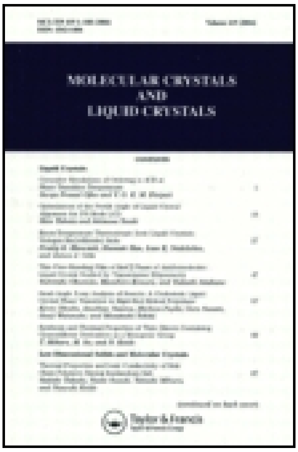

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Photochromism of Quinonfs Experimental and Quantum Chemical Study

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PHOTOCHROMISM OF QUINONES. EXPERIMENTAL AND QUANTUM CHEMICAL STUDY

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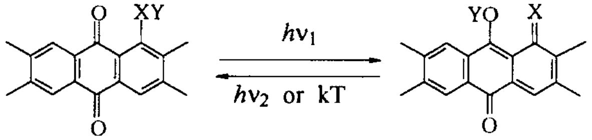
Abstract There are three types of photochromic processes for substituted quinones. They are characterized by photoinduced isomerization of the colorless or yellow para-quinone form to the ana-quinone colored form. Photochemical hydrogen and acyl migration in photochromic 1-alkyl- and 1-acylanthraquinones is the adiabatic process occurring on the triplet potential energy surface. Quantum chemical calculations of the structure of triplet intermediates in the photochromic reactions of phenoxy quinones were performed. It was concluded, that the most preferable mechanism of photochemical phenyl migration is the non-adiabatic process with the formation of the triplet biradical spiro-form. Variation of the lifetime of photoinduced ana-quinones by the orders of magnitude was achieved by the modification of quinone structures.

INTRODUCTION

There are three types of photochromic processes for substituted quinones.[1]



1) $X=CR_1R_2$, Y=H (D); 2) X=O, Y=C(O)R; 3) X=O, Y=Ar

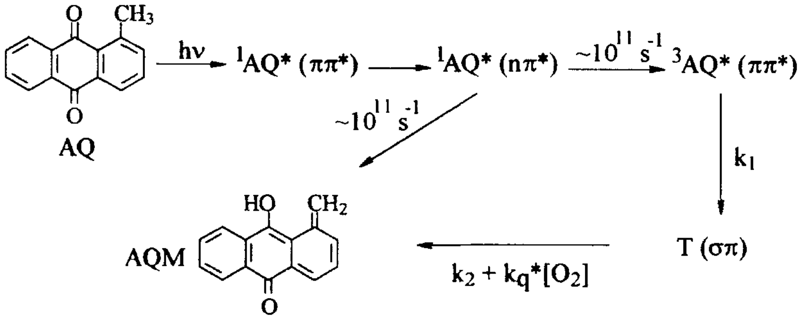
Photochromism of substituted quinones is due to the photoinduced isomerization of either colorless or yellow para-quinone form to the ana-quinone colored form.[1,2,3,4] Photoisomerization of 1-alkyl- and 1-acyloxyanthraquinones is thermally reversible.[1] There is no thermal back reaction in the case of photochromic phenoxy quinones.[1,5] This is very important for the possibility to use phenoxy quinones as materials for both optical and 3D optical memory devices[5].

Photochemical reactions of 1-methyl- and 1-acylanthraquinones were studied in details and the results were published in our previous papers.[1-3] Therefore, these processes will be considered here very briefly. Photochromism of phenoxy quinones was discovered in 1971.[4] Recently, the first results on the mechanistic study of this process were published.[5-9] The different contradictory mechanisms of photochemical phenyl migration were proposed by the authors.[5-9] To choose the most preferable mechanism, we performed the quantum chemical calculations by AM1 method[10], using the modified MNDO85 program[11] The RHF AM1 calculations in half electron approximation[12] were performed for the triplet state intermediates.

MECHANISM OF PHOTOCHEMICAL PROCESSES

1-alkylanthraquinone photolysis

Using the results of nanosecond laser flash photolysis (LFP) set-up we have proposed the adiabatic mechanism of photochemical hydrogen transfer in 1-methyl-anthraquinone.[1,2]



The σπ-biradical structure was proposed for the triplet intermediate. The deepest minimum on the triplet potential energy surface of the product corresponds to this intermediate (Figure 1).

