^{13}C NMR and Electronic Absorption Spectroscopic Studies on the Equilibrium between the Colorless Lactone and the Colored Zwitterion Forms of a Fluoran-Based Black Color Former

Mitsuhiro Yanagita,* **Izuo Aoki, and Sumio Tokita**[†]

R&D Laboratory for Specialty Chemicals, Nippon Soda Co., Ltd., 12-54, Goi-minamikaigan, Ichihara, Chiba 290

†Department of Applied Chemistry, Faculty of Engineering, Saitama University, 255 Shin-Ohkubo, Urawa, Saitama 338

The equilibrium between the colorless lactone (**L**) and the colored zwitterion (**Z**) forms of the fluoran compound **1**, which has been widely used as a typical black color former in data-recording systems, has been studied by ^{13}C NMR and electronic absorption spectroscopies. Fluoran **1** showed no visible absorption in aprotic solvents, while a black color appeared in phenolic solvents. The ^{13}C NMR and signal of the spiro carbon of **1** in CDCl$_3$ appeared at 84.2 ppm, indicating that **1** exists substantially as **L** in aprotic solvents. In phenol d_6 at 50 °C, the signal of the spiro carbon in **1** shifted to a lower magnetic field and appeared in the sp^2-hybridization region ($\delta = 162.7$), suggesting that in phenol-d_6 a cleavage of the C(spiro)–O bond in the lactone ring occurs and that the ring-opened **Z** form is produced. The equilibrium between **L** and **Z** depended strongly on the temperature and solvents. The high temperature and inhibition of the solute (**1**)–solvent interaction by steric hindrance, self-association and intramolecular chelation of the solvent shifted the **L–Z** equilibrium toward **L**. The thermodynamic parameters for the equilibrium reaction in phenolic solvents were also estimated.

Fluorans are well-known chromogenic compounds useful as color formers for pressure and thermosensitive data-recording systems.[1—13] They develop colors by reacting with electron-accepting substances (Lewis acids), such as phenol-related compounds. Among the broad class of fluorans, there is an important group of compounds that develop a black color.[3—9] The typical fluoran-based black color formers have amino substituents in the 2- and 6-positions and an alkyl substituent in the 3-position on the xanthene component. In particular, fluoran compound **1**, 2′-anilino-3′-methyl-6′-(dibutylamino)spiro[isobenzofuran-1(3*H*), 9′-(9*H*)xanthen]-3-one has been widely used in practical data-recording systems, because it possesses various properties necessary for a pressure and thermosensitive recording material. The numbering of each atom in this compound is shown in Table 1 throughout this paper.

While various studies of the application of **1** and its analogs to data-recording systems, such as facsimiles, printers and point-of-sales labels have been performed,[4—13] reports on the chemical and physical properties of **1** from a fundamental point of view have been scarcely provided, except for X-ray crystallographic studies[14—16] and PPP MO calculations of **1** and its analogs.[17]

Herein we describe a study of the equilibrium between the colorless lactone form (**L**) to the colored zwitterion form (**Z**) (Scheme 1) by ^{13}C NMR and electronic absorption spectroscopies which enable us to monitor the position of the equilibrium and structural change in **1**. It was revealed from the NMR data that **1** exists substantially as **L** in chloroform-*d* (CDCl$_3$) at ambient temperature, while in phenol-d_6 at 50 °C

almost 100% of **1** exists as **Z**, and high temperatures shift the **L–Z** equiliblium toward **L**. These are the first examples of the NMR spectra for the colored zwitterion of a fluoran-based black color former formed upon contact with phenol compounds that are most widely used as a typical Lewis acid in practical data-recording systems. The effects of the temperature and solvents on the **L–Z** equilibrium were investigated and the thermodynamic parameters for the equilibrium in phenolic solvents were also determined by an analysis of the temperature dependence of the electronic absorption spectra.
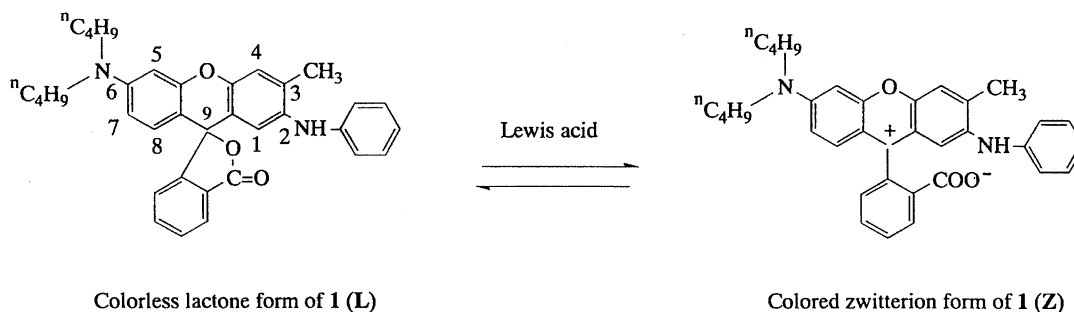
Experimental

