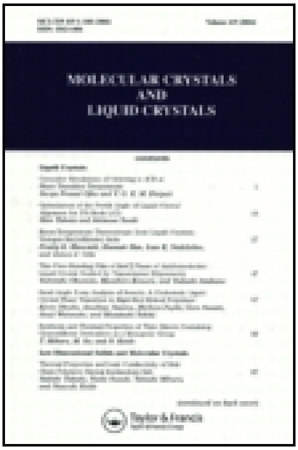

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photochromism of Aryloxyquinones

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To cite this article: Valery A. Barachevsky (1994): Photochromism of Aryloxyquinones, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 95-102

To link to this article: http://dx.doi.org/10.1080/10587259408037794

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 95–102
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Printed in the United States of America

PHOTOCHROMISM OF ARYLOXYQUINONES

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Abstract. The photochromic transformation mechanism, the dependence of properties upon the structure of photochromic compounds of aryloxyquinone class as well as their possibility of application are performed in the present review.

INTRODUCTION

Intensive development of investigation into photochromism of different systems being continued up to the present time is based on the possibility of practical use of this phenomenon[1-4]. Nontheless, the problem of creation of photochromic recording media (PRM) for operative optical memory[5] with necessary characteristics are far from solving. The complexity in solving of this problem is connected, in the first place, with elaboration of the materials being characterized by high recurrence of photochromic transformations, thermal stability of photoinduced form (PF), coincidence of spectral characteristics of initial (IF) and photoinduced (PF) forms with radiation wave length of small overall dimension semiconductor lasers, the most of which, unfortunately, radiates in IR spectral region.

PRM creation satisfying to the pointed demands would allow to realize the operative memory with the maximum resolution unlike the existing reversible light sensitive materials (magneto-optical media, materials on the base of phase transitions)

In the present paper, the analytical review of results under investigation of aryloxyquinones (AOQ)[3,6,7] photochromism and the possibilities for their application for creation of operative optical memory are performed.

MECHANISM OF PHOTOCHROMIC TRANSFORMATIONS OF ARYLOXYQUINONES

Photochromic compounds of this class was revealed during the synthesis process and in course of study of properties of anthraquinone derivaties, intended for use as dyes[8,9]. It is appeared that 1-phenoxyanthraquinone (I) reversibly change its color in crystalline state and in solution (Fig. 1)[8].

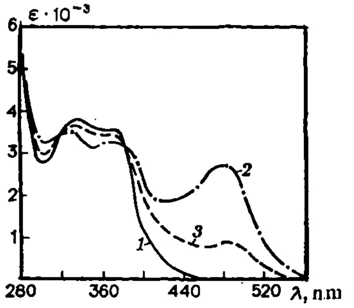


Figure 1. Absorption spectra of compound I in benzene before (1), after UV (2) and VIS (3) excitation.

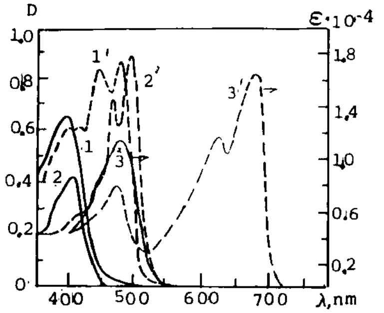
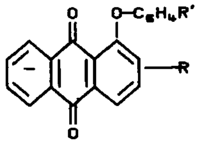
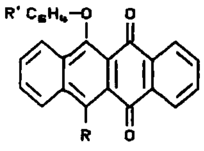


Figure 2. Absorption spectra of initial (1–3) and photoinduced (1'–3') forms for AOQ II(1,1'), III(2,2'), IV(3,3')

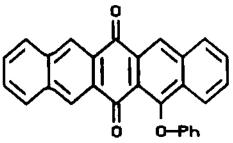
I



II



III



IV

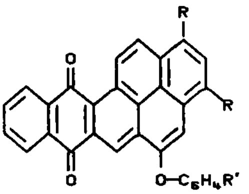


TABLE 1. Spectral data of unsubstituted aryloxyquinones.

