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Photochromism of 1-(2-naphthoxy)anthraquinone

Masahiro Tajima [a], Hiroaki Misawa [b], Haruo Inoue [b]

[a] *General Education Course, Faculty of Engineering, Toyo University, Nakanodai Kujirai, Kawagoe-shi, Saitama 350, Japan*
[b] *Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University, Minamiosawa, Hachioji-shi, Tokyo 192-03, Japan*

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Abstract

The photochromic behaviour of 1-(2-naphthoxy)anthraquinone (**1**) was investigated using electronic spectroscopy and kinetic analysis of the decay of coloured species. The decay of coloured species well obeyed first-order kinetics and consisted of two processes, reversion to the starting substance and the change toward final formation of 1-hydroxyanthraquinone (**2**). The reversion process was revealed to proceed through two different pathways having activation enthalpies of 30.5 and 104 kJ mol^{-1}. The lower value suggests that the reversion proceeds from a rotational isomer of **1** while the higher value comes from a structural isomer of **1**, 9-naphthoxy-1,10-anthraquinone. The activation enthalpy of the change toward final formation of **2** was 49.1 kJ mol^{-1}. The possible formation of the two different coloured species from the two conformers of **1** on light irradiation was discussed.

Keywords: Photochromism; 1-(2-Naphthoxy)anthraquinone

1. Introduction

The photochromism and photocoloration of the phenoxy derivatives of the anthra- and naphthacenequinones have been investigated in detail. The structural change involving the rearrangement of the phenoxyl group, that is the formation of ana-quinone, has been reported to cause these phenomena [1–10]. Thermally reversible photochromism at ambient temperature is only the case for 1-phenoxyanthraquinone [1]. During the other photochromism, coloured species are only photochemically reversible [4–7,9,10]. Some of the coloured species in the photocoloration are isolable [2,3] but the others are not isolable because of thermal instability [4–6]. It is unusual that some phenoxy derivatives of the anthra- and naphthacenequinones do not exhibit photocoloration [4–6,10].

The lack of consistency in the stability and reversibility of coloured species and the difference in reactivity between the quinones do not necessarily permit the explanation that only the formation of ana-quinone causes the photochromism and photocoloration of the anthra- and napthacenequinones. Recently, we have reported that the coloured species during the photochromism of 1-phenoxyanthraquinone consists of not only a structural isomer, 9-phenoxy-1,10-anthraquinone, but also a rotational isomer where the benzene ring of the phenoxyl group orients to the carbonyl group of the quinone within the molecule and that the structural isomer is produced from the rotational isomer (Scheme 1) [11]. Furthermore, we have elucidated that the coloured species in the photochromism of 1-(1-naphthoxy)anthraquinone is only the structural isomer, 9-naphthoxy-1,10-anthraquinone (Scheme 1) [12]. These studies indicate that a difference in the aryl group alters the photochromic behaviour of the 1-aryloxyanthraquinones. The size of the aryl group and spatial relation between the anthraquinone nucleus and the aryl group are important factors in the photochromic behaviour of 1-aryloxyanthraquinones.

In this paper, the photochromic behaviour of 1-(2-naphthoxy)anthraquinone (**1**) as another example of 1-aryloxyanthraquinones has been investigated using electronic spectra and the kinetic analysis of the coloured species' decay. The steric repulsion of the 2-naphthyl group of **1** may be less than that of the 1-naphthyl group of 1-(1-naphthoxy)anthraquinone, although the sizes of both groups are the same. In contrast to the previously investigated 1-aryloxyanthraquinones, the coloured species was revealed to return to **1** through two processes, having lower and higher activation enthalpies. The two conformers of the starting **1** were postulated to form a rotational and structural isomer.

