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A colour sensor system based on the photo- or thermal-isomerisation of anthraisoxazoles to phenoxazinequinones

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Abstract

Photo- and thermal-sensitive irreversible colour sensor systems based on the isomerisation of anthraisoxazoles to the corresponding phenoxazinequinones were examined. This reaction was first reported by Gornostaev in 1979 but its application in colour sensor systems have thus far not been studied in terms of the relative rate of isomerisation in solvents and in polymer matrices. Isomerisation produced colour changes from orange to blue, and these colour changes were easily recognized in various sensor systems. The optimisation of the structures through the reaction pathways were evaluated using the MOPAC method and the rate of isomerisation was correlated with substituent effects. It was found that photo-isomerisation proceeded very smoothly but the thermal process at temperatures above 100°C was accompanied by unwanted side reactions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Colour sensor system; Photo- and thermal-isomerisation; Anthraisoxazoles; Phenoxazinequinones; Half-life; MOPAC method

1. Introduction

Non-impact, heat-sensitive recording using leuco dyes as colour former is currently used widely as a conventional recording system [1]. This technology is achieved by the reaction of leuco dyes with acids to produce cationic dyes by means of heat energy from the thermal print head. The main problem of this particular system, however, is the reversibility of the colour developing reactions, as a result of which, the printed colour images are decolourized by light or in a hydrophobic medium. Consequently, this colour former system cannot be used as a sensor system. We have developed irreversible, colour forming system that uses the addition reaction of isocyanate to imines but this process also cannot be used as a sensor system because of its low sensitivity and lack of reactivity to light [2].

A desired colour-forming or colour-changing process could be used as light-sensitive and/or heat-sensitive sensor label systems which should be simply applied, easily accessible and detectable and of low cost. There are many demands for such

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sensor systems, namely temperature-detectable labels for chilled foods, light-exposure labels for oxidation-sensitive foods and confectioneries as well as, colour sensor labels for textiles and plastics.

We were looking for an appropriate, irreversible colour-change system for such purposes, and have examined the photo-sensitive isomerisation of 3-arylthioanthraisoxazoles to give phenothiazinequinones which was first developed by Gornostaev's group in 1979 [3]. These workers reported a series of reactions in which the photo- and thermal isomerisation of substituted anthra[1,9-*cd*]isoxazole-6-one to the corresponding phenoxazinequinone occurred via a nitrene intermediate [4]. Such an isomerisation causes the colour to change drastically, as example from yellow to blue and, as these large colour changes appeared favourable for use as a colour sensor, we studied their reaction in detail.

In this paper, 3-aryloxy(or arylthioxy)-5-anilinoanthra[1,9-*cd*]isoxazole-6-ones were synthesized from 1-amino-2-aryloxy(or arylthioxy)-4-anilinoanthraquinones and isomerisation of the anthraisoxazoles to 7-anilinonaphtho[2,3-*a*]phenoxazine were examined under either photo-irradiative or thermal conditions. This reaction was irreversible and was accompanied by remarkable colour changes. The half-life times for isomerisation were correlated with substituent effects and the structural changes that occurred during the reaction pathways were evaluated from their optimized structures using the MOPAC method. Furthermore, the relative rates of isomerisation in polymer matrices were also evaluated for practical applications.

