Review

Photochromism of quinoid compounds: properties of photo-induced ana-quinones

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Abstract

The paper reviews the results of studies on the photochromic transformation mechanisms for three classes of quinone derivatives. Photoisomerization of the para-quinone to the ana-quinone structure by photochemical migration of hydrogen, aryl or acyl groups is common to these processes. Characteristic features of each type of photochromic transformation are considered in detail. The effects of substituent, temperature and solvent on the efficiency of the photochemical and thermal stages of photochromic processes are discussed. Data on the spectra and the nature of reactive excited states of photochromic quinones are generalized. Information on the spectra and chemical properties of photo-induced products of ana-quinone structures (including 1,10-anthraquinones) is classified.

1. Introduction

Photochromism is one of the most interesting and technologically important photochemical processes. Photochromism is a reversible transformation of chemical compounds which proceeds, at least in one direction, under the action of light and is accompanied by the appearance of an absorption, or by a change, in the visible spectrum.

$$A(\lambda_1) \xrightleftharpoons[h\nu_2 \text{ and/or } kT]{h\nu_1} B(\lambda_2)$$
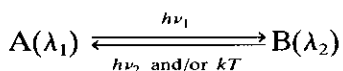
Photochromic transformations of organic compounds have been studied extensively. In 1990, a voluminous monograph was published [1] which contained the most complete review of studies of various photochromic processes, including those important to biology. Studies on photochromism have been carried out in different directions, such as the search for and analysis of new photochromic

compounds [2], detailed investigation of the process mechanisms [3, 4], and the creation of new photochromic materials and processes [5]. The photochromism of different classes of spiropyran has been of greatest interest [1, 4, 5]. Recent years have seen an increasing interest in the photochromic transformations of fulgides [1, 3].

The photochromism of quinoid compounds has received considerably less attention. For instance, the monograph mentioned above [1] gives no examples on the photochromism of quinones. The present review aims to remedy this deficiency.

Three types of photochromic transformation are currently available to quinone derivatives. They are characterized by light-induced isomerization of the para-quinoid to the ana-quinoid structure by photochemical migration of aryl, hydrogen or acyl groups [6–13]

1 X=O, Y=Ph; 2 X=CR₁R₂, Y=H; 3 X=O, Y=–C(O)R

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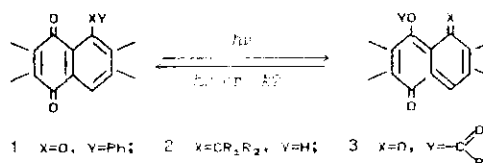
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The bimolecular process was observed only in non-polar aprotic solvents (hexane, toluene), where the rate constant k_{11} turned out to be nearly diffusion controlled [45]. The activation parameters of the rate constant of unimolecular isomerization (k_3) of XX'a in various solvents were determined [45].

Photochromic derivatives of 1-alkylanthraquinone have thus far not found practical use, since image visualization is possible only for frozen matrices. At room temperature, the lifetime of the photo-induced quinone-methides XX'a–i and XXIII'a–e are on the microsecond time scale and, even for compound XXII, it is not more than a few minutes [43–45].

5. Photochromism of peri-acyloxy-para-anthraquinones

In 1982, we discovered a new class of photochromic derivatives of anthraquinone [12, 13]. Irradiation of some 1-acetoxyanthraquinone (XXIV) derivatives and 9-acetoxy-1,4-anthraquinone (XXV) in a glassy matrix at 77 K was found to yield products characterized by an intense visible absorption band (Fig. 2). At 77 K, the photoproducts are stable under long-term irradiation as well as in the dark. The melted samples show the spectra of the initial compounds [12, 13]. The spectra of all the low temperature photoproducts of the XXIV derivatives are similar to the spectra of the corresponding 9-phenoxy-1,10-anthraquinone (I') derivatives (Table 11). Thus, on irradiation, derivatives of XXIV also yield products
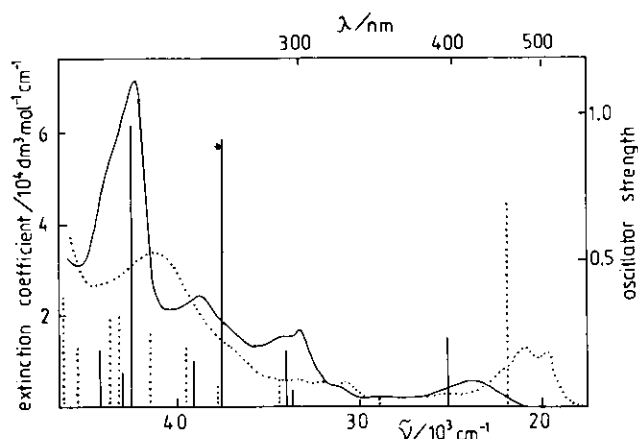

Fig. 2. Electronic absorption spectrum of 9-acetoxy-1,4-anthraquinone (——) and its photolysis product (· · ·) in ethanol at 77 K. Vertical lines show the positions of the band maxima and the oscillator strengths for the transitions in the spectra of 9-acetoxy-1,4-anthraquinone (——) and 4-acetoxy-1,10-anthraquinone (· · ·) as calculated using the PPP (Pariser–Parr–Pople) method.

with the 1,10-anthraquinone (ana-quinone) structure. In addition, experimental absorption spectra of the products are in satisfactory agreement with the calculated spectra of the corresponding 1,10-anthraquinones (Fig. 2) [13]. Hence, the process of photochromic transformation in this case can be described by the schemes
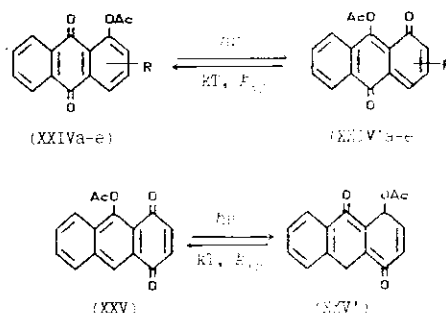
Detailed investigations of the effect of the substituents on the photochemical properties have shown that photochemical migration can take place only in derivatives of XXIV with electron-donor (amino, methoxy group) substituents in the anthraquinone ring and in unsubstituted 9-acetoxy-1,4-anthraquinone (XXV) [13, 47]. The long-term irradiation of unsubstituted XXIV and some of its derivatives at 77 K does not lead to noticeable spectral changes.

To account for the relationship between the reactivity of these compounds and their chemical structure, it was assumed that photochemical migration of the acetyl group occurs adiabatically. The excited $\pi\pi^*$ ($n\pi^*$) state of the initial compound correlates with the $\pi\pi^*$ ($n\pi^*$) state of the reaction product. Energy level diagrams of the initial derivatives of XXIV and the products of their photolysis (ana-quinones) were constructed from experimental absorption spectra and quantum chemical calculations. For hypothetical photoproducts, we used experimental spectral data for the corresponding 9-phenoxy-1,10-anthraquinones. An analysis of the experimental data using energy level correlation diagrams has shown that, for the peri-acetoxy-1,4- and 9,10-anthraquinones studied, there are three possible situations which differ from each other in the type of excited reactive state and relative position of the excited state levels of the initial compound and photoproduct [13, 47].

(1) The lowest excited states (singlet and triplet) of the initial compound are $\pi\pi^*$ in character and are higher in energy than the $\pi\pi^*$ states of the reaction product with which they correlate. In such cases, the adiabatic photochemical migration of the acetyl group occurs with a high quantum yield

TABLE 11. Long wavelength band maxima in electronic absorption spectra for the photoproducts of 1-acetoxy-9,10-anthraquinone derivatives (at 77 K in ethanol) and for corresponding 9-phenoxy-1,10-anthraquinone derivatives [13, 47]

No.	Substituents	λ_{max} (nm)	
		Photoproducts of 1-acetoxy-9,10-anthraquinone derivatives	9-Phenoxy-1,10-anthraquinone derivatives
XXIV'a	2-OCH$_3$	526	506
XXIV'b	2-NHCOCH$_3$	550	546
XXIV'c	2-N(CH$_3$)$_2$	683	670
XXIV'd	2-NC$_5$H$_{10}$	654	—
XXIV'e	4-OCH$_3$	510	486
XXV'	4-acetoxy-1,10-anthraquinone	468	468[a]

[a]Experimental value for 4-phenoxy-9-methoxy-1,10-anthraquinone.