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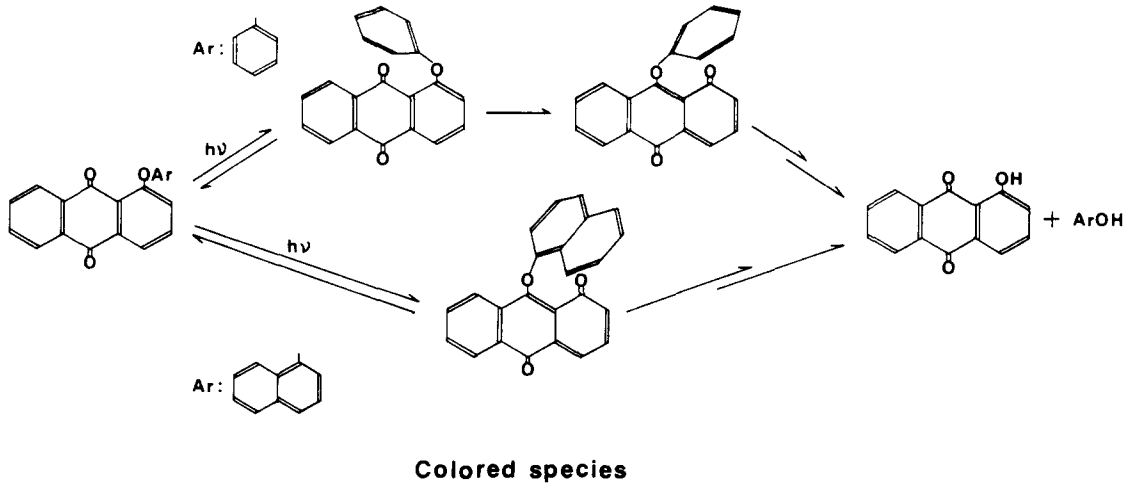


Scheme 1.

2. Experimental details

2.1. Materials

1-(2-Naphthoxy)anthraquinone (**1**) was prepared by the Ullmann condensation [13] of 1-bromoanthraquinone with potassium 2-naphtholate and purified by column chromatography on alumina using benzene as the eluent. 1-Bromoanthraquinone was synthesized by the Sandmeyer reaction from 1-aminoanthraquinone [14]. Benzene was dried over sodium and fractionally distilled before use. 1-bromonaphthalene, 1-cyanonaphthalene and *n*-butanol were purchased from Tokyo Kasei Co. and used without further purification.

2.2. Procedures

Light irradiation was carried out using a 500 W high pressure mercury lamp (Ushio) with a filter (Toshiba D-25) which transmitted the 365 nm spectral line of the lamp. Quantum yield of the coloration was determined in comparison with that of 1-phenoxyanthraquinone in aerated benzene [11]. Electronic absorption spectra were measured using a Shimadzu UV-200 spectrophotometer.

3. Results and discussion

3.1. Photochromic behaviour of 1

Electronic absorption spectra of the benzene solution of **1** (2×10^{-4} mol dm^{-3}) changed on irradiation of the 365 nm light; the colour of the solution turned from pale yellow to orange. The absorbance at 370 nm decreased during the irradiation and a new absorption appeared around 470 nm with isosbestic points at 325 and 377 nm (Fig. 1(a)). When the coloured solutions were allowed to stand in the dark, the orange colour returned to its initial pale yellow. The absorption of the coloured species decreased in the dark without an isosbestic point (Fig. 1(b)). The spectrum of the irradiated solution cannot be completely restored to that of the solution before irradiation. The remaining absorption around 400 nm suggests the formation of 1-hydroxyanthraquinone (**2**), which has λ_{max} at 410 nm in benzene, that is similar to the case of 1-phenoxyanthraquinone [11]. Thin layer chromatography (TLC) analysis (silica gel–benzene) indicates the production of **2** together with 2-naphthol. The coloured species was not recognized by TLC as in the case of the previous quinones [11,12]. Similar to the other cases, the coloured species should decompose on an acidic silica gel TLC plate to produce **2** and 2-naphthol because of its instability against acid. In fact, the addition of hydrochloric acid to the coloured solution just after the light irradiation of **1** caused a rapid disappearance of the colour. The resultant solution was revealed to contain **1**, **2** and 2-naphthol based on the visible absorption spectrum and TLC analysis. These phenomena are also very similar to the cases of 1-phenoxy- and 1-(1-naphthoxy)anthraquinone [11,12]. This indicates the decomposition of the coloured species to **2** in addition to the reversion to **1**. Therefore, the decay scheme of the coloured species could be determined as shown in Scheme 2 containing two processes: the reversion to **1** (k_1) and the change toward the final formation of **2** (k_2).

