterized by the most light-sensitivity as well as the rate constants for photocoloration and photobleaching processes.

The relative analysis of received results shows that the best kinetic characteristics for photocyclization and potorecyclization processes as well as a fatigue were measured for the derivatives of perfluorocyclopentene I, maleic anhydride II and maleimide IV. The measured kinetic and spectral characteristics may be controlled by changing the bridge structure and nature of the substituents R-R<sub>3</sub>.

### Fulgides and Fulgimides

These photochromic compounds manifest the same reversible photocyclization between IIA and IIB forms.<sup>10,11</sup>



We studied the several new thienyl - containing fulgimides with the different substituents R.

Absorption spectra of the open form II A of these compounds exhibit absorption band in the field of 290-340 nm (Fig.3). Maximum of the absorption band for the cyclic form II B is arranged at 520-540 nm. The position of this band depends on the substituent nature. The efficiency of the photocoloration process is reduced after introduction the substituent R undergoing cis-trans photoisomerization.

Much like the dihetarylethenes, fulgimides are characterized by high thermal and photochemical stability of both forms.

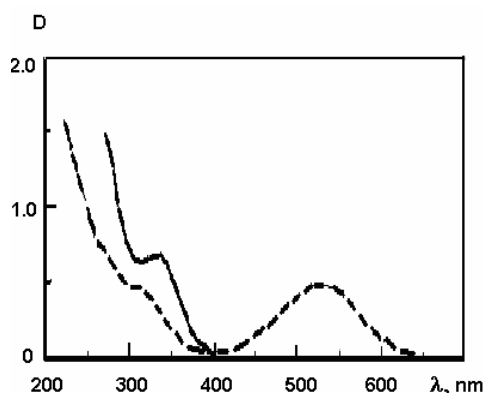
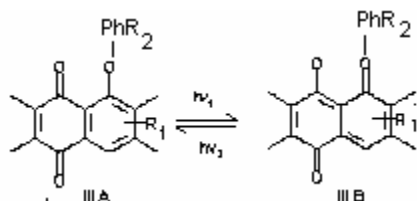


Figure 3. Absorption spectra of the open form II A (solid curve) and photoinduced form II B (dotted curve) for fulgimide with R=NPHCO<sub>2</sub>Bu in toluene

### Quinones

Photochromism of certain quinones namely phenoxy-derivatives naphthacenequinone, penthacenequinone, phthaloylpyrene ,et.al. is caused by reversible photoisomerization of the para - quinone structure III A to the ana - quinone structure IIIB as a result of fast photoinduced and very low thermal intramolecular substitution according to associative mechanism.<sup>12</sup>



Analysis of the spectral characteristics of photochromic quinones showed that the absorption bands of both form strongly depend on the compound structure (Fig. 4).

The substituents in the quinone nucleus most strongly affected the spectral characteristics of the photoinduced form.

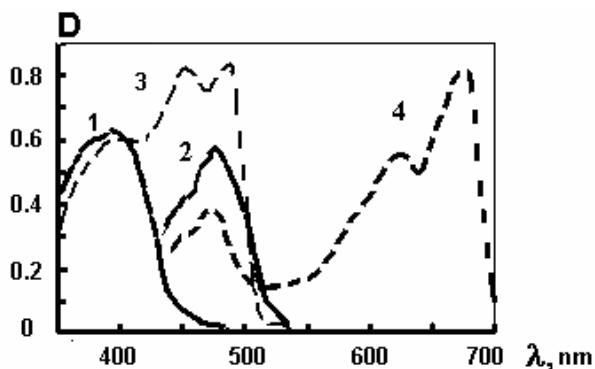


Figure 4. Absorption bands of the para- (1,2) and ana-(3,4) forms of phenoxy-derivatives of naphthacenequinone (1,3) and phthaloylpyrene (2,4) in toluene

The study of the efficiency of quinone photochromism showed that the introduction of the electron- donor substituents in the quinone cycle as well as the bulky substituents in the migratory phenoxy - group reduces the efficiency of the photoinduced rearrangement. At the same time, the introduction of electron-donor substituents in the migratory phenoxy - group is favorable for the photochromic transformations. On the contrary, electron-acceptor substituents decrease the photochromism efficiency.