(2-methoxy, 2-acetylamino, 2-dimethylamino and 4-methoxy derivatives of **XXIV** and unsubstituted (**XXV**).

(2) The lowest excited states (singlet and triplet) of the initial compound are $\pi\pi^*$ in character and are lower in energy than the $\pi\pi^*$ states of the hypothetical reaction product with which they correlate. Such compounds do not undergo any isomerization on irradiation (derivatives of **XXIV** with a substituted amino group in position 3 or 4).

(3) The lowest excited states (triplet and singlet) of the initial compound are $n\pi^*$ in character and are lower in energy than the $n\pi^*$ states of the hypothetical reaction product with which they correlate. In such cases, photochemical migration of the acetyl group is not realized. At room temperature, these compounds abstract a hydrogen atom from the solvent (compound **XXIV** and some of its derivatives with spectra close to the spectrum of the unsubstituted anthraquinone).

A detailed analysis of the process leading to the formation of ana-quinone in the ground state was performed for **XXIVa** by the laser flash photolysis technique [47]. The kinetic curve detected at 510 nm (**XXIV'a** absorption maximum) consists of two parts, corresponding to the accumulation and decay of **XXIV'a**. The kinetic curve of **XXIV'a** accumulation obeys an exponential time dependence and the pseudo-first-order rate constant $\bar{k}'$ is dependent on the oxygen concentration

$$\bar{k}' \sim = k_{14} + k_{15}[O_2]$$

The yield of **XXIV'a** is independent of the oxygen concentration. Hence, the excited state of **XXIV'a** is the precursor of **XXIV'a** in the ground state. This excited state is a triplet — ^{3}(**XXIV'a**)* — since its lifetime is rather long (1–2 μs in the absence of oxygen).

The process leading to the formation of ^{3}(**XXIV'a**)* is detected in the 0–150 ns time domain [47]. The singlet-excited state of **XXIV'a** cannot be the precursor of ^{3}(**XXIV'a**)*, since its lifetime is substantially less than 10 ns. It is reasonable to assume that the triplet-excited state of the initial quinone **XXIVa** is the precursor. The data available confirm the assumption that intramolecular photochemical migration of the acetyl group is an adiabatic reaction at the triplet potential energy surface [47].
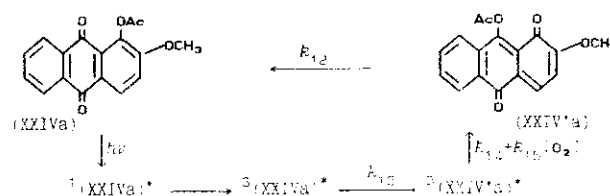
The estimated rate constant k_{13} at 160 K is of the order of 2×10^7 s^{-1}. The rate constants k_{14} and k_{15} and their temperature dependences have been measured ($k_{14} = 10^{6.44 \pm 0.07} \exp\{-(280 \pm 30)/T\}$) [47].

The photochromic materials based on 1-acetoxyanthraquinone derivatives show high sensitivity, good picture contrast and a high number of cycles. However, one should work with these photochromic compounds, as with 1-alkylanthraquinones, at low temperatures, since the lifetimes of the photo-induced products at room temperature are on the microsecond time scale.

A series of O-acyl derivatives of 1-hydroxy-2-methoxyanthraquinone (**XXVIa–c**) has been synthesized and investigated in order to control the rate constant of the thermal stage of the photochromic process [47, 48]. It has been found that the introduction of donor substituents into the migrating acyl group results in a strong decrease in the thermal migration rate constant k_{12}. By

substitution of an ethoxyl group for the methyl group, a decrease in the rate constant by two orders of magnitude is achieved. Replacing a methyl group by a diethylamino group decreases the rate constant by five orders of magnitude (Table 12).

The effect of the nature of the substituents in the phenyl ring also turned out to be significant in the case of the thermal migration of the aroyl group. In this case, the dependence of the logarithm of the rate constant on the Hammett electrophilic constant σ^+ of the substituent in the migrant aroyl nucleus fits satisfactorily to a straight line (Fig. 3) with a slope $\rho = 0.60 \pm 0.02$ (correlation coefficient 0.99) [47, 48]. The positive sign of ρ indicates that the larger the positive charge of the carbon

TABLE 12. Relation between rate constants of thermal migration of acyl group (k_{12}) in toluene at 285 K and nature of substituent in O-acyl derivatives of 1-hydroxy-2-methoxy-9,10-anthraquinone [47, 48]

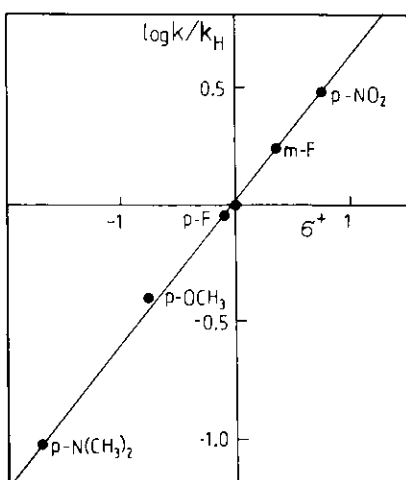| No.	00Migrant group	k_{12} (s^{-1})
XXIVa	O ‖ −C−CH$_3$	5.6×10^5
XXVIa	O ‖ −C−Ph	4.6×10^4
XXVIb	O ‖ −C−OC$_2$H$_5$	3.1×10^3
XXVIc	O ‖ −C−N(C$_2$H$_5$)$_2$	2.9

Fig. 3. Correlation between the rate constant of thermal migration of the benzoyl group at 285 K in toluene and the electrophilic constant of the substituent in the phenyl ring of the migrating acyl group.

atom of the migrating acyl group, the higher is the rate of migration. Thus, one can change over a wide range (from several microseconds to seconds) the lifetime of the photoproduct with the 9-acyloxy-1,10-anthraquinone structure at room temperature.

6. Photochromic transformations of 1-phenoxy-4-acetoxy- and 1-phenoxy-4-hydroxyanthraquinones

Even before starting our systematic studies of photochromic transformations of 1-acetoxyanthraquinone derivatives, we found that the final product of irradiating 1-phenoxy-4-acetoxyanthraquinone (XXVII) was 9-phenoxy-10-acetoxy-1,4-anthraquinone (XXVIII), *i.e.* both the phenyl and acetyl groups migrated [20]
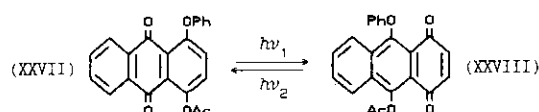
It can be seen from Sections 2 and 5 that photochemical migration of both the phenyl and acetyl groups is possible in the case of XXVII and XXVIII. However, only thermal migration of the acetyl group was detected for quinones. Therefore, it is natural to assume that photochromic transformation of XXVII consists of the photochemical step of the phenyl group migration followed by the thermal acetyl migration. Detailed flash photolysis and low temperature studies were conducted to understand mutual transformations of the compounds XXVII and XXVIII [21].