3.2. Absorption spectrum of the coloured species

The absorption spectrum of the coloured species was estimated by the method [11] based on the quantitative conversion to **2** of the coloured species under the action of hydrochloric acid. The concentration of the coloured species was taken to be the same as that of **2** formed on the addition of hydrochloric acid. The absorption

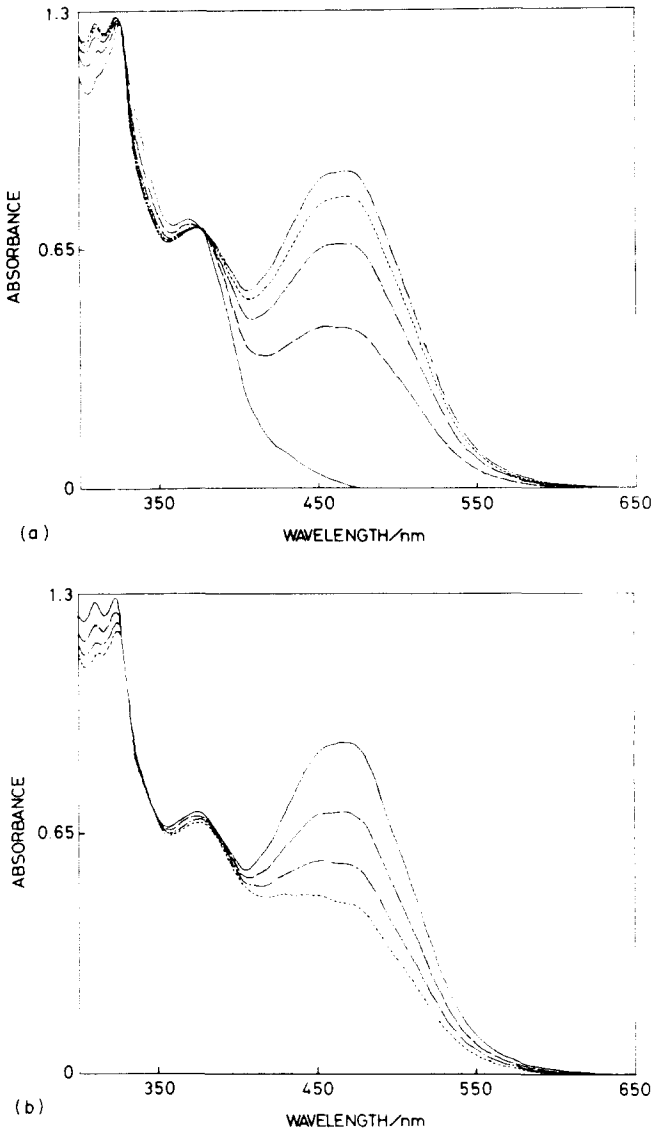


Fig. 1. (a) Spectral change of **1** in benzene (2×10^{-4} mol dm^{-3}) due to light irradiation ($\lambda = 365$ nm) at 295 K for the following times (seconds): —, 0; – – –, 4; – · –, 8; - - -, 12; – · · – · · –, 16. (b) Spectral change of irradiated benzene solution of **1** (2×10^{-4} mol dm^{-3}) in the dark. The solution after irradiation ($\lambda = 365$ nm) for 20 min was allowed to stand at 295 K in the dark for the following times (hours): —, 0; – – –, 2; – · –, 4; - - -, 6.

spectrum of the coloured species was obtained by subtraction of the contribution of remaining **1** from the observed spectrum of the coloured solution.

