광변색성 Spiroxazine 색소의 흡수스펙트럼

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Electronic Absorption Spectrum of Photochromic Spironaphthoxazine Dye

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요 약. Photochromism을 나타내는 spiroxazine 색소의 흡수스펙트라 및 용매 효과에 관해 검토하였다. 그 결과 positive solvatochromism을 나타내었으며 이로부터 spiro 고리가 자외선 조사에 의해 개열되었을 때는 keto형의 분자구조로 되어있음을 나타낸다는 것을 알 수 있었다. 색소골격내에 C 대신 N 원자가 존재하므로서 흡수극대치가 장파장측에 이동한다는 것을 PPP 분자궤도법(Pariser-Parr-Pople Molecular Orbital Method)을 사용해 정량적으로 해석하였다.

ABSTRACT. Absorption spectra of photochromic spironaphthoxazine dye in various solvents were examined and exhibited a positive solvatochromism. The positive solvatochromism of this dye strongly suggests that the structure of open chain forms is keto type structure, 4a. The effect of structural change on the electronic spectra, on replacement of the C=C bond by C=N bond, is discussed.

INTRODUCTION

A photochromic compound is characterized by its ability to undergo a reversible colour change. Although the photochromic compounds have long been attracted significant attention because of their potential ability for sunlight-activated self-coloured glasses as well as for optical memory media, they still await major commercial exploitation. One of the prime reasons for this lack of industrial applications for photochromic materials, particularly organic photochromic compounds is their poor durability. This lack of durability to sunlight irradiation is called light fatigue. There are a unique classes of compounds which show excellent light fatigue resistance among the hundreds of known organic photochromic compounds. This classes of compounds is called spironaphthoxazine 3a[1]. In view of the similarity in the chemi-cal structure between the spiropyans and spiroxazines, it was surprising to find that the photochromic durability of spiroxazines is exceptionally better than that of spiropyrans. For instance, the quantum yield of photodecomposition of a spiroxazine in ethanol irradiated by 366 nm of Hg lamp is 2×10^{-4} which is about 10^3 smaller than most spiropyrans. The only difference in the chemical structure between spiropyran and spiroxazine is that the C=C bond in the pyran ring is replaced by a C=N bond in the case of oxazine (*Scheme* 1). A number of authors have reported important advances towards understanding of the detailed photopysical property involved in the photochromism of spiroxazine dyes[2], but electronic spectral characteristices of these dyes have not yet been reported.

In this paper, we described UV-Vis spectrosco-

Scheme 1.
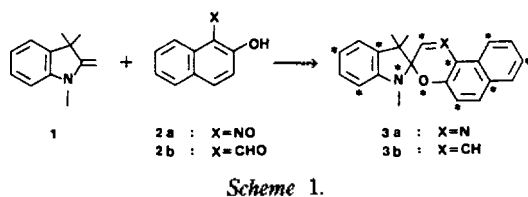
pic studies to determine the exact structure of the photochemically produced coloured species from the influence of solvent on the equilibrium and color-structure relationship for these dyes were discussed by means of the Pariser-Parr-Pople molecular orbital (PPP MO) methods[3].

EXPERIMENTAL AND MO CALCULATION METHOD

The dyes used were synthesised in our laboratory by known method[2] and were purified by repeated recrystallization. The results of elemental analysis were consistent with the theoretical values. Dye 3a was prepared by reacting 1-nitroso-2-naphthol (18 g, 0.104 mol) in MeOH (200 ml) under reflux with a solution of 1,3,3-trimethyl-2-methylene indoline (17 g, 0.098 mol) in MeOH (50 ml). After refluxing for 2 hr, the reaction mixture was cooled. A brown solid was precipitated and purified by recrystallization from acetone and yielled 11 g of oproduct, mp. 119°C (lit. 122~124°C[2]). Similar reaction of 1 with 2b gives the corresponding spironaphthopyran 3b which absorbs at 570 nm in chloroform. The solvents used were of spectrometric grade quality whenever possible. The above solvents were chosen from a spectrum ranging from 32.4 to 51.9 in E_T scale[4]. The absorption spectra were recorded on Shimadzu UV-2100 spectrophotometer. For low temperature measurement, a dry ice-acetone was used. The absorption spectrum of the colored form was obtained by irradiating the sample at low temperature with the 8 watt UV light (Tokyo kogaku Kikai, PAN UV 1B) for 2~3 min. The modified PPP MO calculations were carried out by the method described previously[3].
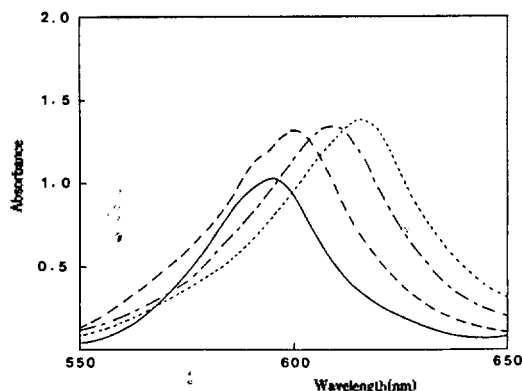
RESULTS AND DISCUSSION