When irradiated at 77 K, XXVII and XXVIII yield products whose spectra are typical of 1,10-anthraquinone derivatives. On pulse excitation of XXVII, the formation of an intermediate was detected with a lifetime of 330 μs and an absorption maximum at 470 nm. On pulse excitation of XXVIII, intermediate absorbance in the visible spectrum also was detected. However, the kinetics of the absorbance decay fit satisfactorily to the sum of the two exponential time dependences, with the exponents independent of the wavelength. Based on these data, the existence of two intermediates on excitation of XXVIII was assumed [21].

The lifetime (330 μs) and spectrum ($\lambda_{max} = 470$ nm) of the first intermediate coincide with the characteristics detected on XXVII pulse excitation. The lifetime of the second intermediate is essentially shorter (about 10 ns) and its spectrum is shifted towards the red ($\lambda_{max} = 520$ nm). It can be

TABLE 13. Lifetime (τ), long wavelength band maxima (λ_{max}) in the absorption spectra of 1,10-anthraquinone derivatives in toluene at 285 K, and PPP-calculated values of the thermal effects for acetyl group migration (ΔH)

No.	Position of substituent in 1,10-anthraquinone	τ (μs)	λ_{max} (nm)	ΔH (kJ mol^{-1})
XXIV'a	9-OCOCH$_3$-2-OCH$_3$	4.0 ± 0.4	520 ± 10	72.5
XXIV'e	9-OCOCH$_3$-4-OCH$_3$	3.5 ± 0.4	500 ± 10	73.0
XXIV'c	9-OCOCH$_3$-2-N(CH$_3$)$_2$	16 ± 2	680 ± 10	71.0
XXV'	4-OCOCH$_3$	325 ± 30	460 ± 10	25.0
XXVIII'	4-OCOCH$_3$-9-OPh (C)	330 ± 30	470 ± 10	23.5
XXVIII'	9-OCOCH$_3$-4-OPh (D)	10 ± 2	520 ± 10	73.0

seen from Table 13 that the characteristics of the first intermediate are similar to the data for 4-acetoxy-1,10-anthraquinone (**XXV'**). The characteristics of the second intermediate are similar to the data for ana-quinones **XXIV'a** and **XXIV'e**. Based on these similarities, it was concluded that the first intermediate is 4-acetoxy derivative of 1,10-anthraquinine (C) and the second is 9-acetoxy derivative (D). Therefore, the photochromic transformation of 1-phenoxy-4-acetoxyanthraquinone could be described by the following scheme [21]:
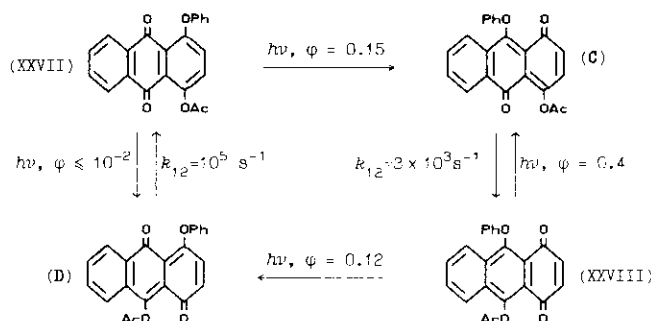

The quantum yields of the photochemical steps were estimated using a value of the extinction coefficient of 10^4 dm^3 mol^{-1} cm^{-1} typical of the acetoxy derivatives of 1,10-anthraquinone [20, 21].

The difference in the lifetimes of the intermediate ana-quinones C and D is due to the difference in the rate constants of thermal migration of the acetyl group, resulting in isomerization to 1,4- or 9,10-anthraquinone respectively. Table 13 presents quantum chemical calculations for the enthalpy of the isomerization reaction. The essential difference in the lifetimes of the investigated acetoxy derivatives of 1,10-anthraquinone is seen to correlate with the difference in the thermodynamic characteristics of the isomerization process [21].

An advantage of the latter photochromic process is that the photo-induced form **XXVIII**, *i.e.* the 1,4-anthraquinone derivative, is stable, which is not the case for the compound with the 1,10-anthraquinone structure. A disadvantage of this

process is the small difference in the long wavelength band maxima of the initial and photo-induced forms.

Irradiation of 1-phenoxy-4-hydroxy-9,10-anthraquinone (**XXIX**) leads to the formation of 9-phenoxy-10-hydroxy-1,4-anthraquinone (**XXX**), which is a product of the migration of both the phenyl group and the proton of the hydroxy group [20]:
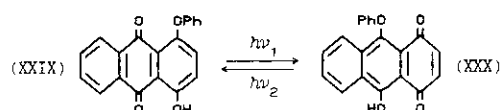
It is natural to assume that the mechanism of photochromic transformation of **XXIX** is similar to that discussed above. In the case of **XXIX**, the final product (**XXX**) is formed at 77 K [20], since, unlike the acylotropic change, the prototropic change occurs usually at high rates without activation energy [49, 50].

The absence of photochromism of the 11-hydroxy (**IV**) and 11-acetoxy (**V**) derivatives of 6-phenoxy-5,12-naphthacenequinone also has been accounted for (see Section 2) by the fact that the photochemical migration of the phenyl group is accompanied by the thermal migration of the proton or acetyl group, with the initial compound and photoproduct being identical. Thermal prototropic and acylotropic tautomerisms also have been observed for a number of other 1,10-anthraquinone and 1,10-anthraquinoneimine derivatives [41, 51–56].

7. Conclusions

Analysis of the available literature data shows that photochromic transformations of quinone derivatives are significant both from the theoretical and practical points of view. A number of new photochromic materials based on 1-phenoxyanthraquinone and 6-phenoxy-5,12-naphthacenequinone derivatives have been proposed, providing

image recording and erasure under the action of radiation of different wavelengths, long-term dark storage of images without additional chemical treatment, and a sufficiently high recyclability of the recording–erasing processes [9, 32].

Photochromic derivatives of 1-alkyl- and 1-acylanthraquinones have not yet found application, as image visualization is possible only in glassy matrices at 77 K. However, these compounds can be used in processes which do not require the prolonged conservation of photo-induced absorption. Variation of the substituents in the anthraquinone ring, in the alkyl group of 1-alkylanthraquinones and, particularly, in the acyl group of 1-acylanthraquinones, makes it possible to change (from several microseconds to seconds) the lifetimes of the coloured, photo-induced products at room temperature. These properties of anthraquinone derivatives may be of practical interest in new applications of photochromic processes.

The investigation of photochromism in the quinone series has revealed some new cases of phototransfer of sizeable (aryl and acyl) groups. These studies have made it possible to obtain 1,10-anthraquinone derivatives previously unavailable and to analyse their reactivities. Analysis of the reactivities of 1,10-anthraquinone and other ana-quinone derivatives obtained during the photolysis of para-quinones broadens significantly our knowledge of the chemistry of quinones.

The mechanism of photochromic transformation of 1-alkyl- and 1-acylanthraquinones has been investigated in detail. The triplet–triplet absorption spectra of the photoproducts were detected on pulse excitation of the initial compounds. Consequently, the primary photochemical steps of these processes — the migrations of hydrogen or an acyl group — are adiabatic photochemical reactions at the triplet potential energy surface. There are currently only a few other examples of triplet adiabatic reaction available in the literature [45, 57–59].

The photochromic transformation mechanism of aryloxy derivatives of anthra-, naphthacene- and other para-quinones has received considerably less attention. Only some empirical trends of the process have been revealed and data on the rate constants of the elementary steps are lacking. It also is necessary to continue studying the reactivity of this new class of quinones, i.e. the ana-quinones. Such investigations could broaden our theoretical knowledge of the chemistry of quinones as well as lead to the synthesis of new interesting photochromic compounds.

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55 V. P. Volosenko, B. E. Zaytsev and S. I. Popov, *Zh. Org. Khim.*, *21* (1985) 1086.