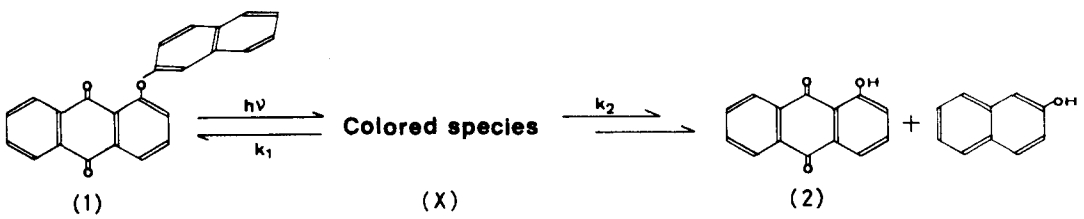
λ_{max} was 470 nm and the molar extinction coefficient at λ_{max} was 1.15×10^{4} dm^{3} mol^{-1} cm^{-1}, which are very similar to those of previous cases [11,12]. The spectra are compared in Fig. 2.

3.3. Kinetics of the coloured species' decay

The coloured species reconverted to **1** together with the decomposition to **2** and 2-naphthol. The decay obeyed first-order kinetics as shown in Fig. 3, although the case of 1-phenoxyanthraquinone deviated from the first-order kinetics [11]. Although the rate constant k_0 has a slight tendency to increase with irradiation time, it can be regarded as almost constant in the range of irradiation time of 15–60 min. The decay rate was determined after a 15 min irradiation. The coloured species would be very sensitive to protic substances in the solution. 2-Naphthol formed from the coloured species can possibly react further with the coloured species. This may cause the decay rate constant to increase.

The estimation of the rate constants of the two processes mentioned above was spectroscopically carried out using the same method as for 1-phenoxyanthraquinone [11], supposing that the rate constant k_0 of the coloured species' decay is expressed as k_1+k_2, where k_1 and k_2 are the rate constants of reversion to the starting compound and of the final formation of **2** respectively.

Some of the estimated rate constants are shown in Table 1. As shown in Fig. 4, the Arrhenius plot of k_1 is obviously curved and that of k_2 is regarded as straight. Since the kinetic data (k_1) are estimated to contain errors within $\pm30\%$, the curvature is clearly out of the range of experimental error. The following are reasonably considered to be candidates for the coloured species in this case based on the analogy with 1-phenoxyanthraquinone [11] and 1-(1-naphthoxy)-anthraquinone [12]; a rotational isomer of **1**, where the naphthoxyl group of **1** is rotated around the C–O single bond in order to orient itself to the adjacent carbonyl group within the molecule, and a structural isomer, 1,10-anthraquinone. The curved Arrhenius plot of k_1 suggests that the decay mechanism of the coloured species in this case is somewhat different from the



Scheme 2.

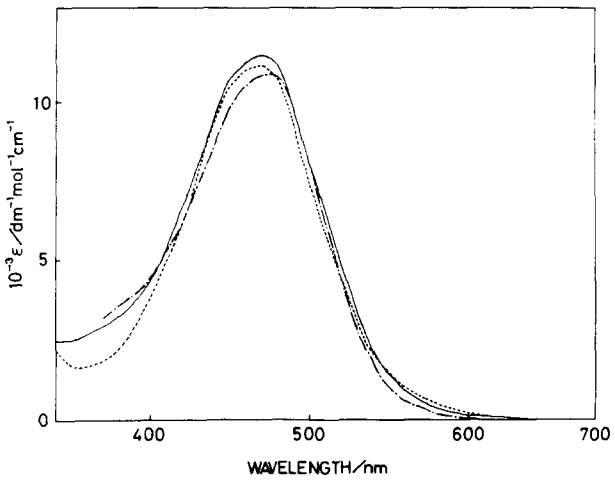


Fig. 2. Estimated absorption spectra of the coloured species (see text): —, **1**; - - -, 1-(1-naphthoxy)anthraquinone; – · –, 1-phenoxyanthraquinone.

