

Quinoxaline 유도체를 포함하는 공액이중결합을 갖는 염료들의 합성과 특성

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Synthesis and characterization of π -conjugated dyes containing quinoxaline derivatives

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1. Introduction

In recent years the interest in research and development of functional dye and π -conjugated polymer containing functional moiety has been larger. there has been many research papers concerning new synthetic method and mechanism of polymer containing quinoxaline as a functional moiety. Because of 1,4-position nitrogen atoms, quinoxalines have electron-accepting properties¹⁻⁴. And it is known that their characteristics can be controlled by modifying substituents and their locations in the structure⁵⁻⁶.

In this study, we designed and synthesized several quinoxaline derivatives varying the connecting groups with electro-donating abilities to research the effects of connecting groups in dyes and functional moieties of polymers. Also their optical properties was investigated.

2. Experimental

2.1 General Methods

¹H NMR spectra were recorded on a Bruker DRX-300 FT-NMR Spectrometer in chloroform-*d*₆ and chemical shifts were reported in ppm unit with tetramethylsilane as an internal standard. UV-visible absorption curve obtained in chloroform/methanol(10/1) on an UNICAM 8700.

All chemicals were reagent grade and used without further purification.

2.2 Synthesis

2,3-Bis-bromomethyl-6,7-bis-(3-methyl-butoxy)-quinoxaline(1)

The reaction mixture of 1-bromobutane-2,3-dion(13.7g, 56mmol), an equivalent amount of 1,2-bis-(3-methyl-butoxy)-4,5-diaminobenzene and a catalytic amount of p-touenesulfonic acid in methanol (40ml) was agitated for 1hr below 5°C. 1,2-bis-(3-methyl-butoxy)-4,5-diaminobenzene was prepared by the literature process. After the reaction was completed, the precipitate was filtered off. The crude product was purified with column chromatography and after removing solvent greenish yellow solid was obtained in 55% yield

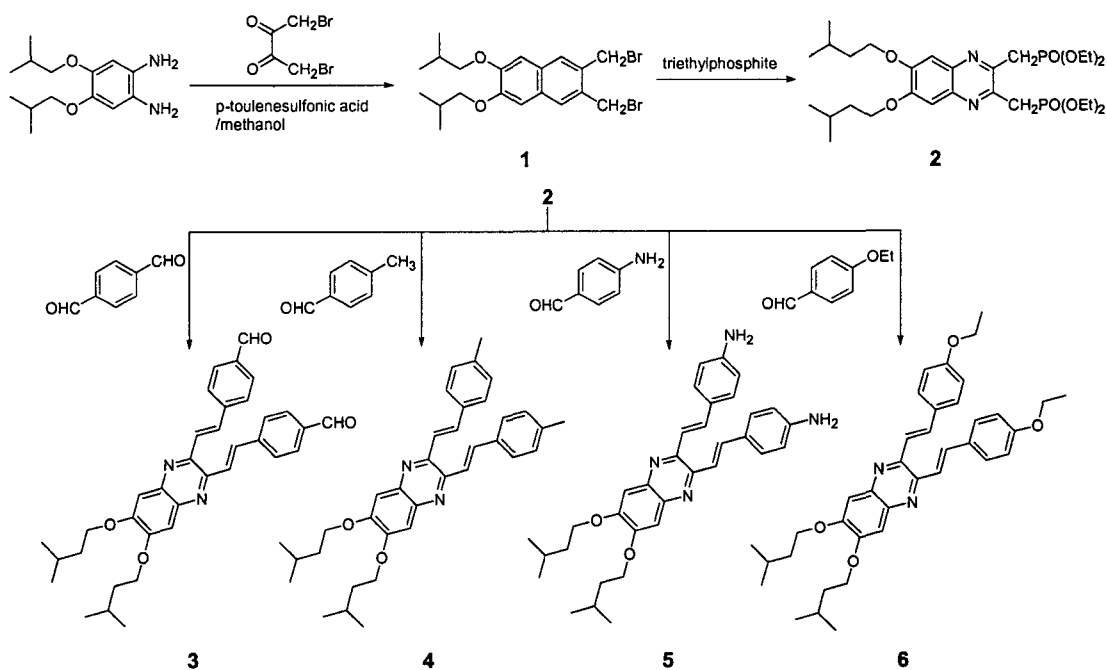
[3-(Diethoxy-phosphorylmethyl)-6,7-bis-(3-methyl-butoxy)-quinoxalin-2-ylmethyl]-phosphonic acid diethylester(2)

The direct phosphorylation of compound 1 gave to [3-(Diethoxy-phosphorylmethyl)-6,7-bis-(3-methyl-butoxy)-quinoxalin-2-ylmethyl]-phosphonic acid diethyl ester(2) in 95% yield. this crude

product was used in next step with out purification.

Synthesis of novel quinoxaline derivatives

2,3-Bis[4-(2-ethenyl)-benzaldehyde]-6,7-bis(3-methyl-butoxy)quinoxaline(3), 2,3-bis-(2-p-aminobenzyl-vinyl)-6,7-Bis-(3-methyl-butoxy)-quinoxaline(4), 6,7-Bis-(3-methyl-butoxy)-2,3-bis-(2-p-tolyl-vinyl)-quinoxaline (5) and Bis-[2-(4-ethoxy-phenyl)-vinyl]-6,7-bis-(3-methyl-butoxy)-quinoxaline(6) were synthesized by the Horner-Wadsworth-Emmons (HWE) reaction. Sodium hydride(0.16g, 6mmol) was added to a solution of 1,4-dibenzaldehyde(4.0g, 30mmol) in 40ml tetrahydrofuran with stirring at 0°C. To the reaction mixture, a solution of 2(3.62g,6mmol) in 40ml tetrahydrofuran was dropwised and 5ml methanol was added. The reaction mixture was refluxed for 2hrs. After the reaction was completed solvents were removed. the crude product was purified by column chromatography in 70% yield. the synthetic routes of 4, 5 and 7 were same as 3 and shown in scheme 1.



Scheme 1 Reaction route of quinoxalines

Halochromism of quinoxaline derivatives

UV-visible spectra of quinoxaline derivatives except 4 in chloroform/methanol(10/1) were measured varying the ratio of quioxaline : *p*-tolunesufonic acid form 1:0 to 1:32. And UV-visible spectra of 4 in same solvent system was measured varying the mole ratio of quioxaline : *p*-tolunesufonic acid form 1:0 to 1:7.5

3. Result and Discussion

The HWE reactions of [3-(Diethoxy-phosphorylmethyl)-6,7-bis-(3-methyl-butoxy)-quinoxalin-2-ylmethyl]-phosphonic acid diethyl ester and several substituents in tetrahydrofuran were successfully carried out

and gave novel quinoxalines in good yield.

The absorption spectra in chloroform/methanol(1/10) is shown Figure 1, 2, 3, 4 and 5. Every Quinoxaline derivatives showed bathochromic shifts with increasing the portion of *p*-toluenesulphonic acid. the absorption spectra shifts at short and long wavelength of 3, 5, 6, 7 decreased and increased uniformly form 1:0 to 1:32(the mole ratio of quioxaline : *p*-toluenesulfonic acid) but the absorption spectrum of 4 shifted dramatically from 1:0 to 1:3 and don't shoft above 1:7. this result was attributed to electron-donating ability of substituent. The stronger the electron-donating ability of substituent is, the easier the 1,4 position nitrogen atoms of quinoxaline with strong electron-withdrawing ability is protonated. In the case of 4, it is supposed that because the amino group of substituent has lone pair electron, the 1,4 position nitrogen atoms of quinoxaline is protonated easier and saturated with electrons by less *p*-toluenesulphonic acid than them of other quinoxalines are. Thus it is expected that quinoxaline derivative substituted with strong electron-donating group can be a good biosensor devise which reflexes sensitively by acidic condition.

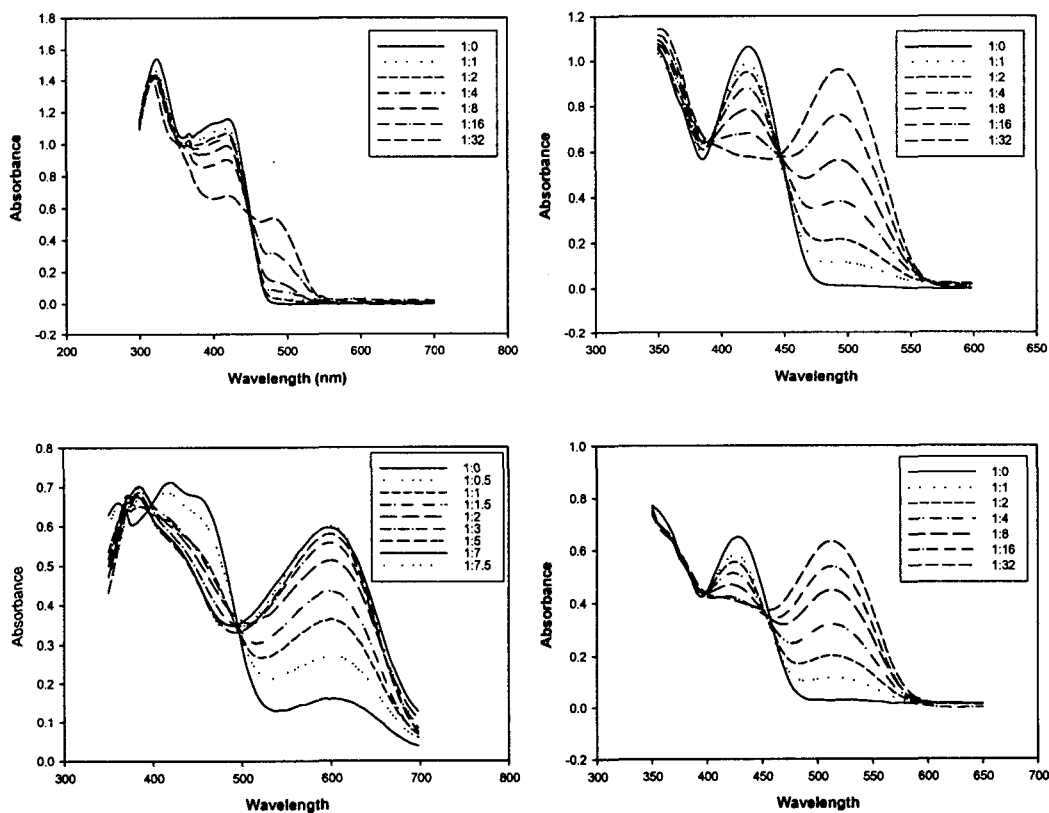


Figure 1. UV-visible spectra of quinoxalines varying the concentration of *p*-toluenesulphonic acid

4. Conclusion

Novel quinoxaline derivatives connected with electron-donating groups were successfully synthesized, and their UV-Visible absorption spectra showed bathochromic shifts. In particular,

UV-Visible absorption spectra of 4 with the strongest electron-donating group has shifted by less p-toluenesulfonic acid.

5. References

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