Fig. 1. Absorption spectra of spiroxaxine dye 3a in various solvents. ———: CCl$_4$, ———: Toluene, ———: CHCl$_3$, -----: EtOH.

As in the case of spiropyrans, a dilute solution of spiroxazine dye in various solvents is colourless and become intensely blue when irradiated by a UV light source or by sunlight. The blue colour of the solution disappears rapidly once the light source is removed. But it is difficult to measure the static absorption spectrum of the coloured form at room temperature since its thermal decay is fairly rapid. Fortunately, the thermal decay of the coloured form decreases slowly as the temperature is lowered. The visible absorption spectra of the coloured form of spiroxazine in various solvents is shown in Fig. 1. Dye 3a is blue in colour and absorbs light at near 600 nm. In principle, a open chain form of spiroxazine dye could exhibit either a bathochromic or a hypsochrmic shift since the ground state could have an electronic configration correspoding largely to the keto type (4a)
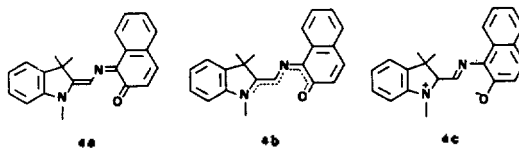
or to an resonance type (4b) or to the zwitter ion type (4c). If the dye molecules possess a permanent dipole, the polar solvent lowers the energy of the ground state more than the excited state, and the solvent produces a hypsochromic shift (negative solvatochromism)[4]. In many coloured molecules, the ground state is less polar than

excited state, and thus a polar solvent will tend to stabilize the exicted state more than the ground state, giving rise to a bathochromic shift (positive solvatochromism). Solvent polarity is of great importance in many areas of chemistry as well as spectroscopy. The solvent induced displacement of UV or Vis absorption band has been used with

Table 1. λ_{max} of the open chain form of spiroxazine in various solvents

Solvent	E_T(kcal·mol^{-1})	λ_{max}(nm)
EtOH	51.9	614
DMF	43.8	608
Acetone	42.2	604
CH$_2$Cl$_2$	41.1(40.7)	608
CHCl$_3$	39.1	609
THF	37.4	607
Toluene	33.9	600
CCl$_4$	32.4	596
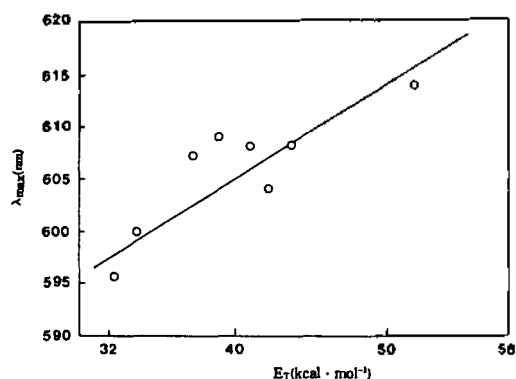
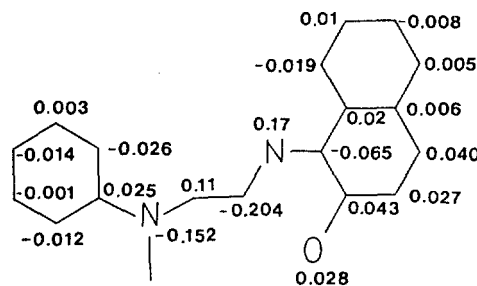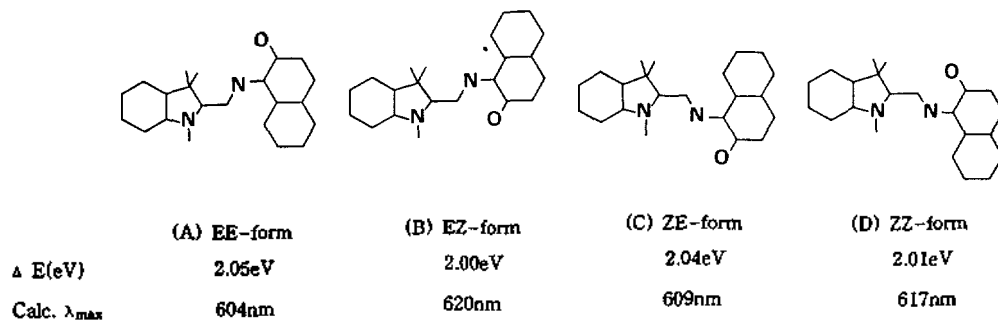Fig. 2. Plots λ_{max}(nm) vs. E_T value for spiroxazine 3a in various solvents.

considerable success to derive empirical scales of solvent polarity. Dimroth et al.[4] have suggested that the transition energy for pyridinium-N-phenoxide betaine dye, expressed in kcal·mol^{-1}, be used as a polarity parameter. This quantity is reffered to as the E_T value. UV-Vis spectral data of the open form of spiroxazine and E_T values of solvents are listed in Table 1. In this present work, on plotting λ_{max} versus the solvent parameter E_T reasonably linear plots were obtained (Fig. 2). As the solvent polarity increase, a bathochromic shift was observed (i.e. positive solvatochromism). The positive solvatochromism indicates that the structure of the open chain form which absorbs near λ_{max} 600 nm is keto type structure 4a. The ring closed form of some spiropyran is well known, but the open form of spiropyran and spiroxazsine has not yet been reported. Although many geometric isomer of open form are known, but the most stable form is not well known. It has also been reported that the transoid isomer is more stable than cisoid isomer. The structure

Fig. 3. The π-electron density changes accompanying the first excitation of spiroxazine compound.

	(A) EE-form	(B) EZ-form	(C) ZE-form	(D) ZZ-form
Δ E(eV)	2.05eV	2.00eV	2.04eV	2.01eV
Calc. λ_{max}	604nm	620nm	609nm	617nm

Scheme 2.

X=CH : λ_{max} 491nm
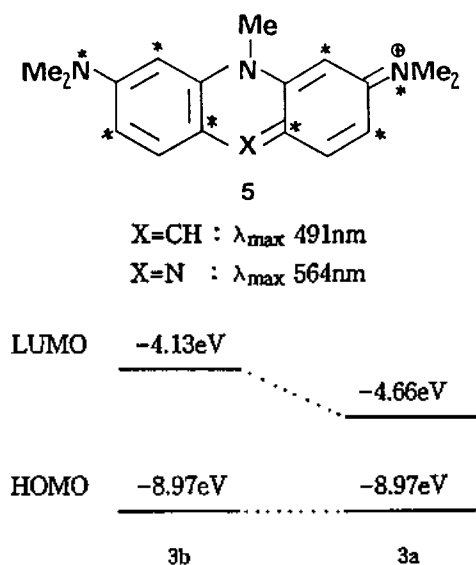
X=N : λ_{max} 564nm

Fig. 4. Energy levels of the HOMO and LUMO (eV) of 3a and 3b.

of the opossible four transoid geometric isomer and the calculated first transition energy of the spiroxazsine are depicted in Scheme 2; A(2.05 eV), B(2.00 eV), C(2.04 eV), D(2.01 eV). The π-electron-density changes accompanying the first excitation of dye 3a is shown in Fig. 3. It was generally found[5] that the indoline fused benzenoid ring in the spiroxazine acts as a strong donor and an intramolecular change-transfer character for the first transition is indicated. Therefore, introduction of donor group to the indoline attached aromatic ring may produce bathochromic shift of the first band. We have attempted to explain the effect of structural change on the electronic spectra, on replace-

ment of the −C= bridge by −N=. Replacement of the carbon bridge in 3b by nitrogen to give 3a produces a bathochromic shift of 40 nm. According to Dewar's rules, an electronegative heteroatom or an electron withdrawing group placed at the unstarred position in 5 should give a bathochromic shift[6]. This reasoning can be extended to dye 3. This finding can be well interpreted by focusing attention on the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) by means of PPP MO[3]. It is apparent that the first excitation energy of spiroxazine predominantly depends on the energy difference between the LUMO and HOMO. From the calculation results, we found that dye 3a and 3b have a same HOMO level (8.97 eV). On the other hand, energy levels of LUMO of 3a and 3b are −4.66 eV and −4.13 eV respectively (Fig. 4). Thus, replacement of a carbon by nitrogen in 3b causes a bathochromic shift.

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