56 M. V. Gorelic, *Chemistry of Anthraquinone and Its Derivatives*, Khimiya, Moscow, 1983, p. 36.

57 N. J. Turro, J. McVey, V. Ramamurthy and P. Lechtken, *Angew. Chem. Int. Ed. Engl.*, *18* (1979) 572.

58 T. Arai, T. Karatsu, H. Misawa, Y. Kurijama, H. Okamoto, T. Hikesaki, H. Furuuchi, H. Zeng, H. Sakuragi and K. Tokumaru, *Pure Appl. Chem.*, *60* (1988) 989.

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The first relatively stable derivatives of 1,10-an-thraquinone were obtained in this way [6, 7].

Unlike para-quinones, whose spectra and chemical properties have been studied extensively, ana-quinones are a novel class of quinoid compounds which became the subject of study only 10–15 years ago. Recent data on spectra and chemical properties of this type of quinone need generalization and systematization. A recent review [14] which, according to its title, is concerned with the spectra and photochemistry of the derivatives of 1,10-anthraquinone (a representative of ana-quinones), contains essentially no data on the properties of 1,10-anthraquinones and describes the properties of the well-known derivatives of 9,10-anthraquinone. Accordingly, the present review also integrates and classifies data on the spectra and properties of ana-quinones, including 1,10-anthraquinone derivatives.

As can be seen from the scheme above, structural changes caused by the photochemical migration of hydrogen, aryl and acyl groups are similar. However, despite the similar structural changes, these processes turned out to differ in the nature of the photoreactive state and in the details of the mechanism of the photochromic transformation. Details of each type of photochromic process will be discussed.

2. Photochromism of aryloxy derivatives of para-quinones

Photochromism was first observed for quinones by Gerasimenko and Poteleschenko in 1971 [6, 7]. On exposure to light, 1-phenoxyanthraquinone (Ia) and 6-phenoxy-5,12-naphthacenequinone (IIa) have proved to change colour both in solution and in the crystalline state [6–9]. The photo-induced product disappears on irradiation by visible light and the spectrum of the initial para-quinone is completely recovered. The photoisomer of 6-phen-oxy-5,12-naphthacenequinone turned out to be rather stable and was isolated in the crystalline state. It was shown to have the structure of 5-phenoxy-6,12-naphthacenequinone (II'a) (ana-quinone) [7, 9].
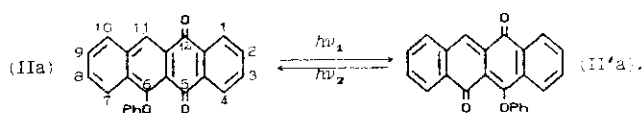

No photoisomer of 1-phenoxyanthraquinone (Ia) has been isolated [6, 7]. It should be noted that ana-quinones of the naphthacene series, unlike 1,10-anthraquinones, have long been known in the literature (see ref. 15).

Most subsequent work by Gerasimenko and Poteleschenko and colleagues was focused on the photochromism of derivatives of IIa. Extensive experimental information has been accumulated on the synthesis and investigation of photochromic transformations of various derivatives of IIa with substituents at position 11 of the naphthacene ring (Table 1) [9, 17–19], such as
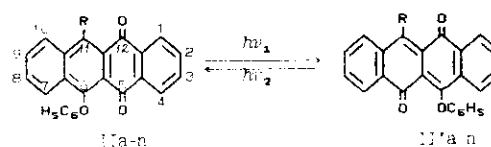
or in the migrating phenyl group (Table 2) [9, 16–18], such as
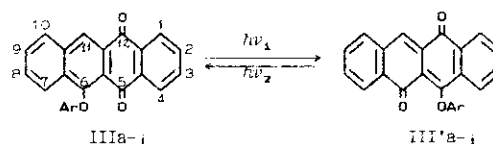
The rate constant of the thermal isomerization of 5-phenoxyana-naphthacenequinones (II'a–n) at room temperature is very small, and for II'a in toluene it is estimated to be about 10^{-8} s^{-1} [18, 19]. The spectral characteristics of the initial compounds and the photo-induced products are listed in Tables 1, 2 and 3. It can be seen from Table 1 that the introduction of a phenoxy group at position 6 of para-napthacenoquinone (or into position 5 of ana-naphthacenequinone) has practically no effect on the position of the long wavelength maximum in the absorption spectrum. The effect of the substituents at position 11 on shifts in the long wavelength maximum is the same for para- and ana-quinones, which is indicative of the same nature of the long wavelength bands of corresponding para- and ana-naphthacenequinone.

11-Hydroxy- (IV) and 11-acetoxy derivatives (V) of IIa are insensitive to light [18, 19]. In our opinion, this is due to the fact that the photochemical migration of the phenyl group is accompanied by thermal migration of the proton or acetyl group, as it is in 4-hydroxy and 4-acetoxy derivatives of 1-phenoxyanthraquinone [20, 21].

TABLE 1. Electronic absorption spectra of 11-substituted 6-phenoxy-5,12-(**IIa–n**), 5-phenoxy-6,12-(**II'a–n**), 5,12-, and 6,12-naphthacenequinones in toluene [18, 19]

R	6-OPh-11-R-5,12-naphthacenequinone		5-OPh-11-R-6,12-naphthacenequinone		11-R-5,12-naphthacenequinone	11-R-6,12-naphthacenequinone
	No.	λ_{max} (log ϵ) (nm)	No.	λ_{max} (log ϵ) (nm)	λ_{max} (log ϵ) (nm)	λ_{max} (log ϵ) (nm)
H	**IIa**	400 (3.78)	**II'a**	480 (4.23)		
Cl	**IIb**	398 (3.74)	**II'b**	444 (4.20) 472 (4.21)	402 (3.73)	451 (4.20) 479 (4.19)[a]
NO₂	**IIc**	394 (3.70)	**II'c**	453 (4.15) 479 (4.07)		
OCH₃	**IId**	400 (3.82)	**II'd**	447 (4.16) 469 (4.16)	401 (3.77)	
OC₆H₅	**IIe**	404	**II'e**	472		
OH	**IIf**	443 (4.00)	**II'f**	Insensitive to light	447 (3.98)	
OCOCH₃	**IIg**	396 (3.89)	**II'g**	Insensitive to light	397 (3.86)	
NH₂	**IIh**	389 (3.55) 468 (3.99)	**II'h**	474 (4.05) 503 (4.24) 538 (4.17)	382 (3.52) 474 (3.99)	490 (4.03) 513 (4.21) 552 (4.10)
NHCH₃	**IIi**	402 (3.73) 502 (4.09)	**II'i**	524 (4.15) 559 (4.07)	396 (3.52) 507 (4.09)	536 (4.11) 572 (4.01)
N(CH₃)₂	**IIj**	408 (3.78) 465 (3.60)	**II'j**	Insensitive to light	393 (3.69) 408 (3.68) 469 (3.57)	
NHC₆H₅	**IIk**	404 (3.84) 496 (3.95)	**II'k**	525 (3.94) 558 (3.86)	401 (3.85) 504 (4.00)	472 (3.91) 536 (3.92) 572 (3.82)
NHCOCH₃	**IIl**	429 (3.87)	**II'l**	504 (4.20)	436 (3.85)	509
NHSO₂C₇H₇	**IIm**	422 (3.77)	**II'm**	509	427 (3.77)	
NCH₃COCH₃	**IIn**	396 (3.85)	**II'n**	448 (4.19) 476 (4.20)	397	455 (4.20) 485 (4.20)

[a]Spectrum of 11-Br-6,12-naphthacenequinone in ethanol.
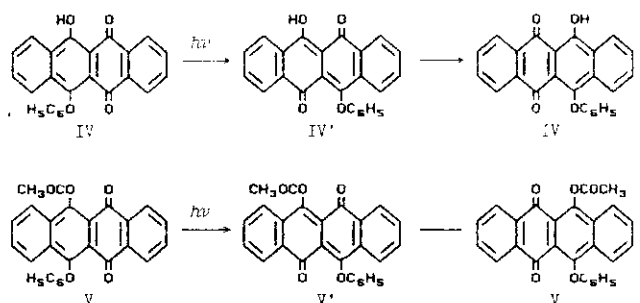
The initial compound and the product are identical.

