Synthesis and Properties of Heptamethine Dyes Having Thiopyran Rings

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Abstract

Meso-chloroheptamethine dye having thiopyran rings has been synthesized by an efficient procedure. Furthermore the reactive chloro-group at meso-position of the dye was substituted with thiadiazolethioether groups to give several new heptamethine thiopyrylium dyes. These heptamethine thiopyrylium dyes having thiopyran rings have longer $\lambda_{\text{max}}$ values exceeding 1 $\mu$m in Vis-NIR spectra and $\lambda_{\text{max}}$ of heptamethine thiopyrylium dyes having thiadiazolethioether groups were shifted about 20 nm in the direction of longer wavelength than that of dye having chloro-substituent. These heptamethine thiopyrylium dyes having thiadiazolethioether groups have higher solubilities than that of thiopyrylium dye having chloro-substituent.

Key-words: Heptamethine dye, Thiopyryl ring, Thiadiazolethioether, Synthesis, Vis-NIR spectra

1. Introduction

Along with development of image processing technology, the system which convert electronically entered information signal to laser light output and image using photosensitive material has began to develop in various fields. In this system, materials possessing photosensitive ability in wavelength of infrared laser such as semiconductor and YAG laser need to have high solubility and high photostability.

It was reported that the thiopyrylium dyes having electron withdrawing group such as halogen atom at the meso carbon in the polymethine chain have a low lasing energy conversion efficiency, but it is thought to be effective for high photostability to introduce an electronic donating group in the polymethine chain of thiopyrylium and cyanine dyes. Heptamethine dyes having thiopyran ring are expected to give high bathochromicity to give $\lambda_{\text{max}}$ value exceeding 1 $\mu$m, and moreover the introduction of an electronic donating group to these dyes is expected to give high photostability and high solubility.

In this paper, heptamethine thiopyrylium dye 4 having thiopyran rings was synthesized by an efficient procedure. Furthermore thiopyrylium dyes 6a-d with substituted thiadiazolethioether at meso-position were synthesized for new IR dyes (Scheme 1).

2. Experimental

2.1. General

The $^1$H-NMR spectra were measured on a JEOL ECP-500 spectrometer or JEOL JNM-AL300. Mass spectra were recorded on a JEOL MS-700. Vis-NIR spectra were measured on a JASCO UVIDEC-610 C. Elemental analyses were obtained using a Perkin Elmer 2400 II element analyzer.

2.2. Preparation of 4-methyl-2,6-diphenylthiopyrylium tetrafluoroborate (2)

3-Methyl-1,5-diphenyl-1,5-pentanedione (1) was prepared by heating the solution of acetophenone and acetaldehyde in NaOH/MeOH at 70°C according to the literature. 1,5-Diketone 1 (4.0 mmol), thioacetic acid (8.4 mmol), and boron trifluoride ether complex (25 mmol) were added in ether (3.50 ml), and the mixture was refluxed for 1.5 h under dry air. To the mixture was added a small amount of water and a large amount of ether and precipitated thiopyrylium salt 2 was obtained.

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by filtration in 78% yield as yellow powder. m. p. 205-206°C; 1H-NMR [300.0 MHz, d-acetone] 9.10 (2 H, s), 8.25-8.22 (4 H, m), 7.88-7.78 (6 H, m), 3.11 (3 H, s); C18H15BF4 requires C, 61.74; H, 4.32; S, 9.16. Found C, 61.73; H, 4.41; S, 8.89; UV-Vis (CH2Cl2) λmax 230, 265, 403 nm.

2.3. Preparation of N-[5-anilino-3-chloro-2,4-(propane-1,3-diy)-2,4-pentadiene-1-ylidene] anilinium chloride (3)

Under N2 atmosphere, phosphorus oxychloride (0.12 mol) was added dropwise in DMF (0.17 mol) keeping at 0°C and the solution was stirred for 30 min. To the solution cyclohexanone (0.053 mol) was added and the mixture was refluxed for 1 h. Next, to the mixture was added aniline/EtOH [1:1 (v/v), 18 ml] mixture dropwise at 20°C with constant cooling. After the reaction mixture was kept at the temperature for an additional 30 min the mixture was poured into ice cold H2O/conc.HCl (10:1, 110 ml) and kept in an ice bath for 2 h. Then the precipitated solid was separated by filtration and washed with cold H2O, Et2O, and acetone. The solid of anilinium salt 3 was obtained as purple powder in 79.4% yield (lit. 87%50); m. p. 212°C (lit.220°C); 1H-NMR [300.0 MHz, DMso-d6] 8.53 (2 H, s), 7.62-7.59 (4 H, d, J = 7.5 Hz), 7.48-7.44 (4 H, t, J = 8.0 Hz), 7.29-7.25 (2 H, t, J = 7.5 Hz), 7.24-7.22 (4 H, t), 1.85 (2 H, m); UV-Vis(CH2Cl2) λmax 230, 265, 403 nm.

2.4. Preparation of 4-[4’-chloro-7’-(2”,6”-diphenyl-4”-H-thiopyrane-4”-ylidene) -3’,5’-(propane-1”-,3”-diyl)-1’,3’,5’-heptatriene-1’-yl]2,6-diphenylthiopyrylium tetrafluoroborate (4)

Thiopyrylium salt 2 (1.0 mmol), anilinium salt 3 (0.50 mmol), and sodium acetate (1.0 mmol) were dissolved in acetic anhydride (6 ml) and the solution was heated at 100°C for 30 min. After chilling, the solid of thiopyrylium dye 4 was separated by filtration, washed with acetic acid and ethanol, and purified by column chromatography on silica gel by using 1,2-dichloroethane : acetone (10:1 (v/v)) as eluent. Thiopyrylium dye 4 was obtained in 12% yield as brown powder. 1H-NMR [300.0 MHz, CF3COOD] 8.69 (2 H, s), 8.62 (2 H, s), 7.87-7.81 (8 H, t, J = 7.7 Hz), 7.72-7.67 (4 H, m), 7.65-7.58 (10 H, m), 7.20-7.14 (2 H, d, J = 15.6 Hz), 2.69 (4 H, m), 1.94 (2 H, m); C44H34BC1F4S2 requires C, 70.54; H, 4.57; S, 8.56. Found C, 70.25; H, 4.84; S, 8.65; (M-BF4)⁺ 662. NIR(CH2Cl2) max 1058 nm (ε 254000).

These spectral data were identical with that of commercial thiopyrylium dye 4.

2.5. Preparation of thiopyrylium dye 6a-d: general procedure

Thiadiazolethiols 5a-d were obtained commercially (Mitsubishi Chemical). Thiopyrylium dye 4 (0.1 mmol) and thiadiazolethiols 5a-d (0.3 mmol) was dissolved in anhydrous DMF (10
Thiopyrylium salts are synthesized from corresponding pyrylium salts and this procedure is widely used\textsuperscript{24, 26}.

4-Methyl-2,6-diphenythiopyrylium salt (perchlorate) is prepared by the reaction of 2,6-diphenylcyclohexanone with methylmagnesium iodide and following dehydration-dehydrogenation\textsuperscript{27, 28}.

In this paper, more convenient procedure for the preparation of thiopyrylium salt 2 was used via only one step reaction from easily obtainable diketone. 3-Methyl-1,5-diphenyl-1,5-pentadiene(1) was prepared from acetophenone and acetaldehyde according to the literature\textsuperscript{29}.

4-Methyl-2,6-diphenythiopyrylium tetrafluoroborate (2) as one starting material for both end groups was prepared directly from 1,5-diketone 1 with thiaoetic acid as sulfuration agent and boron trifluoride, and oxygen in air\textsuperscript{30}. The thiopyrylium tetrafluoroborate 2 was confirmed by the identical $\lambda_{\text{max}}$ with that of corresponding perchlorate. N-[5-Anilino-3-chloro-2,4-(propane-1’,3’-diyl)-1’,3’,5’-heptatriene-1’-yl]-2,6-diphenylthiopyrylium tetrafluoroborate 2 was confirmed by the identical $\lambda_{\text{max}}$ with that of corresponding perchlorate. N-[5-Anilino-3-chloro-2,4-(propane-1’,3’-diyl)-1’,3’,5’-heptatriene-1’-yl]-2,6-diphenylthiopyrylium tetrafluoroborate 2 was confirmed by the identical $\lambda_{\text{max}}$ with that of corresponding perchlorate.

These dyes were identified by $1^H$-NMR, melting point, and absorption spectra. Identification from $1^H$-NMR spectra of thiopyrylium dyes 4 and 6a-c in chloroform was not clear because of their low solubility, and the signals of $1^H$-NMR in DMF gave broad peaks. It is thought that overlapping of the signals was caused by cation radical having a number of localized state in the conjugated system. Therefore, $1^H$-NMR spectra of these dyes were measured in trifluoroacetic acid-$d_6$ as solvent, in which they seem to give a dication form 1) .

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wavelength than thiopyrylium dye 4 having chlorogroup and the molar absorption coefficient $\varepsilon$ of 6a is lower than that of 4. Other thiopyrylium dyes 6b,c having thioether groups gave the same $\lambda_{\text{max}}$ (1078 nm, 1080 nm ; $\varepsilon$ 153000, 136000) with that of 6a. Usually the effect on the $\lambda_{\text{max}}$ shift of electron donating group at meso-carbon in alternate hydrocarbon non-star group is hypsochromic. Therefore this bathochromic shift is thought to be caused by the effect of distortion of C-C bond from the steric hindrance of bulky thiadiazole substituent, which has more influence on the absorbance than the effect of electron donative thioether group at meso-carbon.

The solubility of thiopyrylium dye 4 in cyclohexanone was 0.02 g/l (20°C) and the solubilities of thiopyrylium dye 6a-c having thioether groups in cyclohexanone were 0.4 (6a), 1.0 (6b), 1.2 (6c) g/l(20°C). Thus these thiopyrylium dyes 6a-c having thioether groups have higher solubilities than thiopyrylium dye 4.

4. Conclusion

Meso-chloro heptamethine dye having thiopyran rings was synthesized by an efficient procedure and the substitution of the chloro group with thiadiazolethiols gave their corresponding thiopyrylium dyes having thioether group. These new thiopyrylium dyes have excellent bathochromicity in Vis-NIR spectra to $\lambda_{\text{max}}$ exceeding 1 $\mu$m. These bathochromic shifts are thought to be caused from the steric hindrance of bulky thiadiazole substituent. Moreover these thiopyrylium dyes having thioether group have high solubilities and these properties showed these dyes can be expected to be excellent photosensitive material for IR laser.

References
チオビラン環をもつヘプタメチン色素の合成と性質

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要　旨

チオビラン環をもつメトキシクロロヘプタメチン色素を効率的な方法で合成した。さらにそのクロロ基をチアアジゾールチオエーテル類で置換して一連のチオエーテル基をもつ新ヘプタメチンチオピリリウム色素を合成した。これらのヘプタメチンチオピリリウム色素はこのチオエーテル置換によりクロロ置換のものよりも極大吸収波長が長波長側にシフトし、1μm以上となった。またこれらチオビラン環をもつヘプタメチンチオピリリウム色素はクロロ置換のものより高い溶解性を示した。