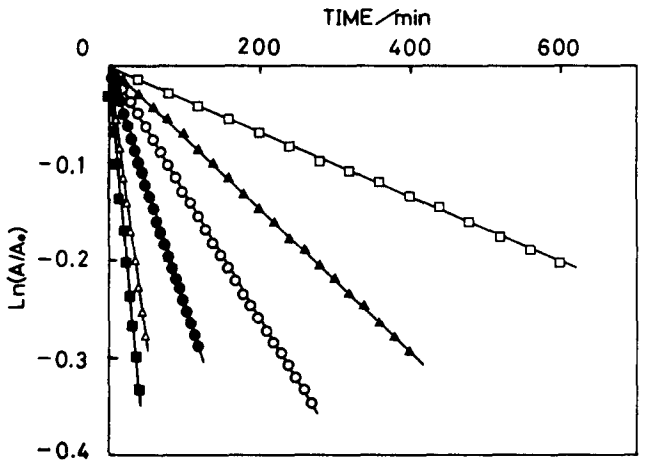


Fig. 3. First-order plot of the decay of coloured species for the following temperatures (kelvins): □, 282.1; ▲, 293.2; ○, 303.5; ●, 313.0; △, 320.8; ■, 328.4.

Table 1
Result of kinetic analysis of the decay of the coloured species based on the mechanism in Scheme 2

Temperature (K)	k_1 ($\times 10^{-6}$ s^{-1})	k_2 ($\times 10^{-5}$ s^{-1})
282.1	0.941	0.468
293.2	1.50	1.07
303.5	4.86	1.67
313.0	8.80	3.20
320.8	19.6	7.36
328.4	42.0	9.90

other cases [11,12]. The Arrhenius plot of k_1 could be analysed using the Marquardt method assuming that k_1 was expressed as the sum of two components. This strongly suggests two reversion processes for the coloured species. The activation enthalpies at 298 K for the two processes estimated from the results of the

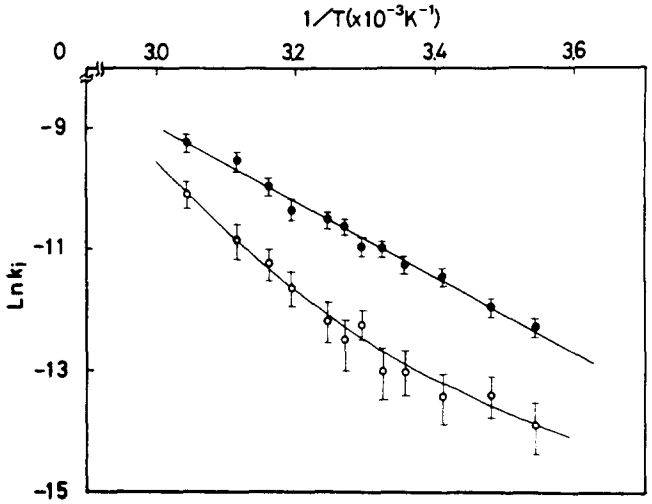


Fig. 4. Arrhenius plots of the rate constants for the decay processes of the coloured species: ○, k_1; ●, k_2.

analysis were the following: $\Delta H_1^{\ddagger} = 30.5$ kJ mol^{-1} and $\Delta H_{1'}^{\ddagger} = 104$ kJ mol^{-1}. The activation enthalpy at 298 K for the change toward the final formation of **2** was found to be 49.1 kJ mol^{-1}. These values were calculated from the activation energy E_a using the relationship

