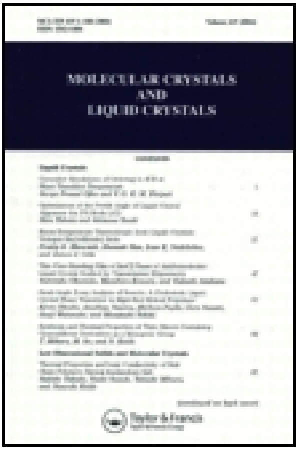

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The Relationship between the Steric Hindrance and Absorption Spectrum of Fluoran Dyes. Part II

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

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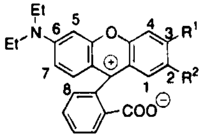
The steric hindrance at the 2-position of the fluoran ring and its influence on the electronic absorption spectrum were studied by semiemprical MO calculations. All fluoran dyes in this study gave two or more conformers by using structure optimization. Spectral changes and band shapes with respect to the steric hindrance of the amino group at the 2-position are discussed on the basis of calculations performed for a variety of conformations. A good correlation between the wavelengths of separated peaks and those of calculated peaks was obtained.

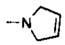
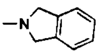
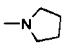
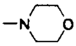
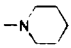
Keywords: fluoran dye; electronic absorption spectrum; steric hindrance; conformer

INTRODUCTION

In the past few decades, fluoran dye is one of the most successful and useful functional dyes as a color former for pressure and thermosensitive dyes. The electronic spectroscopic properties of fluoran dyes have been extensively studied in order to obtain better color tone for recording systems. Recently, Computer-Assisted Quantitative Structure-Property Relationship (QSPR) has been widely used. Although the molecular orbital (MO) calculations have been studied on many dyes using the ZINDO[1)] method, there was no example for fluoran dyes except for the PPP-MO method.[2)] In order to investigate the correlation between the calculated and the observed absorption spectra of fluoran compounds, the theoretical calculations were performed using the MOPAC-AM1 and the ZINDO method. Synthesized fluoran compounds having homologues of an amino group substituted at the 2-position of the fluoran ring are shown in Table 1.

TABLE 1 Structures of fluoran dyes **1a-1** – **1c-5**.



R^2 / R^1					
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**

EXPERIMENTAL

The electronic absorption spectra of all compounds in *m*-cresol were measured with a Shimazu UV-2200 spectrometer using a quartz cell. The concentration in the working solution was 7.5×10^{-5} M. The geometry optimizations were performed with the MOPAC-AM1[3] method. Using these geometries, ZINDO calculations were performed. The peak separations of the observed spectra were performed with the program package ORIGIN[4] by the peak fitting method assuming Gauss functions.

RESULTS AND DISCUSSION

Observed and separated wavelengths are given in Table 2. In addition, calculated wavelengths are given. The geometry optimizations for these fluoran dyes showed the presence of local minima corresponding to the multiple stable conformers *via* rotation about the C-N bond at the 2-position. Each conformer had a different transition energy, oscillator strength and heat of formation as shown in Table 2. In the case where the observed absorption spectra had a shoulder (*i.e.*, **1b-1** – **1c-1**, **1c-4** – **1c-5**), they could be separated into two peaks, and the calculated transition energies could be divided into two groups. On the other hand, in the case where they had no shoulder, they could not be divided into two groups (*i.e.*, **1a-3** – **1a-5**); otherwise, one of the two groups had rather a higher energy (> 2 kcal/mol) of heat of formation than the other (*i.e.*, **1a-1** – **1a-2**). Except for the above compounds (*i.e.*, **1c-2** – **1c-3**), although they did not have shoulders, two separated peaks and two groups of conformer having different transition energies were obtained.

A fair correlation (correlation coefficient : r = 0.83) between the observed transition energies (ΔEobs.) and the calculated lowest transition energies (ΔEcalc.) is obtained in Fig. 1a. An excellent correlation (correlation coefficient : r = 0.97) is obtained between the separated lowest transition energies (ΔEsep.) by extracting through lineshape analysis of the observed peaks and the calculated lowest transition energies (ΔEcalc.) (Fig. 1b). As a typical example, the absorption band of **1c-1** and two separated peaks and the corrected transition energies are shown in Fig. 2.

The electronic absorption spectra are complicated by overlapping peaks due to the steric hindrance between the amino moiety at the 2-position of the fluoran dye and substituent at the 3-position. The calculated transition energi-

TABLE 2 Observed and calculated peaks for fluoran dyes **1a-1 – 1c-5**.