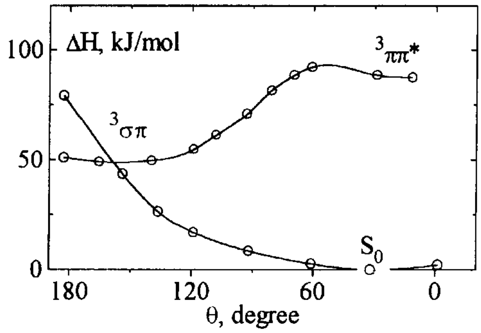
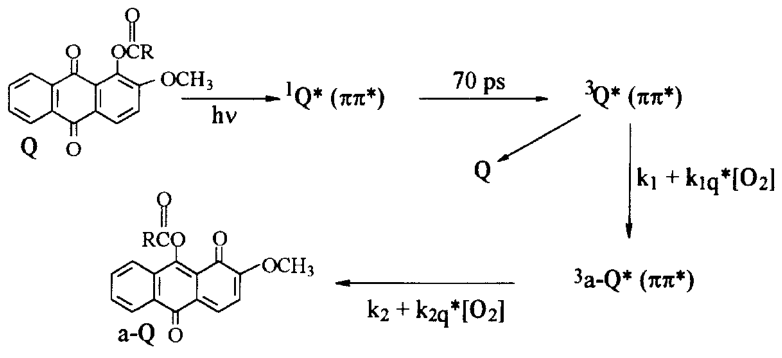


FIGURE 1 Potential energy surfaces for 9-hydroxy-1,10-anthraquinone-1-methide in the ground and triplet state. Reaction co-ordinate is the dihedral angle of hydrogen of OH-group.

Photochemical acyl group migration

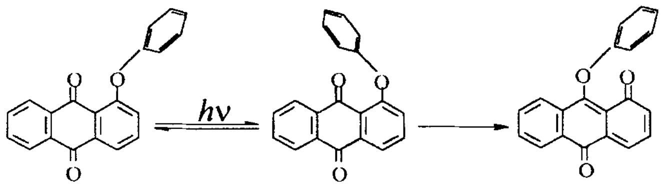
The spectra of three intermediates were detected after the laser excitation of some derivatives of 1-acetoxyanthraquinone.[1,3]



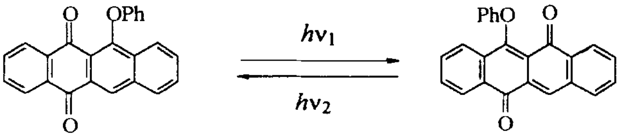
The first short-lived intermediate was assigned to the triplet state of para-quinone, the other two were assigned to the triplet and ground states of the ana-quinone.[1,3] Therefore, the photochemical migration of acyl group is an adiabatic process occurring on the triplet potential energy surface. The process of acyl migration in the triplet excited state is temperature activated, but the activation energy is low (15.9±0.8 and 26.0±1.7 kJ/mol, for $R=OC_2H_5$ and $N(C_2H5)_2$, respectively).

Photochemical phenyl migration.

According to the analysis of spectral data and kinetics of photoproduct decay, Tajima and Inoue[5] proposed very unusual mechanism for 1-phenoxyanthraquinone photochromic reaction. They assumed that primary photochemical stage is the phenyl group rotation around C-O bond.



The first mechanistic study of the photocromic reaction of 6-phenoxy-5,12-naphthacenequinone was performed by Strokach and Barachevskii.[7]



A B

Using a nanosecond LFP set-up they detected[7] the spectrum of one intermediate after excitation of form A and assigned it to the triplet state of spiro-form (^3X). They also detected the spectrum of ^3B after the excitation of form B. It should be noted that the spectra and kinetics of intermediates ^3X and ^3B given in the paper[7] are very similar.