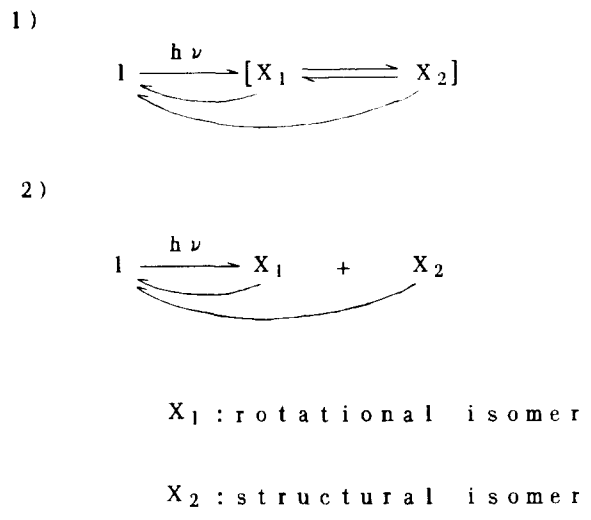
$$E_a = \Delta H^{\ddagger} + RT$$

3.4. Mechanism of the photochromism of 1

As mentioned in the previous section, the decay mechanism of the coloured species is not as simple as those for 1-phenoxyanthraquinone and 1-(1-naphthoxy)anthraquinone. When the reversion of the coloured species to **1** proceeds through only one route, the Arrhenius plot of k_1 is expected to be linear. If the reversion occurs from the rotational isomer, the slope of the plot would have a lower negative value because the process includes no bond dissociation and recombination. In the case of 1-phenoxyanthraquinone, the activation enthalpy for the reversion process was only 8.9 kJ mol^{-1} [11]. If the reversion occurs from the structural isomer, the slope of the plot would have a higher negative value because the process in this case includes bond dissociation and recombination. In the case of 1-(1-naphthoxy)anthraquinone, the activation enthalpy was 83.6 kJ mol^{-1} [12]. Therefore, it would be reasonable to interpret the curved Arrhenius plot of k_1 as having a slope of the tangent to the plot with a smaller negative value in the lower temperature range and, in the high temperature range, it is larger than the negative value (Fig. 4). This interpretation corresponds to the two-component analysis of the previously mentioned plot and suggests that the reversion of the coloured species to **1** consists of two processes having lower and higher activation enthalpies. The lower value of $\Delta H_1^{\ddagger} = 30.5$ kJ mol^{-1} corresponds to the case of

1-phenoxyanthraquinone [11] and the higher value of $\Delta H_1^{\neq} = 104$ kJ mol^{-1} corresponds to the case of 1-(1-naphthoxy)anthraquinone [12].

Reviewing the mechanism in the cases of previous quinones, it is reasonable that the process having a lower activation enthalpy is the reversion from the rotational isomer and the process having the higher activation enthalpy is the reversion from the structural isomer. Therefore, the coloured species in this case has characteristics of both the rotational and the structural isomers. The results suggest the following two cases: (1) the two coloured species of the rotational and structural isomers are in equilibrium and suffer decays via two different pathways from the two isomers (Scheme 3, path 1); (2) the two isomers are simultaneously formed on light irradiation and each species decays independently (Scheme 3, path 2). The rather large activation enthalpy for the conversion from the rotational isomer (X_1) to the structural isomer (X_2) in the case of 1-phenoxyanthraquinone [11] strongly suggests that the former case of equilibrium between the rotational and structural isomers is very unlikely to occur. The discussion, thus, should be focused on the latter case. Two different conformers, A and B, could be equilibrated with each other in equal amounts in the ground state of **1** as shown in Scheme 4. The AM1 calculation indicated that the two conformers have almost the same energy of formation and that the energy barrier between them is very low. On light irradiation of the two conformers, the rotational isomers X_1(A) and X_1(B), and the structural isomers X_2(A) and X_2(B), which correspond, respectively, to the starting conformers A and B, could be formed. Mutual interconversions, $X_1(A) \rightleftharpoons X_1(B)$ and $X_2(A) \rightleftharpoons X_2(B)$, are supposed to be inhibited by a large steric repulsion between the naphthalene and anthraquinone chromophores in X_1 or X_2 for the rotation of the naphthyl–oxygen bond. Supposing Scheme 4 where each conformer, A and B, in equal amounts produces coloured species of either the rotational (X_1) or the structural (X_2) isomer on light irradiation, the obtained results would be most easily explained. Although any definite conclusion about which conformer, A or B, produces which isomer, the rotational or structural isomer, was not obtained, the more serious steric repulsion in X_1(A) than in X_1(B) suggests that conformer A forms the structural isomer, X_2(A), and conformer B forms the rotational isomer, X_1(B). The increase in k_1 with a rise in temperature is caused by a larger increment in velocity of the process from X_2(A or B) to **1**. The kinetic analysis carried out in Section 3.3 is based on the assumption that the extinction coefficients of X_1(A or B) and X_2(A or B) are almost the same. This assumption is supported by the fact that the absorption spectrum of the coloured species of **1** is similar to those of 1-phenoxyanthraquinone and 1-(1-naphthoxy)-anthraquinone as shown in Fig. 2.