Parameter, benzene	I	II	III	IV
IF, λ_{max}, nm (lg ε)	364 (3.70)	400 (3.76)	404 (3.68)	476
PF, λ_{max}, nm (lg ε)	480	480 (4.23)	461, 490	604, 652

The further synthetic investigations leaded to production of a number of compounds from aryloxyquinones (AOQ) class, including aryloxyanthraquinoneone (AOAQ)[8-15]; aryloxynaphthacenequinone (AOHQ)[16-19], phenoxypentacenequinone (PPQ)[16], aryloxynaphthophthacenequinone (AONNQ)[20].

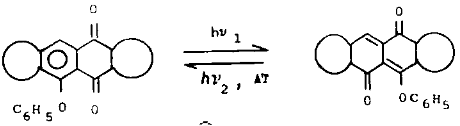
The structure formula and absorption spectra of IP and PF of typical representatives of these compounds are given in Table 1 and Fig. 2, accordingly.

Photochromic transformations of peri-alkyl, peri-acyloxy-p-anthraquinones are discussed earlier in detail[7]. Nowadays, they are not of practical use, that is why they are only slighly mentioned in the present review.

It is appeared that the photochromic transformation mechanism of AOQ depends upon the structure of initial compounds.

Phenoxynaphthacenequinones and Others Unsubstituted Aryloxyquinones.

Experimental data obtained allowed to represent now the general accepted scheme of photochromic conversions of unsubstituted AOQ:



It has been proposed[6] that the reversible photoisomerization is carried out as photo- and thermoinduced intramolecular substitution according the associative mechanism through spirane σ-complex.

The results obtained[22] gave evidence that contrary to the ana-quinone form, T-state arising in course of photoexitation of IF II have not the para-quinone form configuration and, obviously, are the T-state of transient spirane form mentioned above.

Photoexitation of IF leads to molecule isomerization only through T-state of transient spirane form. This is, evidently, due to the high rate of energy conversion of S^*-state[6,23]. Quenching of this T-state and isomerization in T-state is due to one and the same process. As a result, IF as well as PF II forms are produced.

Substituted Phenoxyanthraquinones

Introducing of a number of additional substitutes in phenoxyanthraqiononones leads not only to photoinduced migration of phenyl but also of the other structured fragments[14].

The proposed photochromic conversion mechanism of this type compounds[7] is comprised from photochemical migration step of the phenyl group and the consequent step of thermal migration of the acetyl group for 1-phenoxy-4-acetoxy-9,10-anthraquiononone, or of the proton of hydroxyl group for 1-phenoxy-4-hydroxy-9,10-anthraquinone. These representations have been developed as a result of investigation of these systems using laser photolysis method[15].

As a result of realization of the photochromic conversion mechanism, the more thermal and photochemical stable PF is generated. Unfortunately, its spectral chracterictics almost completely coincide with ones of IF, that exludes the possibility of practical utilization of these photochromic compounds.

INVESTIGATION OF INTERCONNECTION BETWEEN STRUCTURE AND PROPERTIES OF PHOTOCHROMIC ARYLOXYQUINONES

Aryloxyanthraquinones. This subclass of photochromic compounds is the most studied ones.

Among the compounds with mono- and dialkyl-amino-substituites, nonphotochromic ones are revealed, including the compounds, undergoing the unreversible photochemucal transformations[6,7]. Compounds from 1-phenoxy-2- acetylamino-5,12 -anthraquinones are photochromic ones without exeption. The analogous results is obtained for synthesized hydroxy- methoxy-, acetyloxy-, and oxyphenyl-derivatives manifasting photochromism, true, with the exception of 1-phenoxy-8-hydroxy-5,12- anthraquinone[6,7].

Introducing of electron-donor substitutes into position situated near oxygen, leads to longhwave shift of absorbtion bands of IF as well as PF.

Realization of unreversible photoconversions and, as a result of this, limited recurrence of photochromic transformations of AOAQ are explained by the high reactive ability of derivatives of 1,10-anthraquinone generated under action of light due to the high effective interaction between molecules in position 9 and nucleophils[7]. Just for this reason during long time one failed in the synthesis of this type compounds[24]. Derivatives synthesized at last were characterized by absorption bands with maxima over the range 484-491 nm[25]. They coincides with spectral characteristics of PF for photochromic compounds of corresponding structure.