Recently, Dvornikov, Rentzepis et al[5,8] performed the picosecond and nanosecond LFP of quinones A and B. They found that the intermediates detected in the nanosecond LFP of A and B are identical and proposed the adiabatic mechanism of phenyl migration.[5,8]

$$\begin{array}{lcccc} \tau & & \sim 80\text{ ps} & 6\text{ ns} & 6\,\mu\text{s} \\ \mathrm{A} \longrightarrow & \mathrm{A}(S_1) \rightsquigarrow & \mathrm{A}(T_1) \rightsquigarrow & \mathrm{B}(T_1) \rightsquigarrow & \mathrm{B} \\ \lambda_{max} & 380\text{ nm} & 500\text{ nm} & 400,\ 460\text{ nm} & 490\text{ nm} \end{array}$$

This system was studied independently by Born and Wirz[9]. Using the picosecond LFP they detected spectra of three intermediates and assigned them to the singlet and triplet states of the quinone A and to the triplet state of biradicaloid spiro-form (^3X) (non-adiabatic mechanism of phenyl migration).

$$\begin{tikzcd}
A \arrow[r, "\sim 20\ \mathrm{ps}"] & A(S_1) \arrow[r, squiggly, "0.8\ \mathrm{ns}"] & A(T_1) \arrow[r, squiggly, "5\text{-}10\ \mathrm{ns}"] & X(T) \arrow[r, squiggly] \arrow[dr, squiggly] & B \\
& & & & A
\end{tikzcd}$$

It was proposed that ^3B detected in nanosecond LFP of quinone A is the product of two-photon process[9].

Quantum chemical calculations

The mechanism of Tajima and Inoue[5] can be realized only in the case of the double minima potential energy surface for the rotation of phenyl group. Our AM1 calculations show that the potential energy surfaces have only one minimum in the case of 1-phenoxyanthraquinone and 6-phenoxy-5,12-naphthacenequinone (Figure 1).

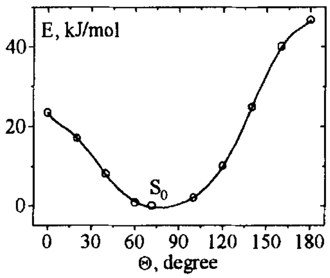


FIGURE 2 Potential energy surface for the ground state of 6-phenoxy-5,12-naphthacenequinone. Reaction co-ordinate is the angle of rotation of phenyl group around CO bond.

Moreover, the back thermal reaction proposed by Tajima and Inoue[5] is absent in the case of 1-phenoxyanthraquinone. The only way of its thermal decay is the reaction with nucleophiles.

We have also performed quantum chemical calculations of energy, geometry and electronic structure of the possible triplet intermediates of phenoxy quionone photolysis. We obtained three minima on the triplet potential energy surface (Figure 3).

fragment (spiropyrans III and IV, V, VII), but is significantly affected by the electron acceptor (II-IV) or electron donor (V-VII) substituents in the 2H-chromene moiety .

