Spiropyran을 도입한 신규 2,3-dicyanopyrazine 유도체의 합성과 물성

이범훈, 정재윤

한양대학교 섬유공학과

Synthesis and characteristics of 2,3-dicyanopyrazine derivatives substituted spiropyran

Bum Hoon Lee and Jae Yun Jaung

Department of Textile Engineering, Hanyang University, Seoul, Korea

1. Introduction

Pyrazines are known to exhibit a range of physiological activities. As we mentioned earlier, the importance of dicyanopyrazine derivatives lies mainly in the chemical industry and many other fields such as food, agricultural, medicinal chemistry because of their specific properties. And then, a large number of research papers have been published about the characteristics of dicyanopyrazine derivatives[1, 2]. Recently, highly functionalized 2,3-dicyanopyrazine derivatives are important in a broad range of chemistry fields concerned with the application of dyestuff, electroluminescence materials and so on[3].

For many years, a large number of spiropyran based on molecular systems have been reported. Spiropyrans exhibit two forms, colorless closed spiro form and colored open merocyaine form(scheme). The physical and photochromic properties of spiropyran are highly depended on their structure and environment.

We have interested in the specific properties of pyrazine derivatives and spiropyran compounds. Therefore, 2,3-dicyanopyrazine derivatives was introduced to 6-position of spiropyran. The coupling reaction of 6-iodospiropyran(**14**) with 2,3- dicyanopyrazine derivatives(**10**) including terminal acetylene gave a novel compound(**15**). In this report, the influence of 2,3-dicyanopyrazine derivatives introduced by direct coupling reaction into 6-position of spiropyran on thermal properties and photochromic characteristics has been studied.

2. Results and Discussion

Wittig reaction of alkoxylbenzaldehyde(**2**) and (4-bromobenzyl)-phosphonic acid diethylester(**5**) in tetrahydrofuran under refluxed conditions gave the 4-[2-(4-alkoxyphenyl)-vinyl]-bromobenzene (**6**) and then 4-[butane-(4-alkoxy-phenyl)-2,3-dione]-bromobenzene (**7**) was prepared by heating corresponding **6** in dimethylsulfoxide with iodine[4]. 1-(4-Alkoxy-phenyl)-2-(4-trimethylsilanylethynyl -phenyl)-ethane-1,2-dione(**8**) and 1-(4-Ethynyl-phenyl)-2-(4-alkoxy-phenyl)-ethane-1,2-dione(**9**) were synthesized by the well-known method in good yield[5]. 2,3-dicyano-5-(4-alkoxy-phenyl)-6-(4-ethynyl-phenyl)-pyrazine(**10**) was synthesized by the condensation reaction of diaminomaleonitrile (DAMN) and **9** in methanol. 6-Iodospiropyran was prepared according to a literature procedure[6]. 2,3-Dicyano-5-(4-octyloxy-phenyl)-6-(4-(6'-indolinobenzopyran)ethynyl-phenyl)-pyrazine(**15a**) and 2,3-dicyano-5-(4-decyloxy-phenyl)-6-(4-(6'-indolinobenzopyran) ethynyl-phenyl)-pyrazine(**15b**) were synthesized by coupling reaction of compound **10** with **14** in the presence of $PdCl_2$, $P(Ph_3)$, and CuI. The results are summarized in scheme 1 and table 1.

The structural assignments for product **10** and **15** were established on the basis of ir, ^{1}H-nmr and mass spectral data as well as microanalyses.

From the ir spectra of **10** and **15**, the stretching vibrations of C≡N for **10** and **15** were observed appearing 2202 and 2240 cm^{-1}, respectively. For the compound **10**, we noticed the band of C≡C-H at 3297 cm^{-1}. These bands disappeared upon **15**. We expect that the coupling reaction was completely(figure 1). Table 2 shows the visible and fluorescence spectra of compound in chloroform solution. The absorption and fluorescence maxima of compound **10** and **15** were observed at 318~387nm and 482~488nm, respectively. The bathochromic shifts of compound **15** compared with **10** are attributed to the extended π-conjugation system and their electron donating ability. The fluorescence maxima were observed at 482 and 488nm. The stokes' shift were 164 and 102nm, respectively.

3. Experimental

^{1}H NMR spectra were taken on a in deuterated chloroform on a Bruker DRX-300 FT-NMR Spectrometer. Infrared spectra were taken on a MAGNA-IR 760 spectrometer using KBr pellets. Melting points were determined on a JISICO melting point apparatus without correction. Mass spectra were obtained using a JEOL JMS-DX303 Mass Spectrometer. Elemental analyses were performed on a CE instruments EA-1110 Elemental Analyzer. The visible and fluorescence spectra were measured on UNICAM 8700 and SHIMADZU RF-5301PC spectrophotometer,

respectively. All chemicals were reagent grade and used without further purification.

General procedure of ***10***

A solution of **9**(12mmol), DAMN (15mmol) and a catalystic amount of p-toluenesulfonic acid in methanol(10mL) was refluxed for 4h. After reaction was complete, the mixture was cooled at room temp.. The precipitate was filtered off and washed with methanol. The crude product was recrystallized from n-hexane as yellow powder (75-82%).

General procedure of ***15***

A mixture of **14**(5mmol) , $PdCl_2$(5mol%), PPh_3(10mol%), CuI(2.5mol%), and triethylamine(15mmol) in THF(10mL) was refluxed. To the refluxing solution was added a **10**(5mmol) over 10min. After the solution was refluxed for 2h, the precipitate was filtered off. The crude product was chromatographed on silica gel using a mixture of ethylacetate and hexane(1:5) as eluant, and concentrated to give yellow powder(45~50%).

4. References

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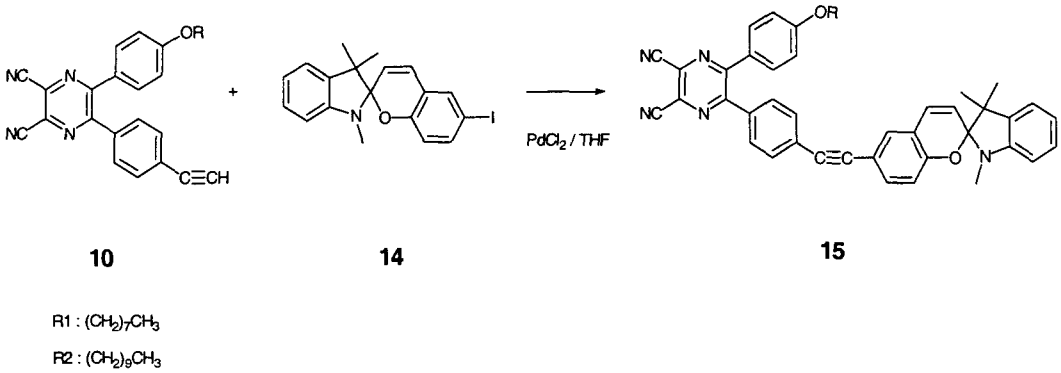
Table 1. Analytical Data for 10 and 15

Comp.	Formula	MP(℃)	Calculated (Found, %)		
			C	H	N
10a	$C_{28}H_{26}N_4O$	59-60	77.39(75.78)	6.03(6.01)	12.89(12.56)
10b	$C_{30}H_{30}N_4O$	79-80	77.89(76.44)	6.54(6.57)	12.11(11.69)
15a	$C_{47}H_{43}N_5O_2$	108-110	79.52(77.42)	6.11(6.09)	9.87(9.46)
15b	$C_{49}H_{47}N_5O_2$	117-120	79.75(77.97)	6.42(6.45)	9.49(9.14)



10 **14** **15**

R1 : $(CH_2)_7CH_3$

R2 : $(CH_2)_9CH_3$

Scheme 1. Reaction route of **15**

Table 2. Visible and Fluorescence Spectra of 10 and 15

Comp.	λmax(nm)[a]	Fmax(nm)[b]	SS[c]
10a	318	482	164
10b	318	482	164
15a	386	488	102
15b	386	488	102

a : In chloroform

b : Fluorescence maximum excited at λmax

c : Stokes' shift

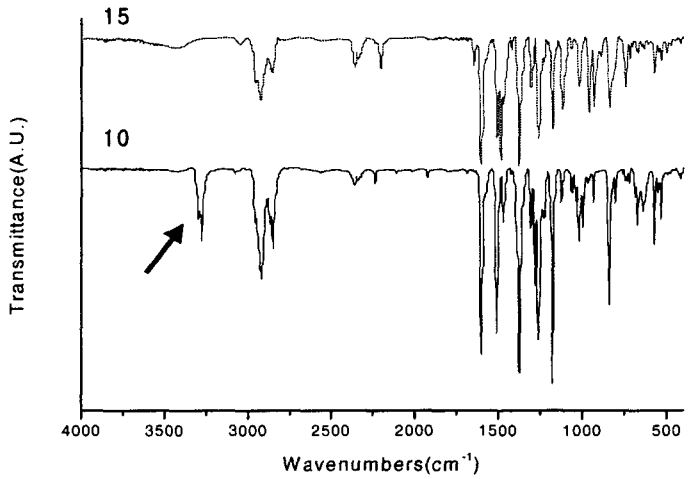


Figure 1. FT-IR spectra of **10** and **15**.