

〈研究論文(學術)〉

Novel Synthesis of Diazaanthraquinone Dye with Infrared Absorption Function

Sung Hoon Kim, Nam Sik Yoon and Yong Jin Lim

Department of Dyeing and Finishing, College of Engineering, Kyungpook National University

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디아자안트라퀴논계 적외흡수 기능성 색소의 합성

김성훈 · 윤남식 · 임용진

경북대학교 공과대학 염색공학과

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Abstract—New Series of diazaanthraquinone near-infrared dye was synthesised by the ring closure reaction between 2,3-dibromodiazaanthraquinone and potassium 2-aminobenzenethiolate. This dye absorbs near-infrared light at 780 nm.

1. Introduction

Quinonoid dyes have been developed as functional dyes for optical information-recording media. A new organic medium incorporating infrared dyes, having a single-layer structure, can be recorded and played back by a laser diode through a substrate, and shows excellent long-term stability properties. As the gallium-aluminum-arsenic diode laser emits infrared light at 800-830 nm, the dyes have to absorb light in the range 700-832 nm. Recently some infrared dyes such as the squarylium and pentamethine cyanine dyes have been reported as suitable for an optical information-recording medium.¹⁾

We have recently reported the synthesis of some phenothiazine and phenoselenazine quinone infrared dyes.²⁾ These dyes absorbed infrared light at about 750-800 nm. In this paper We wish to report the synthesis of new types of diazaanthraquinonoid infrared dye obtained by the reaction with 1,4-dihydroxy-2,3-dibromodiazaanthraquinone and 2-aminobenzenethiolate and to correlate the color structure properties of this dye.

2. Experimental

All melting points are uncorrected. The visible spectra were measured using Shimadzu UV-240 spectrophotometer. Elemental analysis was recorded on a Yanako CHN recorder MT-2

2.1 Preparation of 2,3-pyrazine dicarboxylic anhydride

A solution of glyoxal-sodium bisulfite (40 g) in 150 ml of hot water (80°C) was added dropwise to a suspension of diaminomaleonitrile (14 g) in water (200 ml) for 50 min. The reaction mixture was heated at 60°C for 30 min. After cooling, the resulting solid was separated to give dicyanopyrazine[5] (yield 36%, mp. 131-132°C, lit⁶⁾ 132°C). Compound [7] was prepared by the dehydration of 2,3-pyrazine dicarboxylic acid, which obtained by hydrolysis of [5] with Na₂O₂, with acetic anhydride (yield 30%).

2.2 Preparation of 1,4-dihydroxydiazaanthraquinone

1,4-dihydroxydiazaanthraquinone was synthesi-

sed by the Friedel-Craft reaction of pyrazine dicarboxylic anhydride (0.1 mol) with 1,4-dimethoxybenzene (0.11 mol) at 200°C for 2 hr.

Yield 90%, mp. 280°C, UV (DMF) 630, 650 nm, Elemental analysis, Found; C, 56.21; H, 2.92; N, 13.21; C₁₀H₁₀N₂O₄ requires; C, 55.04; H, 2.75 N, 12.84%.

2.3 Preparation of 1,4-dihydroxy-2,3-dibromodiazaanthraquinone

1,4-dihydroxydiazaanthraquinone (0.1 mol) and iodine (50 mg) were dissolved in conc. sulfuric acid (400 ml), and bromine (11 ml, 0.22 mol) was added dropwise to the solution. The reaction mixture was stirred at 110°C for 6 h, then poured into water. The separated product was collected by filtration, washed with water and recrystallized from benzene to give [10]. Yield 83%, mp. 290-292°C, Elemental analysis, Found; C, 36.18; H, 2.01; N, 9.28; C₁₀H₄N₂O₄Br₂ requires; C, 35.71; H, 1.19; N, 8.33%.

2.4 preparation of diazaanthraquinonoid dye[12]

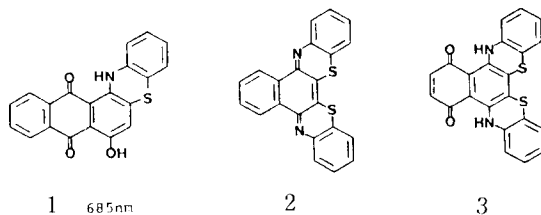
A mixture of 2-aminobenzenethiol (11.1 mmol) and potassium hydroxide (11.1 mmol) in ethanol (100 ml) was added dropwise to a suspension of 1,4-dihydroxy-2,3-dibromodiazaanthraquinone[10] (5.05 mmol) in ethanol (300 ml) at 40°C. The reaction mixture was stirred at 50°C for 7 hr, poured into water and neutralised with aqueous hydrochloric acid. The separated product was collected by filtration, washed with water and recrystallised from chloroform to give [12]. Yield 75%, mp. 249-250°C, Elemental analysis, Found; C, 62.12; H, 2.13; N, 12.15; C₂₂H₁₂N₄O₂S₂ requires; C, 61.63; H, 2.28; N, 13.08%, UV λ_{max} (nm) (CHCl₃) (ε × 10⁻⁴): 780(1.92).

3. Results and Discussion

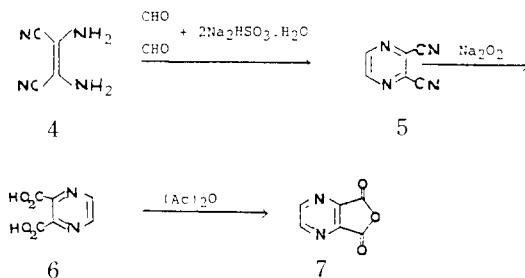
It has been shown that the reaction of 2-bromopyrazinone with 2-aminobenzenethiolate gives 7-hydroxy-14H-naphtho [2,3-a]-phenothiazine-3, 13-dione[1], which has been evaluated as a deep colored disperse dye for polyester.³⁾ On the other hand, the reaction of 2, 3-dichloro-1, 4-naphtho-

quinone with 2-aminobenzenethiol in pyridine gives the bis-ring-closure product, 10,11-dithia-5, 16-diazadinaphtho[3,2a], [2,3-c]-naphthalene [2].⁴⁾ We have also reported that the reaction of 2,3-dibromonaphthazarin with potassium 2-aminobenzenethiolate gives the bis-ring-closure product, 10, 11-dithia-5H, 16H-5, 16-diazadinaphtho [3,2-a], [2, 3-c]-1, 4-naphthoquinone [3], which absorbs near-infrared. light at 725 nm.⁵⁾

The characteristics of dye [3] as an infrared dye for optical recording media are under investigation and the synthesis of diazaanthraquinone analogues of dye [3] is of interest in respect of their characteristics as functional dyes and in their color-structure relationship.



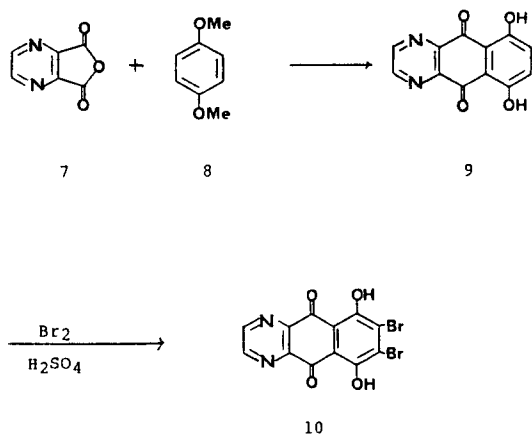
Pyrazinodicarboxylic anhydride [7] was prepared by the hydrolysis and dehydration of dicyano pyrazine [6], which was obtained by the similar method reported by Hinkel *et al.*,⁶⁾ (Scheme 1).



Scheme 1.

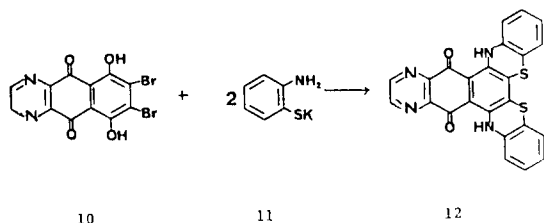
1,4-dihydroxy diazaanthraquinone [9] was synthesised by the Friedel-Craft reaction of pyrazine dicarboxylic anhydride [7] with 1,4-dimethoxybenzene [8]. Bromination of diazaanthraquinone was carried out in sulfuric acid with excess of bromine. Dibromodiazaanthraquinone [10] was obtained mainly at 110°C (Scheme 2).

Reaction of [10] with potassium 2-amino benze-



Scheme 2.

nethiolate [11] resulted in the bis-ring-closure product [12], in 73% yield, and none of the corresponding mono-ring-closure product was obtained.

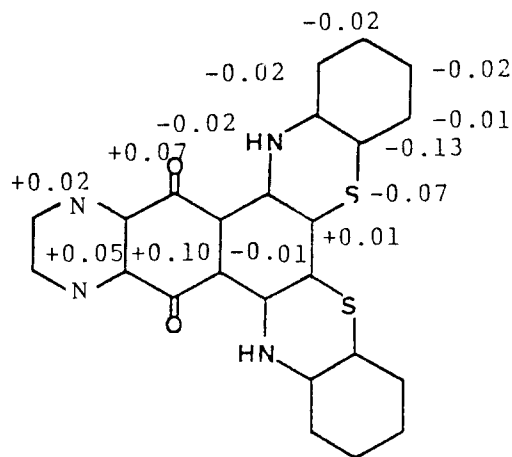


Scheme 3.

Dye [12] absorbs infrared light at 780 nm in chloroform and produces a bathochromic shift of 55 nm in comparison to the corresponding naphthoquinone analogues [3].

We have quantitatively evaluated the color-structure relationship of anthraquinonoid dyes by means of the PPP MO method.⁷⁾

The π -electron density changes accompanying the first excitation of dye [12] are shown in Scheme 4. It was generally found that the epithio group acts as a strong donor together with aryl amino residue, and an intra molecular charge-transfer character for the first transition is indicated.



Scheme 4. π electron density changes accompanying the first excitation of dye [12].

It was concluded that the large bathochromic effect caused by the introduction of the epi-thio group into molecule of phenothiazine quinoid dyes can be attributed to its electron donating properties.

References

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