Compd	observed[a] nm(log ε)	separated[b] nm(log ε)	conformer[c]	calculated[d] /nm(f)	heat of formation[c] /kcal mol^{-1}
1a-1	640(4.05)	645(0.75)	1a-1-1	468(0.36)	160.95
			1a-1-2	463(0.38)	160.18
		567(0.31)	1a-1-3	424(0.78)	163.06
1a-2	635(4.06)	646(0.62)	1a-2-1	464(0.37)	169.42
			1a-2-2	463(0.38)	169.30
		580(0.46)	1a-2-3	424(0.79)	172.00
1a-3	652(3.99)	659(0.69)	1a-3-1	467(0.37)	124.41
			1a-3-2	470(0.35)	124.43
		581(0.25)			
1a-4	569(4.20)	566(1.19)	1a-4-1	449(0.40)	90.68
			1a-4-2	449(0.39)	90.45
			1a-4-3	447(0.53)	90.40
			1a-4-4	449(0.42)	90.56
		511(0.14)			
1a-5	556(4.12)	577(0.56)	1a-5-1	454(0.35)	116.62
			1a-5-2	452(0.36)	116.46
			1a-5-3	453(0.46)	116.41
			1a-5-4	453(0.46)	116.50
		554(0.35)			
		518(0.07)			
1b-1	612(4.17)	631(0.88)	1b-1-1	461(0.40)	159.67
			1b-1-2	465(0.40)	159.76
	560(s)	561(0.60)	1b-1-3	434(0.66)	159.41
			1b-1-4	433(0.69)	159.49
			1b-1-5	422(0.84)	159.88
1b-2	620(s)	630(0.64)	1b-2-1	465(0.40)	169.24
			1b-2-2	465(0.40)	169.17
	574(4.19)	562(1.00)	1b-2-3	428(0.75)	168.33
			1b-2-4	423(0.73)	168.37
1b-3	630(s)	635(0.61)	1b-3-1	470(0.38)	124.46
			1b-3-2	466(0.40)	124.16
	569(4.14)	562(0.87)	1b-3-3	440(0.61)	124.10
			1b-3-4	437(0.65)	124.21
1b-4	557(4.41)	561(1.61)	1b-4-1	440(0.61)	87.59
			1b-4-2	441(0.61)	87.59
	520(s)	518(1.05)	1b-4-3	421(0.84)	90.50
			1b-4-4	432(0.72)	88.00
1b-5	559(4.39)	561(1.42)	1b-5-1	445(0.56)	113.79
			1b-5-2	446(0.55)	113.85
	520(s)	518(0.32)	1b-5-3	438(0.65)	115.31
			1b-5-4	437(0.66)	115.37
1c-1	620(s)	625(0.57)	1c-1-1	456(0.64)	156.05
			1c-1-2	461(0.54)	155.97
	569(4.03)	549(0.56)	1c-1-3	435(0.80)	155.37
			1c-1-4	433(0.82)	155.43
1c-2	563(4.14)	628(0.37)	1c-2-1	462(0.55)	165.54
			1c-2-2	459(0.55)	165.43
		555(0.97)	1c-2-3	434(0.81)	164.28
			1c-2-4	431(0.85)	164.31
1c-3	562(4.35)	609(0.56)	1c-3-1	461(0.55)	120.45
			1c-3-2	460(0.56)	120.53
		553(0.62)	1c-3-3	437(0.78)	120.14
			1c-3-4	437(0.77)	120.21
1c-4	550(4.35)	552(1.55)	1c-4-1	442(0.72)	83.91
			1c-4-2	437(0.77)	84.33
			1c-4-3	436(0.79)	84.33
	520(s)	509(0.76)	1c-4-4	430(0.86)	84.48
1c-5	553(4.36)	552(1.70)	1c-5-1	446(0.66)	110.28
			1c-5-2	442(0.72)	111.66
			1c-5-3	439(0.75)	110.94
	520(s)	508(0.24)	1c-5-4	430(0.87)	110.94

a) in *m*-cresol(7.5X10^{-5} M), b) obtained by peak-fitting procedure[4], c) calculated by MOPAC-AM1 method[3], d) calculated by ZINDO method[1] (f : frequency factor) es and their intensities were in good agreement in the separated peaks of the observed spectrum using the peak-fitting procedure. Taken together, these spectral shifts are caused by a resonance effect between the lone pair electron of nitrogen and the π-electrons of the fluoran ring. Thus, this result includes a conclusion of the previous paper in this series and would provide an important technique for molecular modeling of the color former.

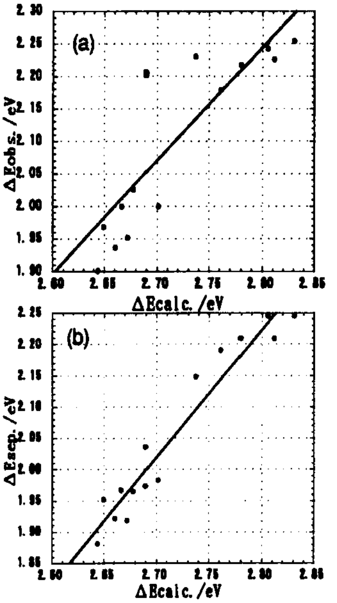


FIGURE 1 (a) Correlation between observed transition energies and calculated transition energies. (b) Correlation between transition energies of separated peaks and calculated transition energies.

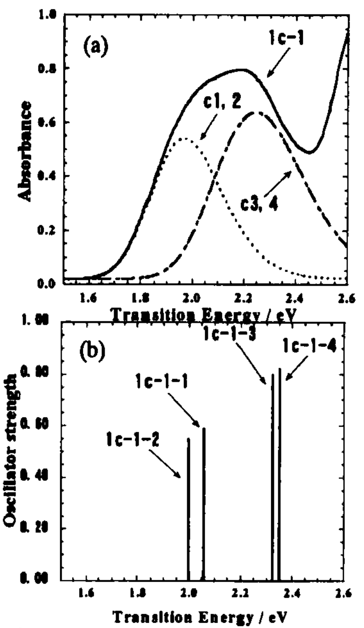


FIGURE 2 (a) Observed absorption spectrum of 1c-1 and separated peaks. (b) Corrected transition energies of calculated values and oscillator strengths of four conformers of 1c-1. $C_{1,2}$ in (a) corresponds to 1c-1-1 and 1c-1-2 in (b), and $C_{3,4}$ in (a) to 1c-1-3 and 1c-1-4 in (b).

References

[1] J. E. Ridley, M. C. Zerner, *Theor. Chim. Acta (Berl.)*, **32**, 111 (1973).

[2] M. Matsuoka, K. Ueda, T. Kitao, *Shikizai Kyokaishi*, **55**, 213 (1982).

[3] M. J. S. Dewar, E. G. Zoebisch, *J. Am. Chem. Soc.*, **107**, 3902 (1985).

[4] Microcal Software Inc.