It is noted also [18, 19] that, in the series 6-acetylamino-, 6-amino-, 6-methylamino-, 6-dimethylamino-11-phenoxy-5,12-naphthacenoquinone, the donor ability of the substituents increases and, consequently, the ability of the quinones to photoisomerize decreases. However, qualitative data on photoisomerization quantum yields for these compounds are lacking.

It can be seen from Tables 2 and 3 that the nature of the substituents in the phenyl ring has a minimal effect on the positions of long wavelength maxima and on the values of the extinction coefficients (ϵ) in the absorption spectra of the aryloxy derivatives of para- and ana-naphthacenequinones. Table 2 does not allow one to establish a correlation between the electronic effect of the substituents and the quantum yields of the direct and reverse photoisomerizations [18].
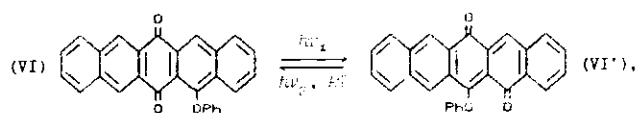
5-Phenoxy-6,13-pentacenequinone (**VI**) [22]

TABLE 2. Electronic absorption spectra of 6-aryloxy-5,12- and 5-aryloxy-6,12-naphthacenequinones in toluene and quantum yields of direct (φ_1) and reverse (φ_2) photoisomerization [16, 18]

Ar	6-OAr-5,12-naphthacenequinone				5-OAr-6,12-naphthacenequinone			
	No.	λ_{max} (nm)	$\epsilon \times 10^{-3}$ (M^{-1} cm^{-1})	φ_1	No.	λ_{max} (nm)	$\epsilon \times 10^{-4}$ (M^{-1} cm^{-1})	φ_2
C_6H_5	IIa	400	6.0	0.30	II'a	480	1.7	0.05
β-naphthyl	IIIa	398	5.7	0.16	III'a	478	1.7	0.07
p-C_6H_5–C_6H_4	IIIb	398	5.4	0.20	III'b	478	1.8	0.10
2',4',6'-$(CH_3)_3$–C_6H_2	IIIc	410	6.7	0.08	III'c	498	1.3	0.05
p-Br	IIId	397	5.9	0.36	III'd	480	1.8	0.10
p-OH–C_6H_4	IIIe	400	5.2	0.06	III'e	480	1.7	0.32
p-OCH_3–C_6H_4	IIIf	400	5.8	0.08	III'f	480	1.6	0.03
p-$COCH_3$–C_6H_4	IIIg	400	6.0	0.27	III'g	480	1.8	0.10
p-NO_2–C_6H_4	IIIh	395	6.0	0.20	III'h	480	1.9	0.05
p-NH_2–C_6H_4	IIIi	395	5.5	0.13	III'i	480	1.7	0.07
p-$NH(C_6H_5)$–C_6H_4	IIIj	396	6.4	0.02	III'j	476	1.8	0.01

λ_{exc} = 366 nm.

TABLE 3. Electronic absorption spectra of 11-aryloxy derivatives of 6-amino-5,12-naphthacenequinone and of its photoproducts in toluene [17]

Ar	6-NH_2-11-OAr-5,12-naphthacenequinone λ_{max} (nm) (log ϵ)	6-NH_2-12-OAr-5,11-napthacenequinone λ_{max} (nm)
C_6H_5	389 (3.55) 468 (3.99)	541
p-CH_3–C_6H_4	392 (3.66) 475 (4.08)	543
p-C_2H_5–C_6H_4	392 (3.66) 473 (4.08)	543
p-OCH_3	393 (3.65) 475 (4.09)	543
o-OCH_3	392 (3.61) 473 (4.05)	543
p-NHC_6H_5–C_6H_4	392 (3.69) 473 (4.07)	543
p-HO–C_6H_4	392 (3.58) 473 (4.01)	543
m-Cl–C_6H_4	390 (3.59) 471 (4.07)	541
p-NO_2–C_6H_4	391 (3.63) 472 (3.98)	543 Insensitive to light
α-naphthyl	385 (3.62) 472 (4.15)	Insensitive to light

and 1-phenoxy-2,3-phthaloyl pyrene (VII), as well as some of its derivatives [23]
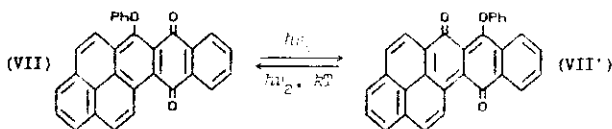
proved to be photochromic. The spectral characteristics of these compounds are given in Table 4. As can be seen from the table, the absorption spectra of ana-quinones I'a, II'a and VI' are similar and the long wavelength band maximum of VII' is strongly shifted (about 170 nm) towards the red.

Following the results of flash photolysis studies of photochromic transformations of IIa, it has been assumed that the photochemical migration of the phenyl group occurs in the triplet state. The triplet state of the spiro-form
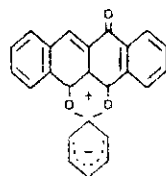

was assumed to be an intermediate [24]. However, this assumption is questionable.

TABLE 4. Electronic absorption spectra of peri-phenoxy derivatives of para- and ana-quinones

λ_{max} (nm) (log ϵ)				Solvents	References
Para-quinone		Ana-quinone			
Ia	364 (3.7)	I'a	480	Benzene	[6, 9]
IIa	400 (3.78)	II'a	480 (4.23)	Toluene	[9, 16]
VI	404 (3.08)	VI'	461 490	Toluene	[9, 22]
VII	476	VII'	604 652	Chlorobenzene	[9, 23]

One of the first derivatives in the series of 1,10-anthraquinones was isolated in a crystalline form by irradiating 2-alkylamino derivatives of 1-phenoxyanthraquinone (Ia), which undergo irreversible photoisomerization [25, 26]. ¹H and ¹³C nuclear magnetic resonance (NMR) data have shown that they have the structure of 2-alkylamino derivatives of 9-phenoxy-1,10-anthraquinone (ana-quinone). Further investigations [20, 26–29] have established a correlation between the photoisomerization ability of 1-aryloxyanthraquinones and the position and electronic nature of the substitutent in the anthraquinone ring.
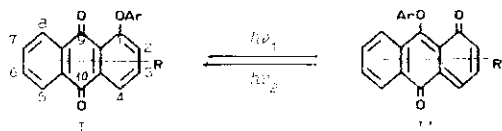
The most pronounced effect of the substituents is observed in 2-amino derivatives: 2-dialkyl- and 2-monoalkyl derivatives of **I** undergo irreversible photoisomerization, whereas 2-acylamino derivatives of **Ia** are reversibly isomerizing compounds with good photochromic characteristics [26–28]. Figure 1 shows an example of the spectral changes observed in the photochromic transformations of 1-phenoxy-2-acetylaminoanthraquinone.