2. Results and discussion

2.1. Syntheses of aminoanthraquinones **1** and anthraisoxazoles **2**

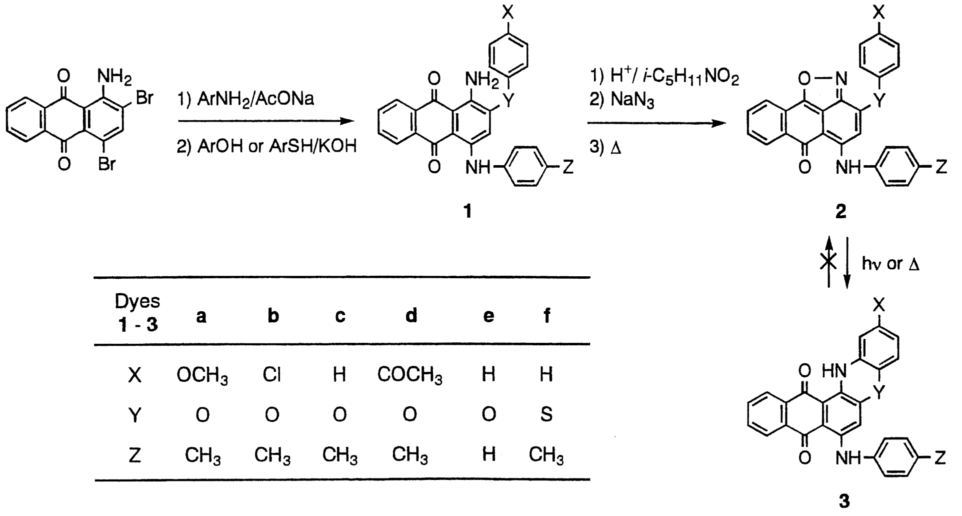
1-Amino-2-phenoxy-(or phenylthioxy)-4-anilinoanthraquinone (**1a**–**1f**) were synthesized from 1-amino-2,4-dibromoanthraquinone by arylamination at the 4-position followed by phenoxylation (or phenylthioxylation) at the 2-position [5]. Diazotisation of **1** with iso-amyl nitrite in acetic acid followed by reaction with sodium azide gave the corresponding 1-azido derivatives which spontaneously decomposed under thermal conditions to give the 3-aryloxy(or arylthioxy)-5-anilinoanthra[1,9-*cd*]isoxazole-6-one **2** (Fig. 1). The yields and some properties of **1** and **2** are summarized in Table 1.

The chromophoric system of the anthraquinones **1** has been studied by the PPP MO method [6]. It is known that the first transition of **1** has strong intramolecular charge-transfer character and the λ_{max} value is affected mostly by the electron donating ability of 1- and 4-substituents rather than the 2-substituent. As a result, the substituent effects of X and Z on the λ_{max} are negligible and that of Y is rather small too. Dye **1f** produces a 17 nm bathochromic shift compared to **1c** due to the stronger donor character of the sulfur atom than the oxygen atom. Anthraisoxazoles **2** no longer have a strong intramolecular charge-transfer chromophoric system, because they lack the quinone acceptor moiety and, consequently, exhibit a large hypsochromic shift of around 90 nm relative to **1**. NMR, MS and elemental analytical characterisation data for **2a**–**2f** are summarised in the experimental section.

2.2. Photo- and thermal-isomerisation of anthraisoxazoles **2** in solution

The photo- and thermal-isomerisation of **2** to the corresponding phenoxazinequinones **3** proceeded smoothly under appropriate conditions. This type of isomerisation of 3-phenoxy-5-hydroxyanthra-[1,9-*cd*]isoxazole-6-one **2g** to give 7-hydroxynaphtho[2,3-a]phenoxazine **3g** is known [3]. In the reaction, a large colour shift from yellow (**2g**) to blue (**3g**) was attained. Changes in colour from orange to blue in the cases of **2a** to **3a** and from red to blue in the cases of **2f** to **3f** were observed. The substituent effects on the relative rate of isomerisation from **2** to **3** were studied from the half-life time ($\tau_{1/2}$) values.

Irradiation of the dye solution at the λ_{max} with monochromatic light (20 nm wavelength range, cf. experimental section) changed the colour of the solution from orange or red to blue. Fig. 2 shows the spectral changes accompanying the photo-isomerisation of **2c** to **3c** in chloroform. The



Dyes 1 - 3	a	b	c	d	e	f
X	OCH$_3$	Cl	H	COCH$_3$	H	H
Y	O	O	O	O	O	S
Z	CH$_3$	CH$_3$	CH$_3$	CH$_3$	H	CH$_3$

Fig. 1. Syntheses and isomerization of anthraisoxazoles **2**.

Table 1
Syntheses and some properties of dyes **1** and **2**

Dye No.	Yield (%)	mp (°C)	λ_{max}[a] (nm)	Dye No.	Yield (%)	mp (°C)	λ_{max}[a] (nm)
1a	69	198–200	603	**2a**	81	205–206	513
1b	67	208–210	603	**2b**	81	>280	514
1c	46	157–159	603	**2c**	52	169–172	514
1d	35	203–204	604	**2d**	46	>280	514
1e	66	196–198	601	**2e**	72	161–162	514
1f	87	237–239	620	**2f**	52	169–170	528

[a] In chloroform

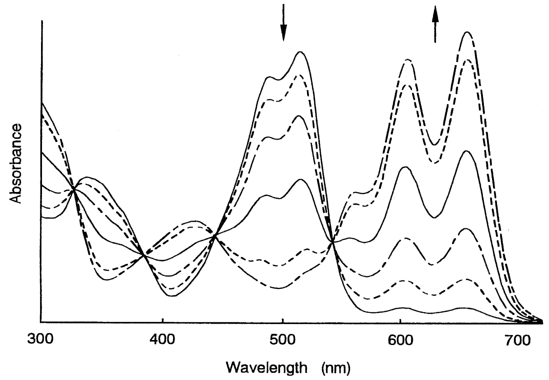


Fig. 2. Spectral changes accompanying the photo-isomerization of **2c** to **3c** in chloroform.

absorbance at 514 nm was lowered and that at 657 nm enhanced as the time of irradiation increased, and isosbestic points at 329, 385, 444 and 543 nm were clearly observed. Similar results were also found in the other cases of **2**. These results indicate that the photo-isomerisation of **2** to **3** proceeds spontaneously without side reactions. The half-life ($\tau_{1/2}$) of each dyes **2a**–**2g** are obtained from their absorption changes. Isomerisation proceeded in the first order reaction and the $\tau_{1/2}$ values are summarized in Table 2.

The $\tau_{1/2}$ values of **2** achieved for photo-isomerisation were little affected by the nature of the substituent *X*; an electron-donating group (**2a**, X=OMe) slightly accelerated the reaction more than that of electron-withdrawing group (**2d**, X=Ac). These results are reasonable from the view point of electrophilic attack of the nitrene in the ring-closure reaction to give **3**. Alternatively, the substituent *Y* largely affected the $\tau_{1/2}$ values; as demonstrated by the value of the phenothiazine (**2f**, 1560 min) compared to the other phenoxazine analogues (**2c**, 4.1 min). The observed large substituent effects ($\tau_{1/2}$, 380 times) found between **2c** and **2f** can be attributed to the size of both atoms involved in the ring-closure reaction ongoing from **2** to **3**. To investigate this result, the optimized structures of **2c** and **2f** were evaluated using the MM2 method (Fig. 3).

It was found that the difference in atomic radius, 0.74 Å for the oxygen atom and 1.04 Å for the sulfur atom, resulted in different optimized structures for **2c** and **2f**; the phenoxy group in **2c** is twisted from the isoxazole moiety but the phenylthioxy group in **2f** is much more twisted and is almost perpendicular from the isoxazole moiety. As a result, the ring-closure reaction to give the phenothiazine ring via the nitrene intermediate may be markedly disturbed in the case of **2f**. The difficulty of the isomerisation reaction was also observed in the thermal reaction of **2f** to **3f** in which the isosbestic points became obscured as the length of longer reaction time increased; other by-products of **3f** were isolated from long range thermal reaction of **2f** in dimethylformamide. Four isolated products were identified in the following yields, **3f** (23%) together with its oxidized product **4** (19%), and the hydrolysis product of the isoxazole ring to give the starting material **1f** (31%) and its oxidized product **5** (7%) (Fig. 4).

Table 2
Half-life time ($\tau_{1/2}$) and activation energy (ΔE) of isomerization from **2** to **3**

Dye No.	$\tau_{1/2}$[a] (min)	$\tau_{1/2}$[b] (min)			$\tau_{1/2}$[c] (min)	ΔE[d] (kJ/mol)
	25°C	110°C	140°C	155°C	140°C	
2a	2.6	407	44	27	67	84
2b	6.0	2100	121	77	113	98
2c	4.1	585	115	39	89	81
2d	30	1729	122	45	95	110
2e	5.8					
2f	1560					
2g	6					

[a] Photo reaction in chloroform at the concentration of 10^{-4} mol/l.

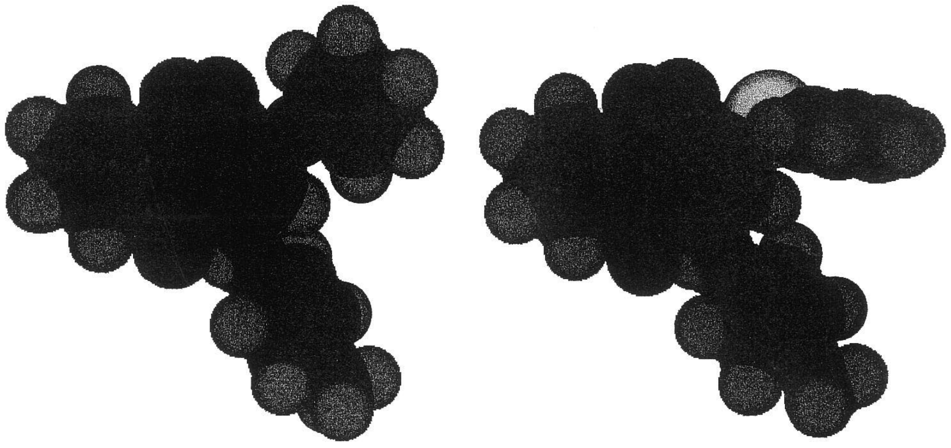
[b] Thermal reaction in dimethylformamide at the concentration of 10^{-4} mol/l.

[c] Thermal reaction in xylene at the concentration of 10^{-4} mol/l.

[d] Activation energy of thermal isomerization in dimethylformamide.

From these results, the oxidation of the aryl ring to give the hydroxy analogues of **3f** and **1f** proceeded after long reaction times due to the difficulty of the ring-closure reaction to give the phenothiazinequinone **3f**.

In the thermal reactions of **2a**–**2e**, the relative rates of isomerisation were accelerated at higher temperatures, in the range 110 to 155°C, but the rates were still slow compared with those for photo-isomerisation. The substituent effects on the value of $\tau_{1/2}$ also differed from those of photo-isomerisation, especially at higher temperatures (Table 2).



2c **2f**

Fig. 3. Differences in the optimized structures of **2c** and **2f** by the MM2 method.

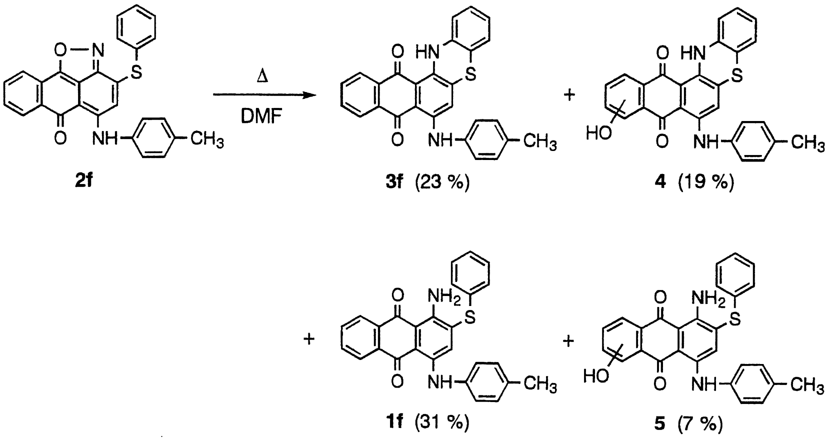


Fig. 4. Thermal reaction of **2f** in DMF at 155°C.

From these findings, it was assumed that, side reactions or decomposition of **2** occured at higher temperatures. The calculated activation energy obtained from the temperature differences in the thermal reaction were 84 kJ mol^{-1} for **2a**, 98 kJ mol^{-1} for **2b**, 81 kJ mol^{-1} for **2c** and 110 kJ mol^{-1} for **2d**. These values are roughly in accord with their $\tau_{1/2}$ value but did not reproduce these quantitatively.

2.3. Simulation of the reaction pathways by the MOPAC AM1 method

The rates of isomerisation of **2c** and **2f** were found to be large because of steric hindrance in their optimized structure (Fig. 3). The MM2 calculation results revealed that the distance between the nitrogen atom at the isoxazole ring and the *ortho*-carbon atom (C'_2) on the phenyl ring of **2f** was much longer (about 1 Å) than that of **2c**. This was in accord with the remarkable differences in their half-life time as well as the decrease in yield of **3f** after thermal reaction which afforded many other by-products (Fig. 4).

The reaction pathways were simulated by the MOPAC AM1 method and the results are shown in Fig. 5. The structural changes from the starting isoxazole (**A**) to the product (**E**) through (**B**) to (**D**) were calculated together with their energy differences; the cleavage of the O–N bond in the isoxazole ring of **A** occurred spontaneously and then was followed by bond rotation around the O–C'_2 axis to form the N–C'_2 bond in **B**, in which the C'_2 atom has sp^3 hybridization. The structure **B** has very distorted phenoxazine ring. Hydrogen atom transfer from C'_2 to C'_3 gave **C** as a meta-stable intermediate which has a non-aromatic ring system. Further hydrogen atom transfer from C'_3 to the nitrogen atom to reproduce the aromatic system gave the product **E**. As a whole, hydrogen abstraction at the C'_2 position by the nitrene affording the N–C'_2 bond gave rise to the phenoxazinequinone **E** which has an almost planar structure and is stable as a dye or a pigment. As a result, an activation energy of 137.9 kJ mol^{-1} was calculated for the first step and another of 92.1 kJ mol^{-1} for the second step. In this preposed mechanism, the nitrene has been reported previously [4].

2.4. Activation energy and solvent effects for the thermal isomerisation

Similar spectral changes to those of the photoisomerisation reaction were obtained for thermal reactions in dimethylformamide at a concentration of 10^{-4} mol^{-1}. The rate of isomerisation under thermal conditions was much slower than that of photo-isomerisation even at 155°C (Table 2). The values of the calculated activation energies (ΔE) suggested that the substituent effects were almost identifical to those in photo-isomerisation in the order of **2d** > **2b** > **2a** > **2c**. Solvent effects

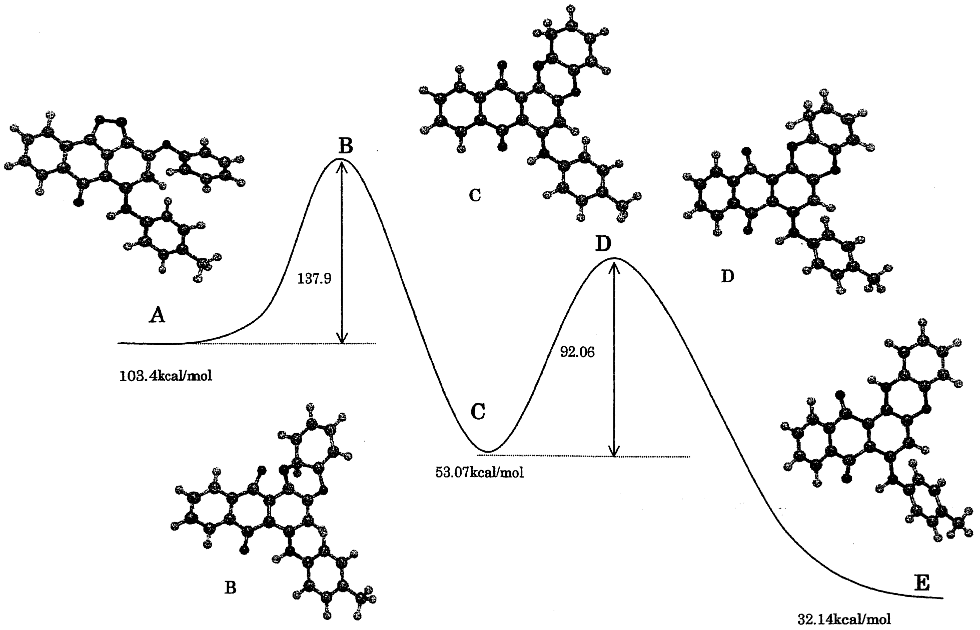


Fig. 5. Stimulation of the reaction pathways by the MOPAC AM1 method.

were observed in the case of thermal-isomerisation and the rate was retarded slightly more in polar solvents (except for **2a**) than in nonpolar solvents. This suggests that the isomerisation was slightly stabilized in polar solvent.

2.5. Isomerisation of **2** *to* **3** *in polymer matrix*

A polystyrene film containing **2c** was prepared by evaporating the solvent from a solution of the two at room temperature. The rate of isomerisation of **2c** in the film was determined under photo- and thermal-conditions. Similar spectral changes having isosbestic points were obtained as reported above in solution. The $\tau_{1/2}$ value for the photo-reaction was 98 min but that for the thermal reaction at 98°C was 204 h. From a comparison of the relative rates of isomerisation in solution (Table 2) and in polymer matrix, the isomerisation reaction was retarded in the polymer matrix because of the restriction of molecular- and/or bond-rotation. The photo-reaction was 125 times faster than the thermal-reaction in the polymer matrix which indicates that both reactions proceeded by different processes; photo-reaction initiated from the first excited state whereas thermal-reaction initiated from the thermal cleavage of the O–N bond in the isoxazole ring.

In conclusion, both the thermal- and the photo-reaction processes can be used as colour sensor systems for various application fields.

3. Experimental

All melting points are uncorrected. Visible spectra were recorded on a Hitachi EPS-3T spectrophotometer at the concentration of 10^{-4} mol^{-1}. ^{1}H NMR spectra were recorded on a Varian Unity-plus 300 NMR spectrometer in deuteriochloroform with tetramethylsilane as an internal standard. Elemental analyses were recorded on a Yanaco CHN Corder MT-3. Column chromatography was carried out on silica gel (Wako gel C-300) using appropriate solvent. Molecular orbital calculations were conducted with MOPAC version 6 [7]. Photo-irradiation was carried out using a Jasco SM-3 type monochromator as a light source. The distance between the light source and the solution cell was kept in constant of 5 cm with all other conditions being kept constant. The rate of isomerisation was calculated from spectral changes in a plot of absorbance versus reaction time.

3.1. Syntheses of **2** *and* **3**

*3.1.1. 3-Phenoxy-5-(4-methylphenylamino)anthra[1,9-*cd*]isoxazol-6-one (***2c***) (general procedure)*

Isoamyl nitrite (286 mg, 2.44 mmol) was added to a solution of **1c** (426 mg, 1.0 mmol) in acetic acid (15 ml) and stirred for 1.5 h at 15–16°C. Sodium azide (83 mg, 1.28 mmol) then added to the solution in the dark and the separated solid was filtered off and then heated in toluene for 5 h under reflux. After removal of the solvent, the product was isolated and purified by column chromatography with toluene as eluent to give **2c**.

2c; ^{1}H NMR (CDCl$_3$): δ 2.25 (3H, s), 6.58 (1H, s), 6.99–7.39 (9H, m, phenyl protons), 7.56 (1H, t, *J*=7.5), 7.68 (1H, t, *J*=7.5), 8.04 (1H, d, *J*=7.5), 8.45 (1H, d, *J*=7.5), 11.48 (1H, s); Mass (*m*/*e*): 418 (M^+); Anal. calcd. for $C_{27}H_{18}N_2O_3$: C 77.51, H 4.34, N 6.70%, found: C 77.34, H 4.46, N 6.55%.

*3.1.2. 7-(4-Methylphenylamino)naphtho[2,3-*a*]phenoxazine (***3c***) (general procedure)*

Dye **2c** (50 mg, 0.12 mmol) in dimethylformamide was heated at 155°C for 75 min in the dark. The reaction mixture was poured into ice-water at room temperature and the separated precipitate was then filtered and purified by column chromatography with toluene as eluent to give **3c**.

3c. 92% yield; mp. 267–268°C; ^{1}H NMR (CDCl$_3$): δ 2.39 (3H, s), 6.58 (1H, s), 6.69–6.71 (2H, m), 6.77 (1H, dt, *J*=7.5, 1.2), 6.87 (1H, dt, *J*=7.5, 1.2), 7.15 (2H, d, *J*=8.4), 7.23 (2H, d, *J*=8.4), 7.66–7.76 (2H, m), 8.29–8.36 (2H, m), 12.07 (1H, s), 12.52 (1H, s); Mass (*m*/*e*): 418 (M^+); UV: λ_{max} (CHCl$_3$): 657 nm; Anal. calcd. for $C_{27}H_{18}N_2O_3$: C 77.51, H 4.34, N 6.70%, found: C 76.81, H 4.67, N 6.75%.

3.2. Characterisation and identification of the products

Dyes **2g** and **3g** were known [3] and were characterized by the following data. **2g**; mp 160–162°C; UV: λ_{max} (CHCl$_3$), 420 nm; ^{1}H NMR (CDCl$_3$): δ 5.98 (1H, s), 7.28 (2H, d, *J*=7.8), 7.37 (1H, t, *J*=7.8), 7.51 (2H, t, *J*=7.8), 7.78 (1H, t, *J*=7.8), 7.90 (1H, t, *J*=7.8), 8.37 (1H, d, *J*=7.8), 8.58 (1H, d, *J*=7.8).

3g; mp. 270–272°C; UV: λ_{max} (CHCl$_3$), 644 nm.

2a. ^{1}H NMR (CDCl$_3$): δ 2.28 (3H, s), 3.76 (3H, s), 6.56 (1H, s), 6.87 (2H, d, *J*=9), 7.01–7.10 (6H, m, phenyl protons), 7.58 (1H, t, *J*=7.5), 7.69 (1H, t, *J*=7.5), 8.07 (1H, d, *J*=7.5), 8.49 (1H, d, *J*=7.5), 11.51 (1H, s); Mass (*m*/*e*): 448 (M^+); Anal. calcd. for $C_{28}H_2ON_2O_4$: C 74.99, H 4.50, N 6.25%, found: C 75.29, H 4.65, N 6.05%.

2b. ^{1}H NMR (CDCl$_3$): δ 2.23 (3H, s), 6.63 (1H, s), 7.03–7.37 (8H, m, phenyl protons), 7.59 (1H, t, *J*=7.8), 7.71 (1H, t, *J*=7.8), 8.07 (1H, d, *J*=7.8), 8.50 (1H, d, *J*=7.8), 11.48 (1H, s); Mass (*m*/*e*): 452 (M^+).

2d. Anal. calcd. for $C_{29}H_2ON_2O_4$: C 75.65, H 4.35, N 6.09%, found: C 75.64, H 4.42, N 5.95%.

2e. ^{1}H NMR (CDCl$_3$): 6.67 (1H, s), 7.19–7.36 (6H, m, phenyl protons), 7.42 (2H, d, *J*=7.8), 7.45 (2H, d, *J*=7.8), 7.65 (1H, t, *J*=7.5), 7.76 (1H, t, *J*=7.5), 8.13 (1H, d, *J*=7.5), 8.55 (1H, d, *J*=7.5), 11.58 (1H, s); Mass (*m*/*e*): 404 (M^+); Anal. calcd. for $C_{26}H_{16}N_2O_3$: C 77.22, H 3.96, N 6.93%, found: C 76.08, H 4.23, N 6.68%.

2f. ^{1}H NMR (CDCl$_3$): δ 2.27 (3H, s), 6.56 (1H, s), 6.84 (2H, d, *J*=8.1), 6.96 (2H, d, *J*=8.1), 7.35–7.58 (5H, m, phenyl protons), 7.55 (1H, t, *J*=7.8), 7.68 (1H, t, *J*=7.8), 8.04 (1H, d, *J*=7.8), 8.44 (1H, d, *J*=7.8), 11.28 (1H, s); Mass (*m*/*e*): 434 (M^+); Anal. calcd. for $C_{27}H_{18}N_2O_2S$: C 74.63, H 4.18, N 6.45%, found: C 75.79, H 4.57, N 5.72%.

3a. 91% yield; mp. 258–260°C; ^{1}H NMR (CDCl$_3$): δ 2.32 (3H, s), 3.64 (3H, s), 6.24 (1H, d, *J*=2.7), 6.34 (1H, dd, *J*=8.7, 2.7), 6.55 (1H, d, *J*=8.7), 6.61 (1H, s), 7.08 (2H, d, *J*=8.1), 7.15 (2H, d, *J*=8.1), 7.59–7.64 (2H, m), 8.19–8.29 (2H, m), 12.14 (1H, s), 12.51 (1H, s); Mass (*m*/*e*): 448 (M^+); UV: λ_{max} (CHCl$_3$): 677 nm; Anal. calcd. for $C_{28}H_{20}N_2O_4$: C 74.99, H 4.50, N 6.25%, found: C 74.62, H 5.05, N 6.15%.

3b. 96% yield; mp. >280°C; ^{1}H NMR (CDCl$_3$): δ 2.40 (3H, s), 6.65 (1H, d, *J*=8.4), 6.74 (1H, d, *J*=1.5), 6.77 (1H, s), 6.87 (1H, dd, *J*=8.4, 1.5), 7.16 (2H, d, *J*=8.1), 7.24 (2H, d, *J*=8.1), 7.64–7.70 (2H, m), 8.33 (1H, d, *J*=8.4), 8.34 (1H, d, *J*=8.4), 12.04 (1H, s), 12.47 (1H, s); Mass (*m*/*e*):

452 (M^+); UV: λ_{max} ($CHCl_3$): 655 nm; Anal. calcd. for $C_{27}H_{17}N_2O_3Cl$: C 71.68, H 3.76, N 6.18%, found: C 71.97, H 4.25, N 5.95%.

3d. 66% yield; mp. >280°C; Mass (*m*/*e*): 460 (M^+); UV: λ_{max} ($CHCl_3$): 649 nm.

3e. 82% yield; mp. 268–270°C; ^1H NMR ($CDCl_3$): δ 6.55–6.68 (3H, m), 6.73 (1H, s), 6.81–6.86 (1H, m), 7.16–7.27 (3H, m), 7.36 (2H, t, $J=7.2$), 7.66–7.69 (2H, m), 8.26 (1H, d, $J=7.2$), 8.30 (1H, d, $J=7.2$), 12.00 (1H, s), 12.51 (1H, s); Mass (*m*/*e*): 404 (M^+); UV: λ_{max} ($CHCl_3$): 650 nm.

3f. 23% yield; mp. 279–281°C; ^1H NMR ($CDCl_3$): δ 2.32 (3H, s), 6.74–6.79 (3H, m), 6.96–7.25 (6H, m), 7.68–7.71 (2H, m), 8.27–8.30 (2H, m), 12.43 (1H, s), 13.12 (1H, s); Mass (*m*/*e*): 434 (M^+); UV: λ_{max} ($CHCl_3$): 693 nm; Anal. calcd. for $C_{27}H_{18}N_2O_2S$: C 74.63, H 4.18, N 6.45%, found: C 74.23, H 4.90, N 5.85%.

Compounds **4** and **5** obtained as by-products in preparation of **3f** were identified from the following data. The position of the hydroxyl group was not be determined for **4** and **5**.

4. mp. 263–265°C; UV: λ_{max} (benzene) 664 nm; Mass (*m*/*e*): 450 (M^+).

5. mp. 145–148°C; UV: λ_{max} (benzene) 639 nm; Mass (*m*/*e*): 452 (M^+).

References

[1] Muthyala R, editor. Chemistry and applications of leuco dyes. Plenum, 1997.

[2] Kabashima K, Hiraishi S, Tanaka M, Matsuoka M. New heat-sensitive irreversible colour former derived from aromatic isocyanate and imino compounds. Dyes and Pigments 1993;23:33.

[3] Gornostaev LM, Levdanskii VA, Fokin EP. Synthesis and thermal and photolytic transformations of 1-azido-2-arylthioanthraquinones. Transcyclisation of 3-arylthioanthra-[1,9-*cd*]isoxazol-6-ones. Zh Org Khim (English version) 1979;15:1692.

[4] Gornostaev LM, Levdanskii VA. Transformations of 1-azido-2-aryloxyanthraquinones and 3-aryloxyanthra[1,9-*cd*]isoxazol-6-ones. Zh Org Khim (English version) 1980;16:2209.

[5] Venkataraman, K. editor. The chemistry of synthetic dyes, vols. 1–8. Academic Press, 1978.

[6] Kogo Y, Kikuchi H, Matsuoka M, Kitao T. Colour and constitution of anthraquinonoid dyes part 1, modified PPP MO calculations and substituent effects. J Society Dyers Colourists 1980;96:475.

[7] Stewart JJP. MOPAC ver. 6, QCPE #455 (revised as ver. 6.01 by Hirano T. JCPE Newsletter 1991;2:26.