Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Relationship between the Steric Hindrance and Absorption Spectrum of Fluoran Dyes. Part I

Mitsuhiro Yanagita [a], Satoru Kanda [a], Kazue Ito [a], Reiko Shibuya [a] & Sumio Tokita [a]

[a] Department of Applied Chemistry, Saitama University, 255 Shimo-Ohkubo, Urawa, Saitama, 338-8570, Japan

Version of record first published: 24 Sep 2006

To cite this article: Mitsuhiro Yanagita, Satoru Kanda, Kazue Ito, Reiko Shibuya & Sumio Tokita (1999): The Relationship between the Steric Hindrance and Absorption Spectrum of Fluoran Dyes. Part I, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 327:1, 49-52

To link to this article: http://dx.doi.org/10.1080/10587259908026778

Mol. Cryst. Liq. Cryst., 1999, Vol. 327, pp. 49-52
Reprints available directly from the publisher
Photocopying permitted by license only

The Relationship between the Steric Hindrance and Absorption Spectrum of Fluoran Dyes. Part I

MITSUHIRO YANAGITA, SATORU KANDA, KAZUE ITO, REIKO SHIBUYA and SUMIO TOKITA

Department of Applied Chemistry, Saitama University, 255 Shimo-Ohkubo, Urawa, Saitama, 338–8570 Japan

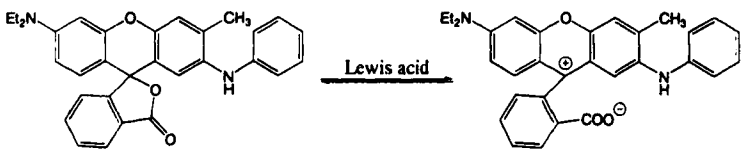
(Received June 30, 1998; In final form July 30, 1998)

Fluoran compounds used for the thermosensitive data-recording systems usually have substituted amino groups at the 2-position of the fluoran ring. Their absorption spectra are significantly affected by the electron-donative ability of the 2-amino groups. We investigated the relationship between the steric effects around the 2-amino groups and the absorption spectra of fluoran dyes.

Keywords: fluoran dye; electronic absorption spectra; steric hindrance

INTRODUCTION

Fluoran dyes are well-known as leuco dyes or colored cationic dyes for thermosensitive recording papers and have an equilibrium between the colorless lactone form **L** and the colored zwitterion form **Z** [1),2)]. They develop



Colorless Lactone Form (**L**) — Colored Zwitterion Form (**Z**)

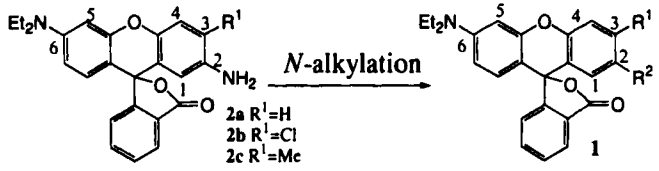
SCHEME 1 Equilibrium between Lactone Form and Zwitterion form

their colors by reacting with a Lewis acid, such as phenol derivatives (Scheme 1). In particular, 2-anilino-3-methyl-6-diethylaminofluoran (**L** in scheme 1) is one of the typical fluoran-based black color formers.

The absorption spectrum of the colored zwitterion form **Z** has two main bands in the visible region. It is previously accounted for by the PPP-MO calculation which the first absorption band is shifted hypochromically in proportion with the decrement of the electron-donating ability in the 2-amino substituents[3]. The relationship between the steric hindrances around the 2-amino groups and the absorption spectra of fluoran dyes, however, has not been investigated in detail. In this paper, we have synthesized several fluoran derivatives having steric hindrances between substituted amino groups R^2 at the 2-position and substituents R^1 at the 3-position. The absorption spectra of these fluoran dyes are discussed in terms of the resonance ability between the lone-pair electrons on the amino nitrogen and the π-electrons of the fluoran ring.

EXPERIMENTAL

All fluoran compounds **1** (Scheme 2) were prepared by *N*-alkylation of the intermediates **2** which were obtained by the reaction of 2-(4-diethylamino-2-hydroxy)benzoyl benzoic acid with *p*-aminophenol derivatives in conc. H_2SO_4. For example, **1a-3** was prepared by the reaction of **2a** with 1,4-dibromobutane refluxed in 2-butanone in the presence of anhydrous potassium carbonate for 72 h. The structures of all intermediates and target compounds were identified by ^1H NMR and MASS spectroscopy. The UV-Vis spectra of all compounds were measured in *m*-cresol with a Shimadzu UV-2200 spectrophotometer.