The formation of the corresponding derivatives of 1,10-anthraquinone on irradiating 2-dialkylamino derivatives of 1-phenoxyanthraquinone was observed only chromatographically. After long irradiation of 1-(p-tert-Bu-phenoxy)-2-dimethylaminoanthraquinone solution, 1-hydroxy-2-dimethylamino-, 1-hydroxy-2-methylamino- and 1-hydroxy-2-formylaminoanthraquinones were obtained. The final products seem to be formed in the course of further photochemical transformations of the intermediate 1,10-anthraquinone
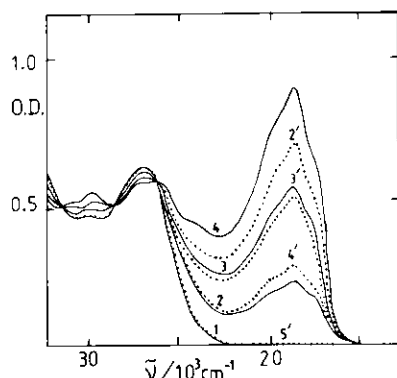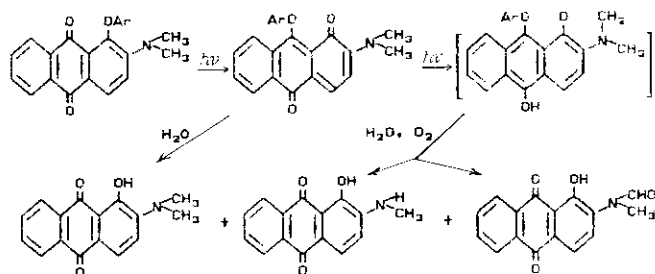
Fig. 1. Electronic absorption spectrum of 1-tert-butylphenoxy-2-acetylamino-9,10-anthraquinone (1) in toluene at room temperature and changes on 365 nm irradiation for 7 s (2), 20 s (3), 60 s (4) and on subsequent 546 nm irradiation for 3 s (2'), 6 s (3'), 20 s (4') and 60 s (5').

The transformations are similar to those of 2-dialkylamino derivatives of 1,4-naphthoquinone [30, 31].

The series of 2-, 3-, 4-, 5- and 8-amino derivatives of 1-aryloxyanthraquinone also has been studied [26, 27] (Table 5). 1-Aryloxy derivatives with dimethylamino substituents at positions 4, 5 and 8 do not isomerize photochemically. As regards photochromism, the 1-phenoxy-2-acylaminoanthraquinones are the most interesting compounds of all the amino derivatives of **I** studied. 2-Monoalkylamino derivatives are interesting as model compounds, yielding sufficiently stable 1,10-anthraquinones.

The photochromic properties of the series of 2-, 4-, 5- and 8-hydroxy, methoxy and acetoxy derivatives of 1-aryloxyanthraquinones have been

TABLE 5. Long wavelength band maxima in electronic absorption spectra of 2-, 3-, 4-, 5-, 8-amino derivatives of 1-(p-tert-butylphenoxy) anthraquinone before and after irradiation in benzene [26–28]

Substituents	λ_{max} (nm) (log ϵ)	
	Before irradiation	After irradiation
2-NH₂	404 (3.74)	587 (3.87)
2-NHCH₃	423 (3.86)	616 (3.94)
2-NHCOCH₃	373 (3.72)	543
2-NHCOCF₃	354 (3.72)	527
3-NH₂	415 (3.64)	434[a]
3-NHCH₃	438 (3.64)	442[a]
3-N(CH₃)₂	459 (3.74)	443, 466[a]
3-NHSO₂C₆H₄(p-CH₃)	380 (3.66)	466
4-NH₂	478 (3.86)	581[b]
4-NHCH₃	518 (3.91)	621[b]
4-NHCOCH₃	436 (3.87)	532
4-NHCOC₆H₅	445 (3.86)	541
5-NH₂	466 (3.76)	575[b]
5-NHCH₃	504 (3.89)	—
5-NHCOCH₃	415 (3.86)	502, 523
5-NH₂OC₆H₅	418 (3.84)	506, 532
8-NH₂	472 (3.75)	—
8-NHCH₃	501 (3.79)	—
8-NHCOCH₃	416 (3.84)	556
8-NHCOC₆H₅	421 (3.88)	566

[a]Irreversible isomerization; [b]optical density of photoproduct in the mixture is small.

investigated [20] (Table 6). On exposure to light, practically all the compounds studied photoiso-merized reversibly to the corresponding derivatives of 9-aryloxy-1,10-anthraquinone. The exception was 1-phenoxy-8-hydroxyanthraquinone, which, like the 1-phenoxy-8-amino(methylamino)anthra-quinones described above, does not photoisomerize under the action of light. It has been found that, in the case of the 2-hydroxy(methoxy, acetoxy) derivatives of **Ia**, the photo-induced form is un-stable and has not been isolated in the crystalline state, which is not the case for the 2-amino(methylamino) derivatives of **Ia**.

The mechanism of phototransformation of the 4-hydroxy- and 4-acetoxy derivatives of **Ia** com-prises two stages: the primary stage of photo-isomerization to the corresponding 1,10-anthra-quinone derivatives and the thermal stage of prototropic or acylotropic transitions to the en-ergetically more stable 1,4-anthraquinones [20, 21]. This mechanism will be considered in more detail in Section 6.

Thus, photoarylotropic transformations of aryl-oxy derivatives of anthra-, naphthacene- and other polycyclic quinones turned out to be of both sci-entific and practical interest. A number of deriv-atives of **I** and **II** have served as bases of novel photochromic materials, allowing recording and erasing of information under the action of a wide range of radiation, the dark storage of the image without additional chemical treatment, and a rather high number of cycles of regeneration [9, 32].

A substantial disadvantage of photochromic ma-terials based on 1-phenoxyanthraquinone and its derivatives is the limited number of cycles of

recording and erasure possible, owing to destruc-tion of the photoisomer by the attack of traces of water. These degradative processes are deter-mined by the unusually high reactivity of ana-quinones towards nucleophilic agents. The next section provides a brief review of data on the reactivity of 1,10-anthraquinone derivatives.

3. Reactivity of ana-quinones

Owing to their high reactivity, 1,10-anthraqui-none derivatives were unknown for a long time and attempts to synthesize them failed [33, 34]. Boldt and coworkers [33, 34] tried to stabilize the 1,10-anthraquinone molecule by stabilizing the qui-noid system with methyl groups. However, 2,3,4,5,8-pentamethyl-1,10-anthraquinone (**VIII**) was de-tected only in solution and attempts to isolate this substance failed. An adduct of **VIII** with ethanol was isolated, which had the structure of semi-ketal **IX**:
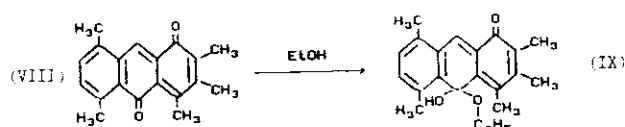
Later, Boldt and Setiabudi [35, 36] isolated crystalline 3-tert-butyl-5,8-dimethyl-1,10-anthra-quinone (**X**) and identified it by ^{1}H NMR and mass spectrometry data. The electronic absorption spectrum of **X** in chloroform exhibits a long wave-length band with a maximum at 491 nm. In the presence of even traces of water, ana-quinone **X** transforms to 1-hydroxy-3-tert-butyl-5,8-dimethyl-9,10-anthraquinone (**XI**):
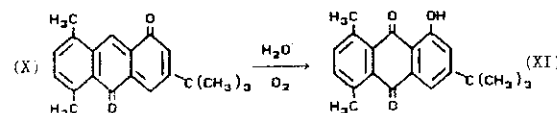
It should be noted that Boldt and Schmand [37] also have isolated crystalline ana-naphthaquinone-3,7-di-tert-butyl-1,5-naphthaquinone (λ_{max} = 475 nm in CCl_4).