It was shown[26] that, in the case of PF of 9-aryloxy-1,10- anthraquinones, the nature of substitutes in anthraquinone structures influences on its stability. Electron-accepter substitutes (nitro- group) increase, and electron-donor substitutes (amino- and methoxy- groups) decrease the stability of photoinduced form.

In the case of photochromic derivatives of AOAQ, 'high values of rate constants of thermal conversation of PF into IF are typical. The reaction of thermal bleaching, in the best case, is conducted during several minutes[6,7].

Aryloxynaphthacenequinones. The photochromic transformations are not observed for 6-amino-, 6-phenylamino-,6-hydroxy- and 6-acetoxy-11-phenoxy-5,12-naphthacenoquinones[17]. The absence of photochromism in two last compounds can be connected with coincidence of spectral characteristics of IF and PF[7].

The nature of substitutes in phenoxyl group practically influences weakly on the position of absorption bands of both forms of photochromic compounds, as it is for the case of AOAQ[17]. At the same time, considerable influence on the spectral characteristics have the substitutes in naphthacenic structure [18]. Maximum bathochromic shift of absorption bands is observed for aminosubstituted derivatives of phenoxynaphthacenoquinone (PNQ). Electron - acceptor substitutes have less considarable impact.

Quantum yields of photocolouring under action of UV radiation (366 nm), as a rule, exceed the quantum yields of photobleaching[17,27]. For II they are equal to 0.30 and 0.05, correspondingly[28]. It is of principal importance that at transfer from liquid to polymer solution the quantum yields are not changed practically.

The distinctive feature of AONQ photochromism is a long life time of PF. For the compound in toluene, outlined above, at 25°C in the darkness the life time of PF is equal to a many years one ($k_T = 10^{-8}s^{-1}$)[29]. In addition, PF can be transformed into the other compound as a result of chemical interaction with nucleophyls, for example, with amines[17].

Phenoxypentacenequinone, just 5-phenoxy-6,13-pentacenquinone, is characterized by spectral characteristics being close to that for II (Fig. 2)[16]. However, the thermal reaction of PF convertion into IF is carried out at higher rate in comparison with the last compound.

Aryloxynaphthonaphthacenequinones. Spectral characteristics of these compounds are distinguished from ones earlier considered by longwave shift of absorption bands of both forms, especially, of PF (Fig. 1, Table 1)[28]. As in the case of AOAQ and AONQ, replacement of substitutes in phenyl groups do not change spectral characteriscics of IF and PF.

INVESTIGATION INTO THE POSSIBILITY FOR REALIZATION OF RECORDING MEDIA ON THE BASE OF ARYLOXYQUINONES

The analysis of synthesized compounds from AOX class shows that due to unusually high thermal stability of PF and relative variety of spectral characteristics of both forms depending upon the structure of the compound, AONQ and AONNQ can represent practical interest for PRM creation. Special investigations showed that these compounds are characterized by high recurrence of reversible photoconversions of para- and ana-quinone forms[6,30].

On the base of II there were created the polymer photochromic materials, in which polymethylmetacrylate and other polymers were used as a matrix[29]. The possibility of their utilization for hologram recording using radiation of helium-cadmium laser (441.6 nm) and nondestroyed reading in the light of helium-neon laser (632.8 nm) is shown[30].

In order to investigate the possibility of realization of operative optical memory on optical disks, the experiments for obtaining the polymolecular layers of AONQ derivatives using Langmuir-Blogett (LB) method were carried out[31].

In LB films based on the compound with the C_9H_{19} group in phenoxyl substitute the effective photochromic transformations under action of activated radiation being absorbed by IF and PF (313 and 500 nm, correspondingly) were observed. Life time of PF was practically unlimited. After 30 cycles of IF and PF mutual transformation, spectral characteristics did not change. Photoproducts of side reactions were not revealed. The availability of isobestical point in the family of spectral-kinetic curves is the additional argument. Light-sensitivity of polymer layers depended upon the method of their production.

CONCLUSION

In connection with the problem of the creation of operative optical memory with high resolution, photochromic AONQ are represented the special interest due to the high recurrence of photochromic transformations, practically nonlimited life time of PF, dependencies of spectral characteristics upon the compound structures.

At the same time, it is necessary to performed the further intense synthetic and photochemical investigations in order to carry out the purposeful synthesis of photochromic compounds of this class taking into account the demands for concrete application.

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