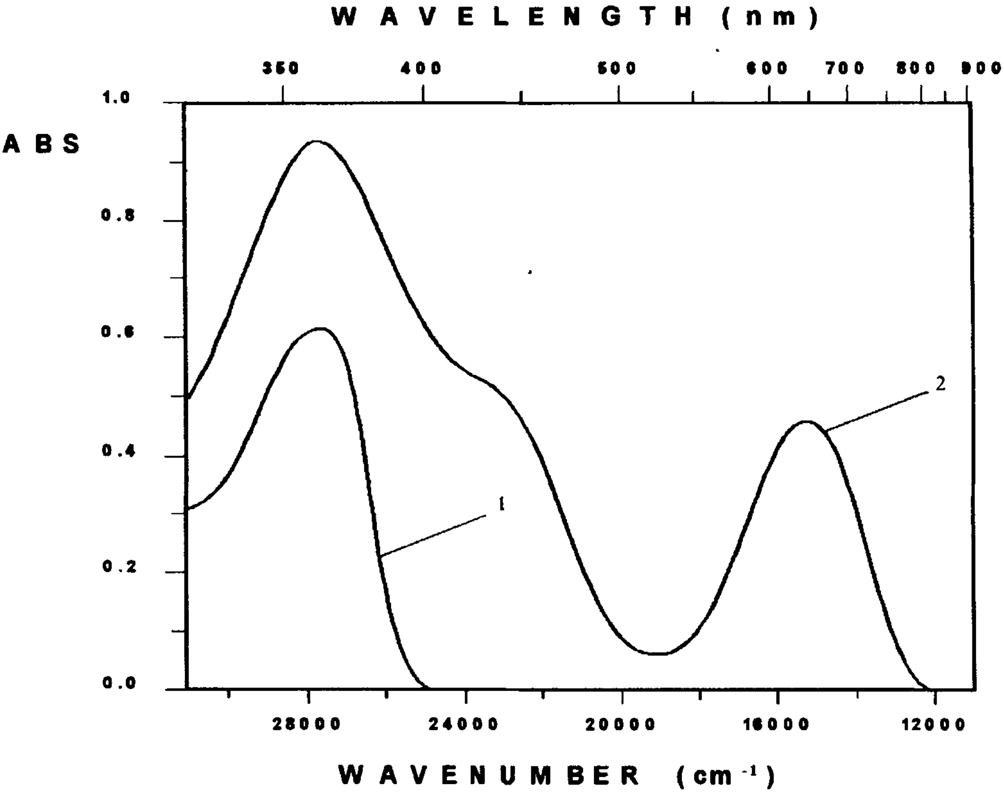


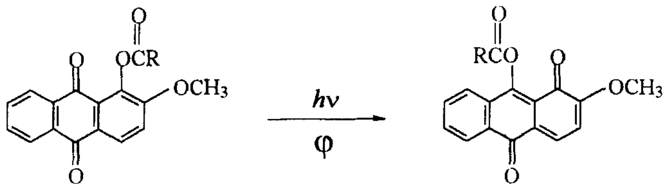
FIGURE 1. Absortion spectra of a vacuum-deposited film of spiropyran III before (1) and after irradiation (365 nm) for 300 s

On the contrary position of the longwave absorption band of the colored merocyanine form B, λ_{max} =584 - 672 nm (Figure 1) having, is affected by introduction of substituents to any of these fragments. With inclusion of an electron acceptor substituent in the 8-position (III) or an electron donor substituent in the 6-position (V,VI) the longwave absorption band of the isomer B is shifted bathochromically, whereas an electron acceptor group in the position 6 (II) exerts an opposite action at the position of this band.

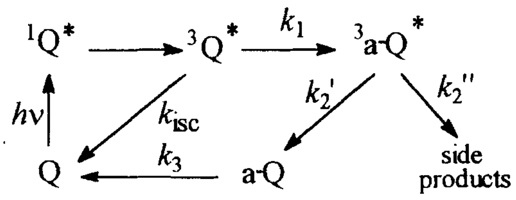
Whereas, the presence of electron acceptor and, in particular, formyl group in positions 6 and /or 8 of a chromene fragment of spirobenzopyranindolines enhances

PHOTOCHEMICAL SIDE REACTIONS

The fatigue of photochromic materials can be due to the existence of either photochemical or thermal side reactions. The thermal side reactions of photochromic quinones will be described in other our articles of this issue. Here we will discuss briefly the side photochemical reaction of 1-acyloxyanthraquinones.



It is seen from Table II, that the diethylamino group in the migrating acyl reduces the quantum yield of photochemical reaction. It was found, that it is due in part to the existence of side photoreaction. In the absence of oxygen the quantum yield of irreversible decomposition is high and equal to 0.25±0.05. The saturation of solution by oxygen results in the significant (68±13 times) decrease of the quantum yield of irreversible decomposition. This is consistent with the assumption that the side reaction occurs mainly in the triplet state of ana-quinone (^{3}a-Q).



Indeed, the quenching by oxygen of both triplets (^{3}Q and ^{3}a-Q) should lead to a very effective decrease in the quantum yield of the side reaction (60±13 times).

TABLE II Quantum yields (φ) of ana-anthraquinones formation

R	CH_3	Ph	OC_2H_5	$N(C_2H_5)_2$
φ	0.85±0.17	0.92±0.18	0.91±0.18	0.10±0.02

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