Gorelik *et al.* [38, 39] have succeeded in isolating two chloro derivatives of 1,10-anthraquinone — 2,4,9-trichloro- (**XII**) and 2,3,4,9-tetrachloro-1,10-anthraquinone (**XIII**) — from the mixture formed in the reaction of 1,4-dihydroxyanthraquinone with thionyl chloride in the presence of triethylamine. When stored in the crystalline state, ana-quinones **XII** and **XIII** are stable for a long time. These compounds were the first 1,10-anthraquinone de-rivatives to be isolated in the free state. Their

TABLE 6. Long wavelength band maxima in electronic spectra of hydroxy, methoxy and acetoxy derivatives of 1-aryloxyanthra-quinone before and after light irradiation in benzene [20]

Substituent in anthraquinone	R (OC₆H₄R)	λ_{max} (nm) (log ϵ) Before irradiation	After irradiation
2-OH	p-C(CH₃)₃	369 (3.74)	389, 532
2-OCH₃	p-C(CH₃)₃	374 (3.68)	506
2-OCOCH₃	p-C(CH₃)₃	326 (3.65)	483
4-OCH₃	p-C(CH₃)₃	390 (3.74)	490
5-OH	H	373 (3.71)	477
5-OCH₃	H	375 (3.75)	479
5-OCOCH₃	H	334 (3.79)	470
8-OH	H	415 (3.89)	—
8-OCOCH₃	H	351 (3.60)	475
2,4-OCH₃	p-C(CH₃)₃	395 (3.88)	525

λ = 280–400 nm.

TABLE 7. Positions of long wavelength band maxima in electronic absorption spectra of 1,10-anthraquinone derivatives obtained non-photochemically

No.	Substituents	λ_{max} (nm) (log ϵ)	Solvents	References
X	3-tert-Bu-5,8-Me$_2$	491	Chloroform	[35]
XII	2,4,9-Cl$_3$	484 (4.06)	Benzene	[40]
XIII	2,3,4,9-Cl$_4$	489 (4.04)	—	—
XV	9-C$_6$H$_5$-2,4-Cl$_2$	485 (4.06)	Benzene	[41]
XVI	9-p-ClC$_6$H$_4$-2,4-Cl$_2$	485 (3.90)	—	—
XVII	9-(2,4,6-Me$_3$C$_6$H$_2$)-2,4-Cl$_2$	485 (4.13)	—	—
XVIII	9-(2,4,6-Me$_3$C$_6$H$_2$)-2,3,4-Cl$_3$	485 (4.08)	—	—

spectra feature long wavelength bands at 484 nm and 489 nm respectively (Table 7).

It has been established that position 9 of ana-anthraquinone is the most active in reactions with nucleophiles [35, 39, 40]. For example, passing hydrogen chloride through a solution of XII in a non-polar solvent leads to the formation of 9,9-dichloro-1-hydroxy-10-anthrone (XIV). The removal of hydrogen chloride and heating reduce the initial compound [39, 40].
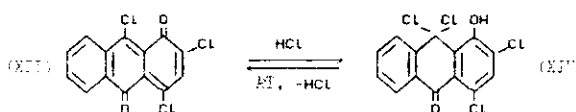

The series of 9-aryl-1,10-anthraquinones (XV–XVIII) (Table 7) also has been synthesized [40, 41]. Analysis of the data given in Table 7 shows that variation of the 9-substituents of 1,10-anthraquinone (hydrogen, chlorine, aryl and phenoxy groups) has practically no effect on the position of the long wavelength band maximum. A similar situation was observed for ana-naphthacenequi-nones (Table 1). Moreover, comparison of the data in Tables 1, 4 and 7 shows that long wavelength maxima of ana-quinones I'a, II'a, III', VI', XII, XIII, XV–XVIII and 1,5-naphthaquinone [37] practically coincide and lie within the range 480±10 nm.

Unlike ana-quinones XII, XIII, XV and XVI, 9-mesityl-1,10-anthraquinones (XVII, XVIII) add neither hydrogen chloride, nor other nucleophilic reagents at position 9. The mesityl group (2,4,6-Me$_3$C$_6$H$_2$), bearing methyl groups at the ortho-positions, completely screens position 9, thus preventing the attack of the reagent and increasing the stability of the compounds. Under the attack of strong nucleophiles (sodium hydroxide, ammonia, aliphatic and aromatic primary amines) at room temperature, the chlorine atom at position 4 of ana-quinones XVII and XVIII is substituted by a hydroxy or amine group respectively [40, 41]. In 9-mesityl derivatives XVII and XVIII, the sub-stitution of chlorine at position 4 can be followed by substitution of the chlorine atom at position 2 owing to excess ammonia [40, 41]. The exper-imentally determined sequence of site reactivities with respect to nucleophilic attack for the 1,10-anthraquinone molecule, namely 9 > 4 > 2, is con-sistent with data of quantum chemical calculations for the π-electron density in the molecule [34].

However, information on the rate constants of these reactions and quantitative comparison of the reactivities of these compounds are lacking [40, 41]. We recently have undertaken the first attempt to perform a kinetic study of the reactivity of some 1,10-anthraquinone derivatives. One aim of this study was to determine the effect of substituents in the anthraquinone nucleus on the stability of the photo-induced 9-aryloxy-1,10-anthraquinone. The reaction of 9-aryloxy-1,10-anthraquinones with alcohols was used as a model. For 2-alkylamino derivatives, we have established a stepwise mech-anism of the reaction with alcohols, starting from 1,4 addition of the alcohol molecule [42].
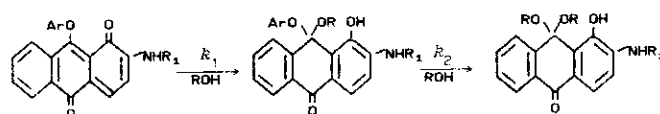
The kinetic studies have shown substituents in the anthraquinone ring to have a substantial effect on the rate constant k_1 (Table 8). The nitro group, an electron-withdrawing substituent, increases k_1 by more than an order of magnitude. Electron-donor substituents (amino and methoxy groups) decrease k_1 by 2–3 orders of magnitude and, hence, enhance the stability of the photo-induced form [42].

4. Photochromism of peri-alkyl-para-quinones

Thermally reversible photoenolization of methyl derivatives of para-quinones was discovered first

TABLE 8. Rate constants of nucleophilic addition reaction of methanol at 298 K in toluene (k_1) to 9-(p-tert-Bu-phenoxy)-1,10-anthraquinone derivatives [42]

| Substituents	k_1 $(10^{-3}$ dm^3 mol^{-1} s$^{-1})$	Substituents	k_1 $(10^{-3}$ dm^3 mol^{-1} s$^{-1})$
H	300	2-NH$_2$	1
H[a]	200	4-OCH$_3$	6.6
2-NO$_2$	4200	4-NHCOCH$_3$	0.4
2-NHCOCH$_3$	40		

[a]With pentafluorophenoxy group in position 9.

TABLE 9. Isomerization rate constants (k_3) of anthraquinone-methide derivatives in ethanol (95%) at 290 K and π-electron densities at methylene-group carbon atom for different substituents in the anthraquinone ring [43, 44]

No.	Substituents	k_3 $(10^3$ s$^{-1})$	$p_\pi - 1$
XXa	Unsubstituted	6.6±0.2	0.051
XXb	3-(cyclohexene-1)	8.4±0.3	0.052
XXc	4-CH$_3$-	29.4±0.6	
XXd	2,3,4-(CH$_3$)$_3$-	83.0±6.0	
XXe	4-CH$_3$-5,6,7,8-Cl$_4$-	20.8±1.9	
XXf	4-CH$_3$-5,6,7,8-F$_4$-	10.1±0.5	
XXg	4-OCH$_3$-	4.4±0.1	0.045
XXh	4-piperidino-	0.51±0.01	0.040
XXi	4-Cl-	10.5±0.5	
XIX	4-hydroxy-1,5-naphthoquinone-5-methide	0.27±0.01 (1.25[a][10])	0.033

[a]Measurements in absolute ethanol.

for 5-methyl-1,4-naphthaquinone (XIX) [10] and shortly after for 1-methylanthraquinone (XXa) [11]. For 1-methylanthraquinone and its series of derivatives with substituents in the anthraquinone ring, it has been established that 9-hydroxy-1,10-anthraquinone-1-methides resulting from photochemical migration of hydrogen are stable in alcohol matrices at 77 K. At room temperature, the thermal process leads to reformation of the initial structure [11, 43, 44].
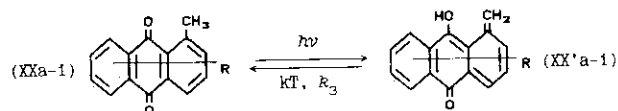
Substituents in the anthraquinone ring have a significant effect on the rate constant k of the thermal migration of hydrogen [44] (Table 9). It has been found that this effect is related to a change in the π-electron density at the carbon atom of the methylene group: k_3 increases with increasing π-electron density and decreases with decreasing π-electron density [43, 44]. The value of k_3 also is affected strongly by the temperature and nature of the solvent. An increase in the

polarity and, in particular, in the proton-donor ability of the solvent decreases k_3 by several orders of magnitude [10, 43–45].