For the several compounds of this type was found fluorescence for one from two forms.

Thermally irreversible photochromic quinones are characterized by very high stability to photodegradation.

Thus, as result of our study it was shown that the new photochromic compounds from the thienyl-containing diarylethenes and fulgimides as well as phenoxy-derivatives of photochromic quinones may be characterized by the different spectral characteristics of both forms depending on the molecular structure, the acceptable efficiency of photochromic transformations, high stability to thermal relaxation and photodegradation. It was found that one from two forms of certain photochromic compounds may exhibit fluorescence. These properties open the perspectives of their application in the information technologies.

### Application of Thermally Irreversible Photochromic Compounds

The analysis of the properties for the investigated photochromic compounds from above discussed classes shows that the main potential field of their applications is the light-sensitive polymer media for recording, multiplying, storing and processing optical information.

It was established that thermal irreversible photochromic compounds can meet the concrete requirements for preparation recording media for three-dimension two-photon bitwise working optical memory namely large cross-section of light absorption; high efficiency of photochemical transformations; thermal stability of forms A and B; high stability of both forms to the irreversible phototransformations; nondestructive and efficient readout of recorded information by the certain method (fluorescent,

refractive, reflective, polarization et al.). The prepared samples of polymer recording media based on the above mentioned photochromic compounds were tested with the positive results. In principle, the multilayer optical disks using photochromic polymer coatings may provide information density up to 1 TBit/cm<sup>3</sup>.

From our experiments follows that thermally irreversible photochromic compounds may be used to advantage in holographic photopolymerizable recording media as the photosensitizers. Application of photochromic compounds provides writing deep holograms in the thick photopolymerizable recording media and, consequently, three-dimensional holographic archive optical memory on the optical disks with the high information capacity (10-100 TBites).

Application of the thermal irreversible photochromic compounds with different spectral characteristics of the form absorbing in the visible spectral range opens perspectives for making the bitwise and holographic frequency-selected volume four-dimensional optical memory with the super high information capacity.

Polymer films based on the thermal irreversible photochromic compounds may be used as recording media into the intermediate carriers of optical information, for example, in holographic optical memory devices for the formation of the information pages for hologram writing.

These films are suitable for gradation masking of negative images during photoprinting. In this case, the maximum density of the mask should not exceed the value at which the effective gradient of the photochromic film with respect to the photochromic medium becomes equal to unity.

Evident application of the developed photochromic polymer materials is the photocontrolled optical switchers in the different information devices.

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## Author Biographies

*Valery Barachevsky received his Ph. D in Physics from the St.- Petersburg State University, Russia. Now he is Head of Lab of the Photochemistry Center of the Russian Academy of Sciences. His work has primarily focused on the development and application different light-sensitive systems and materials, including of non-silver organic light-sensitive media for information technologies with use of bit-by-bit and holographic methods. He is a member of the SPIE and the editorial staff of the journal "Optical Memory & Neural Networks" (USA). He is author of 535 publications including 70 Russian and European patents.*

*Mikhail Krayushkin is Head of Lab of Heterocyclic Compounds of N.D.Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, D.Sc., Professor. Area of his research interests includes chemistry of azoles and thiophene, condensed aromatic heterocycles, reactions of 1,3-dipolar cycloaddition, high pressure (10-14kbar) chemistry. Last years he focuses on synthesis of photochromic compounds on the basis of thiophene (diarylethenes, fulgides) as perspective organic materials for optical data storage. He is a member of Council on Organic Synthesis of Russian Academy of Sciences, author of above 350 publications including 50 Russian and European patents.*