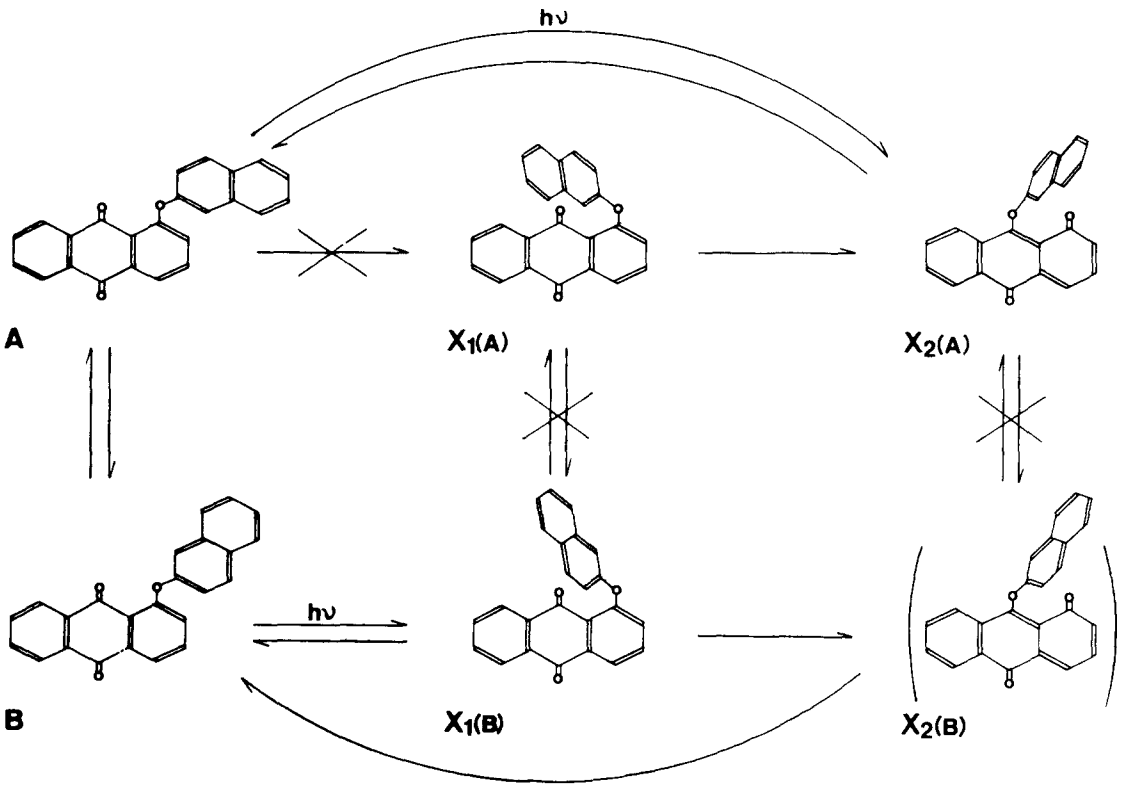


Scheme 3.