Interesting photochromic transformations have been observed for 1-hydroxy-4-methylanthraquinone (XXI) [11, 43]. The photochemical step of hydrogen atom transfer from the methyl group, in this case, is accompanied by a thermal step of proton transfer from the OH group:
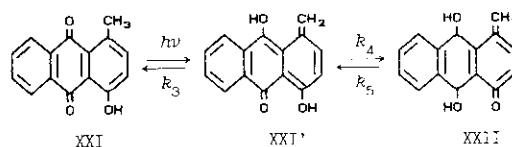

The effective rate constant of thermal decolorization of photoproduct XXII

$$k_{\text{eff}} \approx k_3 k_5 / k_4$$

is about six orders of magnitude lower than k_3 in the case of 4-methoxy derivatives of 1-methylanthraquinone. This is determined by the high thermodynamic stability of 1,4-anthraquinone compared with that of 1,10-anthraquinone [11, 43].

Thermally reversible photoenolization also has been observed for the series of 1-alkyl- and 1-benzylanthraquinones (XXIIIa–e) [44, 46]. (With two hydrogen atoms substituted by phenyl groups, photoenolization does not occur either at 77 K or at room temperature.)
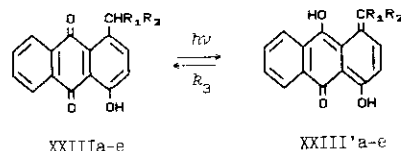
Kinetic studies have shown that the effect of the substituent in the methylene group of XXIII' on k_3 is determined by both electronic (change in the π-electron density of the carbon atom) and purely steric effects [44]. For the case of two different substituents in the methylene group, we have detected two structural isomers (A and B) of 1,10-anthraquinone-1-methylenes. The k_3 values for these isomers differ by approximately an order of magnitude [44, 45] (Table 10).
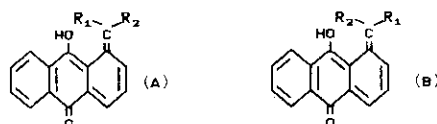
Recently, we have conducted [45] a detailed laser flash photolysis investigation of the photoenolization mechanism of 1-methylanthraquinone (XXa) and its deutero analogue, 1-trideuteromethyl-2,3,4-trideuteroanthraquinone (XXa-

TABLE 10. Relation of isomerization rate constant to methylene-group structure for 9-hydroxy-1,10-anthraquinone-1-methylene derivatives in ethanol (95%) at 290 K [44]

No.	Methylene	k_3 (10^3 s^{-1})	
		A	B
XX'	=CH$_2$	6.6±0.2	—
XXIII'a	=C(CH$_3$)$_2$	—	0.36±0.03
XXIII'b	=CHCH$_3$	3.4±0.2	0.40±0.03
XXIII'c	=CHPh	28±2	—
XXIII'd	=CCH$_3$Ph	59±3	5.9±0.3
XXIII'e	=CHC$_6$F$_5$	56±3	5.9±0.3

d_6) over a wide temperature range (120–340 K). The accumulation of **XX'a** in the ground state and its decay were detected. However, immediately after the laser flash for wavelength $\lambda \geqslant 550$ nm, an absorption is observed, giving a spectrum co-inciding with that of **XX'a**. Within the range 550–700 nm at 206 K, the ratio of the optical density at zero time to the optical density after 3.5 μs equals 0.49±0.02. This value depends on the temperature and, particularly, on **XXa** deu-teration. For **XXa-d$_6$** it changes from 0.43 at 320 K to 0.12 at 120 K. This result was accounted for by assuming that absorption in the range 550–700 nm, arising immediately after the laser flash, cor-responds to **XX'a** formed from the singlet-excited state of **XXa**.

The kinetic curve of additional accumulation of **XX'a** from the precursor is dependent on the concentration of the dissolved oxygen. The pseudo-first-order rate constant $\bar{k}$ can be expressed in the form

$$\bar{k} = k_9 + k_{10} \times [O_2]$$

Although $\bar{k}$ increases strongly with the dissolved oxygen concentration, the **XX'a** yield is indepen-dent of the oxygen concentration and remains equal to unity. The precursor lifetime at 120 K in ethanol is 1.1 μs for **XX'a** and 1.4 μs for **XX'a-d$_6$**. Therefore, the precursor of **XX'a** is its triplet-excited state (T).

The yield of **XX'a** formed from the T is quenched by piperylene admixtures. The intermediate ab-sorption at zero time is independent of the pi-perylene admixtures. Based on the present results, we have concluded [45] that photochemical mi-gration of hydrogen occurs in both triplet- and singlet-excited states of **XXa** and **XXa-d$_6$**. Ac-cording to the identity of the electronic absorption spectra for **XXa** and unsubstituted anthraquinone, and considering the structure of the lower excited states of the unsubstituted anthraquinone available

in the literature, we have made a conclusion about the nπ^* nature of the triplet and singlet reactive states of **XXa** and **XXa-d$_6$** [45].

Migration of the hydrogen (or deuterium) atom in the singlet nπ^* state results in the formation of the quinone-methide **XX'** in the ground state. If the hydrogen (or deuterium) atom migrates in the ^{3}nπ^* state, the primary product is the triplet-excited quinone-methide (T). Therefore, migration of the hydrogen atom is an adiabatic photochemical reaction at the triplet potential energy surface. AM1 calculations [45] for the potential energy surface of quinone-methide **XX'a** in the triplet state have shown that the short-lived intermediate T is a σ,π-biradical with a twisted CH$_2$ fragment. One of the unpaired electrons in this intermediate is localized at the methylene group carbon atom (in the σ orbital), with the plane of the methylene group being practically perpendicular to that of the anthraquinone rings. The photoenolization pro-cess of **XXa** and its deutero analogue **XXa-d$_6$** can be presented in the following rather complex scheme [45]:
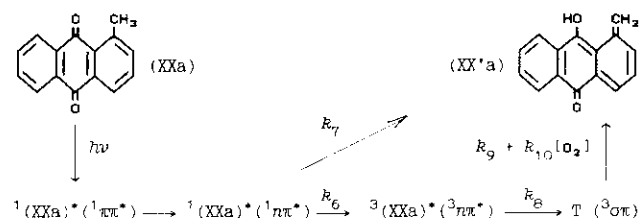
The rate constants k_6 and k_7 were estimated from the quantum yield of the photoproduct in the singlet state, and typical values of k_6 for aromatic ketones are about 10^{11} s^{-1}. The rate constants of ^{3}nπ^* hydrogen atom transfer (k_8) estimated from experiments in the presence of an excitation quencher (piperylene) are 3×10^{10} s^{-1} for **XXa** and 1×10^{10} s^{-1} for **XXa-d$_6$** [45]. The rate constants k_9 and k_{10} and their dependence on temperature, deuteration and solvent also have been measured [45].

It has been found that the thermal step of the photochromic transformations of **XXa** and of its deutero analogue can occur not only as a result of intramolecular migration of hydrogen atoms, but also via a bimolecular channel, i.e. by simul-taneous or sequential transfer of two hydrogen atoms on the encounter of two quinone-methide molecules: