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Syntheses and Properties of Functional Aminosquarylium Dyes

Sung Hoon Kim,[a]* Seok Hwan Hwang,[a] Jae Joon Kim,[a]
Cheol Min Yoon[b] & Sam Rok Keum[b]

[a]Department of Dyeing and Finishing, College of Engineering, Kyungpook National University, Taegu, 702-701, Korea
[b]Department of Chemistry, College of Science and Technology, Korea University, Jochiwon, Choong-nam, 339-700, Korea

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ABSTRACT

Aminosquarylium dyes(6a–d) were prepared by condensation of aminosquarates (3a–d) and 1-ethyl-2,3,3-trimethylindolenium iodide (5) and structure of dye 6 was discussed on the basis of IR and solvatochromism. A new aminosquarylium dye 6a absorbed at a longer wavelength (18 nm) than the corresponding squarylium dye 7. The light absorption characteristics of representative examples are well accounted for with the PPP-MO calculation. The photostability properties of dye 6d was also investigated in solution with a high pressure mercury lamp when iodine was replaced by benzene dithiol metal complex as a counter anion, the photochemical stability being better than that of dye 7. © 1998 Elsevier Science Ltd

Keywords: aminosquarilium dyes, inodine, cyanine dyes.

INTRODUCTION

Squarylium dyes are 1,3-disubstituted products synthesized by condensing one equivalent of squaric acid with two equivalents of various types of electron donating carbocycles and heterocycles such as azulenes [1], pyrroles [2], or heterocyclic methylene bases [3] in an azeotropic solvent.

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*Corresponding author.

This class of cyanine dyes has attracted much attention because of their potential application in xerographic photoreceptors [4, 5], optical recording media [6], and organic solar cells [7], on account of their special properties such as photoconductivity and sharp and intense absorption in the visible or near infrared regions [8]. We have reported the synthesis [9] and electrochromic properties [10] of squarylium dyes containing an indoline moiety.

Aminosquarylium dyes, a class of cyanine dyes synthesized from aminosquarate and pyrylium, thiopyrylium, selenopyrylium, benzpyrylium, benzthiopyrylium, benzselenopylium nuclei, have also been found to be useful near infrared dyes (Scheme 1) [11]. These dyes absorb in the near infrared region in dichloromethane and can be used in a laser-addressed thermal imaging system. In comparison with the parent (neutral) dyes, the cationic aminosquarylium dyes are typically more soluble and exhibit similar wavelength, tunable by at least ± 20 nm by changes in the nature of the amino substituent.

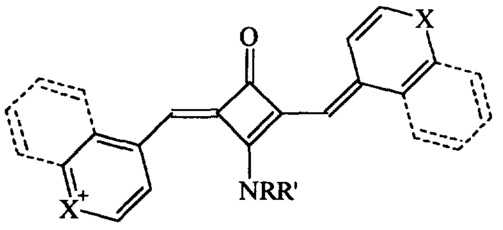
In this study, we report on the synthesis, properties and colour–structure relationships of aminosquarylium dyes **6a–d** containing an indoline ring in the molecule.

EXPERIMENTAL

Melting points were determined using an Electrothermal IA 900 and are uncorrected. The visible and IR spectra were measured using a Shimadzu UV-2100 and a Nicolet Magna-IR 500 Spectrophotometer, respectively. Elemental analysis were recorded on a Carlo Elba Model 1106 Analyzer.

Materials

Squaric acid was reagent grade and used without further purification. 2,3,3-trimethyl indolenine, methyl-, ethyl-, propyl-, and butyl-amines, and ethyl iodide were used without further purification. Organic solvents were reagent grade and used after distillation.



X = O, S, Se

Scheme 1.

Synthesis of aminosquarylium dyes and intermediates

Preparation of 1-ethyl-2,3,3-trimethylindolenium iodide (5)

2,3,3-Trimethyl indolenine (3.9 g, 25 mmol) and ethyl iodide (4.6 g, 30 mmol) were refluxed for 8 h in 250 ml acetonitrile. After the reaction, 1-ethyl-2,3,3-trimethylindolenium iodide was obtained in 56% yield (4.4 g) by filtration.

Preparation of alkylaminosquarates (3a–d) (general method)

Squaric acid (6.84 g, 60 mmol) was refluxed for 14 h in a mixture of 1-butanol (100 ml) and toluene (100 ml). Water was distilled off azeotropically and after the reaction, solvents were removed on a rotary evaporator. Dibutyl squarate was then isolated by vacuum distillation.

Methylamine (0.3 g, 9.4 mmol) was added to a solution of dibutyl squarate (1.06 g, 4.7 mmol) in dicloromethane (20 ml) at room temperature, and the reaction mixture was stirred for 3 h. The slightly cloudy mixture was evaporated to give the aminosquarate as a yellow solid (0.5 g, 56% yield). Ethyl, propyl, butyl aminosubstituted compounds were obtained using a similar procedure. Relevant data for compounds **3a–d** are summarized in Table 1.

Preparation of aminosquarylium dyes (6a–d) (general method)

Methylaminosquarate (**3a**) (0.32 g, 1.7 mmol) and 3.4 mmol of 1-ethyl-2,3,3-trimethylindolenium iodide (**5**) were heated under reflux for 7 h in a mixture of *n*-butanol/benzene (4:1/v:v) containing 0.3 ml quinoline. Water was removed azeotropically using a Dean-Stark trap. The reaction mixture was evaporated and submitted to column chromatography on silicagel with a chloroform/ethanol (5:1/v:v) mixture, to give eluent dye **6a**. Dyes **6b**, **6c**, **6d** were obtained using a similar procedure.

TABLE 1
Yield and Characterization Data for the Alkylaminosquarates

Comps.	*Yield (%)*	*M.p. (°C)*	*MS* M^+	*Formula*	*Analysis (%) Found/Calc.*		
					C	*H*	*N*
3a	56	97	183	$C_gH_{13}NO_3$	59.03	7.34	7.64
					59.01	7.10	7.65
3b	97	55	197	$C_{10}H_{15}NO_3$	59.01	8.14	7.40
					60.91	7.61	7.10
3c	98	54	211	$C_{11}H_{17}NO_3$	62.27	8.86	7.83
					62.56	8.06	6.64
3d	67	40	225	$C_{12}H_{19}NO_3$	64.52	9.32	6.26
					63.90	8.43	6.21

Determination of photochemical stabilities

Solutions of dye (5×10^{-6} mol l^{-1}) in DMF were prepared. These solutions were placed in a UV cell and the cell mounted in a cell holder at room temperature during irradiation using a 100 W high-pressure mercury lamp (Ushio UM-102). The cell was kept at a distance of approximately 10 cm from the light source. The optical densities of the solution were measured before exposing the solutions to the source of irradiation, and after irradiation. The difference between the two measurements, expressed as a percentage of the original optical density, corresponds to the amount of dye decomposed during exposure.

RESULTS AND DISCUSSION

Synthesis of intermediates and dyes

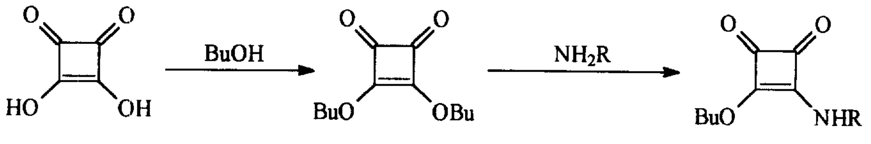
Compounds (**3a–d**) were prepared successfully according to the procedure shown in Scheme 2.

Dibutyl squarate (3) was synthesized by the published procedure [3], and was then reacted with an alkylamine to give **3a–d** as yellow solids. The results are summarized in Table 1. The general procedure used to prepare the aminosquarylium dye is shown in Scheme 3.

The reaction of 2,3,3-trimethylindolenine (4) with ethyliodide in acetonitrile gives 1-ethyl-2,3,3-trimethylindolenium iodide (5). A mixture of **5** and aminosquarates (**3a–d**) in butanol/benzene (4:1/v:v) containing a small amount of quinoline as catalyst was refluxed 7 h to give dyes **6a–d**. The absorption spectra and analysis data are shown in Table 2.

Visible and IR spectra of the aminosquarylium dyes

We have synthesized the squarylium dyes **7** and studied their properties [9]. The IR spectra of **7** do not show any evidence of carbonyl absorption at



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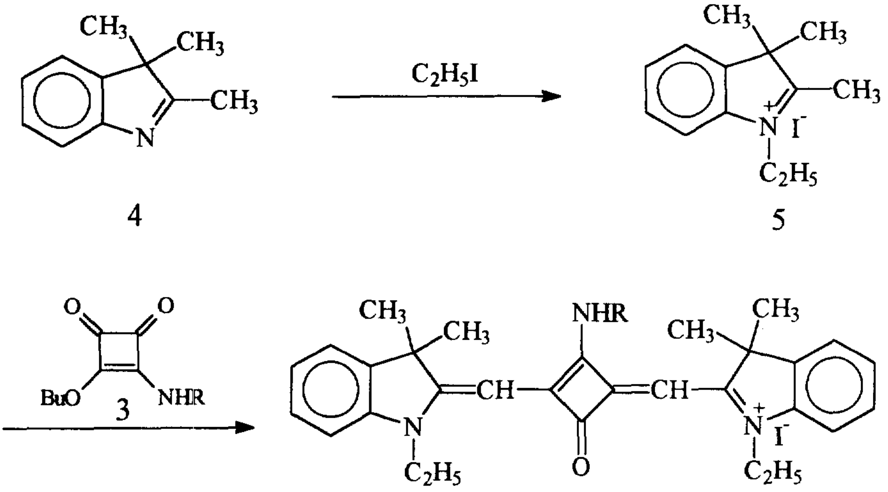
3a, R = CH_3 3b, R = C_2H_5
3c, R = C_3H_7 3d, R = C_4H_9

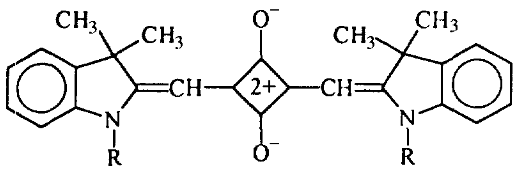
Scheme 2.



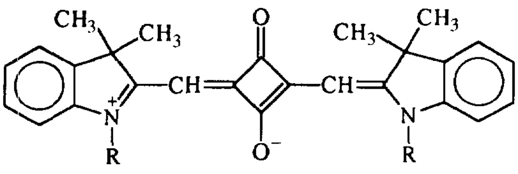
$6a, R = CH_3$ $6b, R = C_2H_5$
$6c, R = C_3H_7$ $6d, R = C_4H_9$

Scheme 3.

approximately $1700\,cm^{-1}$, but exhibit strong absorption bands in the region of $1600\,cm^{-1}$, indicating a strong bonding-delocalization within the four-membered ring system. As the solvent polarity increased, a hypsochromic shift was observed (i.e. negative solvatochromism). From the solvatochromism and IR spectra, it was concluded that structure of the squarylium dyes **7** is the more polar structure **7–I**.



7- I



7- II

TABLE 2
Data for Aminosquarylium Dyes

Dye	*Yield (%)*	*M.p. (°C)*	λ_{max} *(nm)*	ε^a $(\times 10^{-5})$	$\Delta\lambda$	*Analysis Found/Calc.*		
						C	*H*	*N*
6a	9	77	653	0.93	18	63.68	6.41	8.15
						62.76	6.06	7.08
6b	11	231	650	1.47	15	63.71	7.53	5.58
						63.29	6.26	6.92
6c	14	193	651	1.57	16	64.80	7.41	7.61
						63.80	6.43	6.76
6d	15	110	650	1.87	15	63.80	7.21	5.79
						64.28	6.61	6.61
7	66	299	635	8.30	—	78.52	6.75	7.28
						78.60	6.98	7.42

[a] Measured in $CHCl_3$.

Whilst dyes **7** exhibit a strong IR absorption band at $1600\,cm^{-1}$ (Fig. 1) dye **6b** shows characteristics of carbonyl absorption at $1730\,cm^{-1}$ (Fig. 1) and in addition, the IR spectrum shows a broad NH-band at around $3446\,cm^{-1}$.

Visible absorption data for the dyes **6a–d** are summarized in Table 2. Dye **6a** (γ_{max}: 653 nm) absorbs at longer wavelength than dye **7** (λ_{max}: 635 mn), in chloroform, introduction of the methylamino group thus giving a bathochromic shift of 18 nm.

We quantitatively evaluated the colour–structure relationship of these dyes by means of the PPP-MO method. By using slightly modified carbonyl and amino parameters, it was found that a good agreement between experimental and calculated λ_{max}, and f, the oscillator strength, could be obtained (Scheme 4). A good relation was observed between the calculated oscillator strength (f) and the observed molar extinction coefficient (ε).

The f value of dye **6a** was less than that of dye **7**, and this is in agreement with the small observed ε value in dye **6a**. The π electron density changes accompanying the first excitation are shown in Fig. 2.

It was generally found that the alkylamino group acts as a stronger donor than the oxygen residue, and an intramolecular charge-transfer character for the first transition is indicated. From these results, it was concluded that the bathochromic effect caused by the introduction of the alkylamino group in place of the oxygen residue can be attributed to its strong electron-donating property. Solvent effects on dyes **6a–d** in their visible absorption spectra are shown in Table 3. As the solvent polarity increased, a hypsochromic shift was observed (i.e. negative solvatochromism). The negative solvatochromism indicated that these dyes have a larger dipole moment in the ground state than in the excited state.

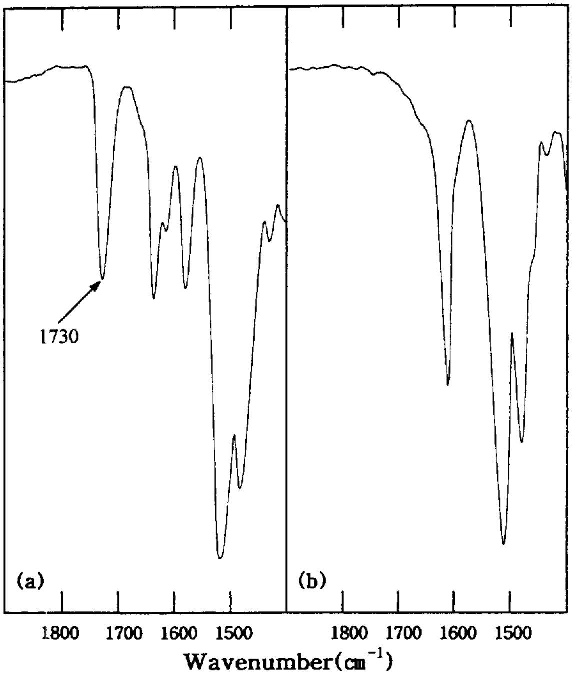
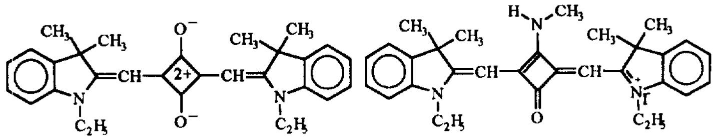


Fig. 1. IR spectra (KBr) of dye **6b** (a) and **7** (b).



7 **6a**

Cal. λ_{max} (nm)	644	672($\Delta\lambda$ = 28)
Obs. λ_{max} (nm)	635	653($\Delta\lambda$ = 18)
Oscillator strength (f)	1.44	1.10
Molar extinction coefficient ($\varepsilon \times 10^{-5}$)	8.30	0.93

Scheme 4.

Photostability properties

The stability of dyes and pigments to light in both solution and polymeric media encompasses a number of problems of technological interest and importance. In this work, the photostability properties of aminosquarylium

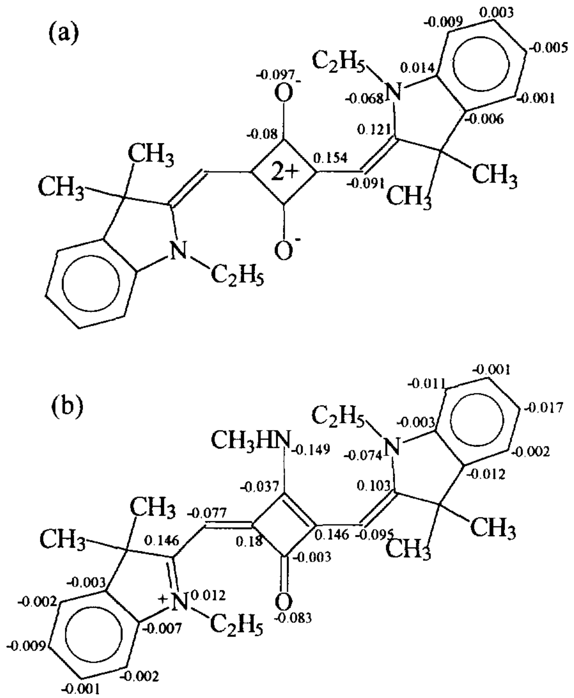


Fig. 2. π-Electron density changes accompanying the first excitation of (a) dye **7** and (b) dye **6a**.

dyes in solution were investigated. The photostability properties of dyes **6a–d** were poor and were inferior to those of the reference dye **7** (Fig. 3). Bisbenzenedithiol derivatives of metal complex have been reported to be superior quenchers for dye media in the optical disk. Namba has reported a highly reflective light resistent cyanine dye film for optical disks consisting of the ionic salt formed between the cationic cyanine dye and the benzenedithiol metal complex anion. This type of cyanine dye is very stable against photon mode degradation, both by environmental light and by the reading light of

TABLE 3
Solvent Effects on Visible Spectra of Dyes **6a–d**

Solvents	*(E_T/kcal·mol^{-1})*	**6a** *(nm)*	**6b** *(nm)*	**6c** *(nm)*	**6d** *(nm)*
MeOH	(55.4)	645	644	645	645
BuOH	(50.2)	650	650	647	647
CH_3CN	(45.6)	652	651	650	647
$CHCl_3$	(39.1)	653	650	651	650
1,4-Dioxane	(36.0)	653	652	654	652
Benzene	(34.3)	657	656	656	656

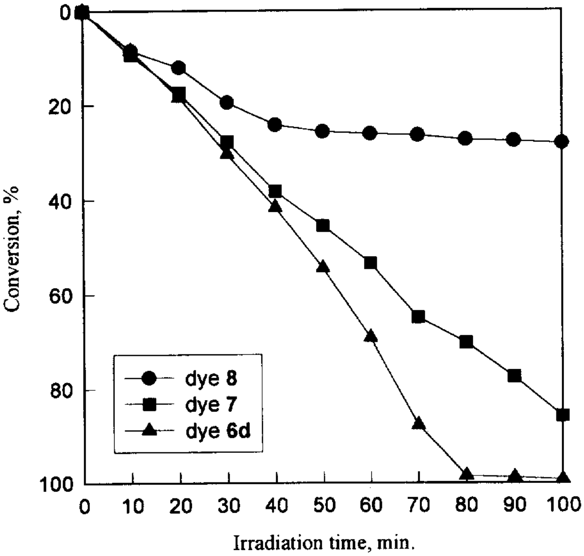
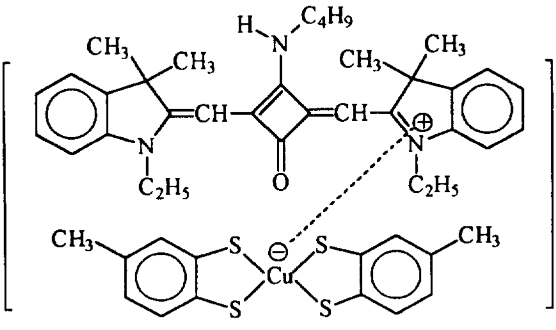


Fig. 3. Photostability of dye **6d**, **7** and **8** in DMF.

the laser diode, compared with the conventional cyanine dye with, for example, perchlorate and halogen anions [12].

Benzene 1,2-dithiol derivatives easily react with a metal salt to give a square-planar bis(benzene-1,2-dithiol) metal complex [13, 14]. The reaction of toluene-3,4-dithiol with copper(II) chloride in the presence of potassium hydroxide or potassium gave a 2 : 1 copper complex which was subsequently heated with tetra-*n*-butyl ammonium bromide to give a cation exchanged 2 : 1 copper complex. Dye **8** was prepared by the reaction of the 2 : 1 copper complex with dye **6d**. Dye **8** gave spectral data in agreement with proposed structures and satisfactory analytical data.



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The influence of the dithiol metal anion on the photostability in DMF solution was investigated and is shown in Fig. 3. When dye **7** was exposed for 50 min, it showed about 50% conversion, but in the case of the dye **8**, it showed 22% conversion. Introduction of a dithiol metal complex as a counter anion thus results in a significant improvement in the photostability.

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