Since the coloured species X_2(A or B) reverted to the starting **1** without formation of 1-(1-naphthoxy)anthraquinone, this strongly suggests that the naphthyl group migrates at the same carbon atom of the ipso position in the colouring and reversion processes.

Since the coloration was not quenched by 1-bromonaphthalene ($E_T = 247$ kJ mol^{-1}), 1-cyanonaphthalene ($E_T = 241$ kJ mol^{-1}), having a lower triplet energy than that of **1**, which is estimated to be of a similar value to that of anthraquinone ($E_T = 261$ kJ mol^{-1}), it occurred through the singlet state of **1**. The quantum yield of the coloration was estimated to be about 0.08 assuming the extinction coefficients of X_1 and X_2 are almost the same. The value is less than one-half that for the case of 1-phenoxyanthraquinone.

In the case of the 1-phenoxyanthraquinone rotational isomer, it is initially produced by light irradiation as the first coloured species and then converted to the second coloured species, the structural isomer. In the case of 1-(1-naphthoxy)anthraquinone, only the structural isomer is produced as a coloured species. In the present case of the 1-(2-naphthoxy)anthraquinone rotational isomer and structural isomer, they are considered to be formed at the same time. These differences in the coloured species during the photochromism of 1-aryloxyanthraquinones may be related to the steric repulsion and electronic interaction between the anthraquinone nucleus and the aryl group when they come close to each other. Access of the aryl group to the carbonyl is required during the first stage of migration of the aryl group from the oxygen at the 1-position to that at the 10-position for the formation of the structural isomer. Destabilization due to the steric repulsion between the aryl group and the anthraquinone nucleus, especially the carbonyl group, and stabilization based



Scheme 4.

on electronic interaction between the aryl group and the anthraquinone nucleus are both expected. If the steric repulsion is larger than the stabilization, the migration may further proceed to make 9-aryloxy-1,10-anthraquinone without stopping at the rotational isomer. Since the coloration proceeds through the excited singlet state of **1**, more strictly speaking, the destabilization and stabilization previously mentioned would largely affect the level crossings from the excited states to form either the rotational or structural isomer. Considering that light irradiation triggers movement of the aryl group, the quantum yield of the coloration based on the production of the rotational isomer should be larger than that of the structural isomer, since the structural isomer would be formed through the rotational isomer on the reaction pathway. The difference in the stability of 1-aryloxyanthraquinones in the first stage of the migration process of the aryl group may be one of the factors governing the quantum yield magnitude of the coloration. The actual quantum yields were in the order 1-phenoxyanthraquinone (0.2) > **1** (0.08) > 1-(1-naphthoxy)anthraquinone (0.05).

The coloured species formed during the photochromism of 1-aryloxyanthraquinones are very sensitive to proton-donating reagents. The addition of *n*-butanol to the coloured solution after light irradiation caused a prompt disappearance of the colour. The bimolecular rate constants of the reaction of the coloured species and *n*-butanol were measured in benzene by following the decay in absorption at $\lambda = 470$ nm (Table 2). They were in the order 1-phenoxyanthraquinone > **1** > 1-(1-naphthoxy)anthraquinone. This result may also reflect a difference in the characters of the coloured species.

Table 2
Rate constants of the reaction of the coloured species with *n*-butanol in benzene at 293.3 K

Compound	Rate constant ($\times 10^{-1}$ dm^3 mol^{-1} s^{-1})
1-phenoxyanthraquinone	1.16
1	1.00
1-(1-naphthoxy)anthraquinone	0.657

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