

신규 2,3-dicyanopyrazine유도체의 합성과 특성

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Synthesis and characteristics of 2,3-dicyanopyrazine derivatives.

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1. Introduction

2,3-Dicyanopyrazine derivatives have been synthesized by condensation of diaminomaleonitrile(DAMN) and α -diketone compounds. Diaminomaleonitrile (DAMN) is well known as a tetramer of hydrogen cyanide and a useful compound in the chemical industry not only as a starting material for synthesis of various heterocyclic compounds but also as an intermediate for synthesis of glycine, adenine, guanine et al[1]. The condensation reactions of diaminomaleonitrile (DAMN) and α, β -dicarboxyl compounds have been reported by Begland. Tetrafunctional pyrazines, as a major product, could be prepared by various reaction conditions[2, 3]. Pyrazines are known to exhibit a range of physiological activities. The reactivity and biological activity of mono-substituted or bis-substituted dicyanopyrazines have been reported by Hou and co-workers[4, 5]. As mentioned earlier the importance of dicyanopyrazine derivatives lies mainly in the chemical industry and many other field such as food, agricultural, medicinal chemistry caused by their specific properties. And then, a large number of publications and patents had been issued on the characteristics of dicyanopyrazine derivatives[6, 7, 8, 9]. For example, they could be usefully used as agricultural fungicide, active ingredients of herbicides and fluorescing agents. Recently, highly functionalized 2,3-dicyanopyrazine derivatives are important in a broad range of chemistries involved the application of dyestuff, electroluminescence material and so on[10]. Certain compounds can be usefully used as monomer or crosslinking materials to prepare conductive polymer[11] and as precursor to synthesize phthalocyanines. Because of the specific properties of 2,3-dicyanopyrazine derivatives result from the two strong electron withdrawing cyanogroup on the pyrazine ring.

We were interested in the electro deficiency of the pyrazine ring, and then synthesized novel push-pull type 2,3-dicyanopyrazine derivatives, which have alkoxyphenyl substituent as an electron donor group at 5-position, and nitrophenyl substituent as an electron acceptor group at 6-position of the pyrazine. These compounds should show specific chemical, spectral properties, owing to the extension of π -conjugate system and intramolecular π - π interaction. If these compounds have fluorescence in solution and/or solid state, they could be used as electroluminescence and nonlinear optical materials.

2. Experimental

1-Bromomethyl-4-nitrobenzene(**2**) was synthesized from p-nitrotoluene(**1**) by bromination in carbon tetrachloride using N-bromosuccinimide at reflux in 83% yield according to a literature procedure[12]. Reaction of **2** with triethylphosphite to give (4-nitrobenzyl)-phosphonic acid diethylester (**3**). And octyloxybenzaldehyde (**5a**), decyloxybenzaldehyde (**5b**) and dodecyloxybenzaldehyde (**5c**) were synthesized from 4-hydroxybenzaldehyde(**4**) by Williamson synthesis in good yield (95-97%).

Wittig reaction of **3** and **5** in tetrahydrofuran under reflux conditions gave the 4-[2-(4-octyloxyphenyl)-vinyl]-nitrobenzene (**6a**), 4-[2-(4-decyloxyphenyl)-vinyl]-nitrobenzene (**6b**) and 4-[2-(4-dodecyloxyphenyl)-vinyl]-nitrobenzene (**6c**). 4-[butane-(4-octyloxyphenyl)-2,3-dione]-nitrobenzene (**7a**), 4-[butane-(4-decyloxyphenyl)-2,3-dione]-nitrobenzene (**7b**) and 4-[butane-(4-dodecyloxyphenyl)-2,3-dione]-nitrobenzene (**7c**) were prepared by heating corresponding **6** in dimethylsulfoxide with iodine[13]. 5-(4-nitrophenyl)-6-(4-octyloxyphenyl)-2,3-dicyanopyrazine (**8a**), 5-(4-nitrophenyl)-6-(4-decyloxyphenyl)-2,3-dicyanopyrazine (**8b**) and 5-(4-nitrophenyl)-6-(4-dodecyloxyphenyl)-2,3-dicyanopyrazine (**8c**) were synthesized by the condensation reaction of diaminomaleonitrile(DAMN) and **7** in ethanol. The reaction route are summarized in scheme 1.

Melting points were determined using a JISICO melting point apparatus. The ir spectra were taken with a MAGNA-IR 760 spectrometer using KBr pellets. The ^1H nmr spectra were obtained in deuterated chloroform on a VARIAN, 300MHz UNITY INOVA. The mass spectra were recorded on a JEOL, JMS-AX505WA, HP 5890 Series II. Elemental analyses were performed on a CE, EA 1110. The visible and fluorescence spectra were measured on UNICAM 8700 and SHIMADZU RF-5301PC spectrophotometer.

General procedure of **6**

The procedure by Wittig reaction was modified as follows. To a solution of

(4-nitrobenzyl)-phosphonic acid diethylester(3) (38.3g, 0.14 mole) and 4-alkoxybenzaldehyde(5) (0.14 mole) in THF was added 60% sodium hydride (5.6g, 0.14 mole), and then dropwised methanol(10 mL) slowly and kept solution temperature at 5-10°C . The reaction mixture was refluxed until all of 5 disappeared by tlc. After reaction was complete, solvent was removed under reduced pressure. Methanol was added to the residue and precipitate was filtered off. The crude product was recrystallized from methanol as yellow powder (68 ~ 73%).

General procedure of 7

A solution of 6 (0.093 mole) and iodine (18.78g, 0.74mole) in dimethylsulfoxide (20 ml) was heated at reflux for 5hr using dean-stark trap. After reaction was complete, the resulting mixture was cooled at room temp. and then methanol was added to the residue and precipitate was filtered off. The crude product was recrystallized from carbon tetrachloride as ivory powder (45 ~ 53%).

General procedure of 8

A solution of 7 (0.036 mole), DAMN (4.73g, 0.044 mole) and p-toluenesulfonic acid (0.02g) in ethanol (50 ml) was refluxed for 5hr. 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 carbon tetrachloride as yellowish-green powder (66 ~ 72%).

3. Results and discussion

The structural assignments for product 6, 7 and 8 were established on the basis of ir, ¹H-nmr and mass spectral data as well as microanalyses.

From the ir spectra of 6, 7 and 8, the stretching vibrations of NO₂ for all the products were observed as sharp and strong absorption bands appearing in 1592, 1596 and 1607 Cm⁻¹, respectively. For the 6, we noticed the band of C=C at 1630 Cm⁻¹. These bands disappeared upon 7. The absorption bands at 1677 Cm⁻¹ were characteristic of the ketone. Stretching vibrations of cyano groups for all of the 8 were observed appearing 2223 Cm⁻¹.

In the nmr study, the trans structure of the intermediates was clearly established by the value of the coupling constant($J=16.2$) for compounds 6.

The absorption and fluorescence maxima of compound 6, and 8 were observed at 427~444nm and 453~494nm, respectively. The stokes' shift indicated the difference between λ_{max} and F_{max} to correspond with the energy loss in the first excited singlet state.

4. References

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Scheme 1.