R^1 \ R^2					
H	**1a-1**	**1a-2**	**1a-3**	**1a-4**	**1a-5**
Cl	**1b-1**	**1b-2**	**1b-3**	**1b-4**	**1b-5**
Me	**1c-1**	**1c-2**	**1c-3**	**1c-4**	**1c-5**

SCHEME 2 Structure of fluoran dyes **1a-1** – **1c-5**

RESULTS and DISCUSSION

The absorption spectra of 2-pyrrolidino-6-diethylaminofluoran **1a-3**, 2-piperidino-6-diethylaminofluoran **1a-5** and 2-pyrrolidino-3-methyl-6-diethyl-aminofluoran **1c-3** are shown in Figure 1. The wavelength of the first absorption maximum of **1a-5** is hypochromically shifted by 100 nm compared with that of **1a-3**. Changing from the five-membered ring in **1a-3** to the bulky six-membered ring in **1a-5** may cause rotation about the C-N bond at the 2-position to relieve steric strain. The bond rotation in **1a-5** may cause

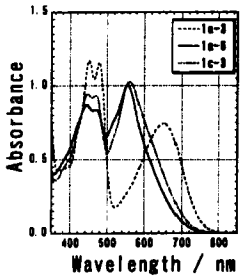


FIGURE 1 Electronic absorption spectra of **1a-3**, **1a-5** and **1c-3** in *m*-cresol (7.5×10^{-5} M)

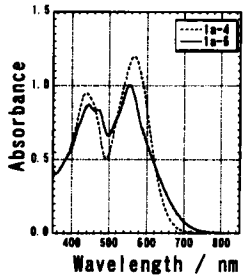


FIGURE 2 Electronic absorption spectra of **1a-4** and **1a-5** in *m*-cresol (7.5×10^{-5} M)

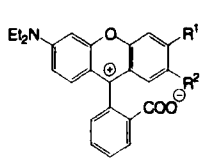
a reduction in the overlap effects between the lone-pair electron on nitrogen and the π-electrons of the fluoran ring. Similar effects of electron-donating ability were suggested from ^{13}C NMR and ^{1}H NMR studies of relevant derivatives of aniline [4,5]. In addition, the wavelength of the first absorption maximum of **1c-3** having a methyl group in place of hydrogen at the 3-position of the fluoran ring shows a hypochromic shift of about 90 nm compared with that of **1a-3**. This result suggests that the enlarging van der Waals radius of *ortho*-sustituent gives significant influence for the absorption spectra of the fluoran dyes.

The absorption spectra of 2-piperidino-6-diethylaminofluoran **1a-5** and 2-morpholino-6-diethylaminofluoran **1a-4** are shown in Figure 2. Compared with the piperidine compound, the wavelength of the first absorption maxi-

mum of the morpholine analogue **1a-4** shows a bathochromic shift of 13 nm. This shift is considered that the sizes of the six-membered ring are slightly smaller in the case of morpholino group than piperidino group so that rotation about C-N bond to relieve steric hindrance may lead to an increase in electron-donating ability of the heterocyclic nitrogen atom.

The wavelengths of the first absorption maxima of all fluoran compounds are shown in Table 1. These results suggest that the absorption spectra of fluoran compounds are significantly influenced by the steric factors arising between *ortho*-substituent R^1 of the fluoran ring and the α-methylene proton of the five or six-membered ring. In general, the wavelength of the first absorption maximum shows a hypochromic shift depending on changing from a five-membered ring to a six-membered ring in the 2-amino groups R^2 and the enlarging van der Waals radius of the 3-substiuent R^1. It became obvious that the steric hindrance between the 2- amino group R^2 and the bulky substituent R^1 at the 3-position had a remarkable effect on the absorption spectrum of fluoran dyes.

TABLE 1 The fist absorption maxima λ_{1max} / nm (absorbance) of **1a-1** - **1c-5** in *m*-cresol (7.5 x 10^{-5} M)



Colored zwitterion form of **1** (**Z**)

R^1 \ R^2	-N	-N	-N	-N	-N O
H	640 (0.84) **1a-1**	635 (0.86) **1a-2**	652 (0.74) **1a-3**	569 (1.20) **1a-4**	556 (1.00) **1a-5**
Cl	612 (1.11) **1b-1**	574 (1.17) **1b-2**	569 (1.04) **1b-3**	557 (1.91) **1b-4**	559 (1.85) **1b-5**
Me	569 (0.80) **1c-1**	563 (1.08) **1c-2**	562 (1.68) **1c-3**	550 (1.68) **1c-4**	553 (1.73) **1c-5**

References

[1] P. Gregory, *High Technology Applications of Organic Colourants*, Plenum Press, New York 1991, p.124.
[2] M. Yanagita, I. Aoki and S. Tokita, *Bull. Chem. Soc. Jpn.*, **70**, 2757 (1997).
[3] M. Matsuoka, K. Ueda, T. Kitao, *Shikizai Kyoukaishi*, **55**, 213 (1982).
[4] C. P. Nash and G. E. Maciel, *J. Phys. Chem.*, **68**, 832 (1964).
[5] F. Effenberger, P. Fischer, W. W. Schoeller and W. D. Stohrer, *Tetrahedron*, **34**, 2409 (1978).