Materials. The fluoran compound **1** was synthesized as follows. To 81.3 g of concentrated sulfuric acid were added 13.5 g of 2-(4-dibutylamino-2-hydroxybenzoyl)benzoic acid and 8.3 g of 4-methoxy-2-methyl-*N*-phenylaniline. The resulting mixture was reacted with stirring at 15 to 25 °C for 24 h. The reaction mixture was then poured into 300 ml (1 ml = 1 cm^3) of ice water and the deposited reaction product was filtered for collection. The filtered deposit was heated under reflux for 1 h while stirring with 200 ml of a 2.5 M (1 M = 1 mol dm^{-3}) sodium hydroxide aqueous solution and 160 ml of toluene for extraction. The toluene layer was washed with water several times, filtered and concentrated. The obtained light-yellow crystals were refluxed in hexane, cooled, filtered and dried to give 18.1 g of compound **1** (white crystals, yield 93%). The structure and the purity of this compound were confirmed by IR, NMR, MS, and elemental analysis: Mp 182.8—184.3 °C; IR (KBr) 3359 (NH), 1748 cm^{-1} (COO); ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, $\delta_{TMS} = 0$ ppm) $\delta = 0.95$ (6H, *t*, Bu), 1.35 (4H, *m*, Bu), 1.57 (4H, *m*, Bu), 2.22 (3H, *s*, ArCH$_3$), 3.27 (4H, *t*, Bu), 5.21 (1H, *s*, NH), 6.32 (1H, *d* of *d*, xanthene), 6.42 (1H, *d*, xanthene), 6.55 (1H, *d*,

Table 1. ^{13}C NMR Chemical Shifts (δ in ppm from SiMe$_4$) of **1** in CDCl$_3$ at 25 °C, and Relative Chemical Shifts ($\Delta\delta$ in ppm) of Each Carbon in Phenol-d_6 at 50 °C [$\Delta\delta$ = (δ Observed in Phenol-d_6) − (δ Observed in CDCl$_3$), at Each Carbon][a]
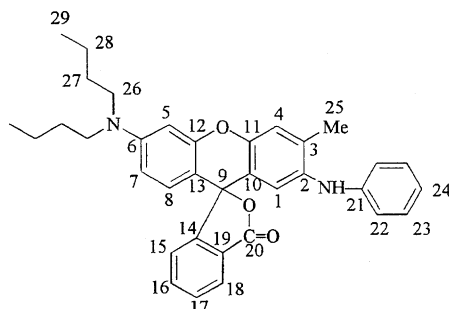
Carbon no.	δ in CDCl$_3$	$\Delta\delta$ in phenol-d_6	Carbon no.	δ in CDCl$_3$	$\Delta\delta$ in phenol-d_6
1	121.3	-5.6	16	134.7	-4.0
2	136.0	4.8	17	129.4	-0.6
3	135.0	8.0	18	124.9	5.7
4	118.9	0.4	19	127.2	12.6
5	97.7	-1.6	20	169.5	4.5
6	150.1	7.4	21	144.9	-2.1
7	108.4	9.0	22	115.1	3.3
8	128.8	3.7	23	129.2	0.4
9	84.2	78.5	24	119.4	2.7
10	117.6	3.7	25	18.0	0.8
11	148.0	2.4	26	50.8	1.2
12	153.0	6.0	27	29.4	0.1
13	104.8	13.2	28	20.3	-0.2
14	153.2	-21.2	29	14.0	-0.3
15	123.9	5.4			

a) ^{13}C NMR signals observed in the CP/MASS spectrum of **1**: 172.0 (COO), 156.7, 152.2, 151.3, 149.4, 148.7, 146.7, 136.0 (doublet), 130.9, 129.5, 127.4, 123.3 (doublet), 119.0, 117.0, 114.5, 109.0, 103.5, 96.5, 83.7 (spiro), 51.0, 47.9, 29.9, 26.1, 20.1, 17.2, 14.0, 13.0 ppm.

Colorless lactone form of **1** (**L**)   Lewis acid   Colored zwitterion form of **1** (**Z**)

Scheme 1.

xanthene), 6.56 (1H, *d*, anilino), 6.58 (1H, *s*, xanthene), 6.72 (1H, *t*, anilino), 7.06 (2H, *d* of *d*, anilino), 7.14 (1H, *s*, xanthene), 7.19 (1H, *d*, isobenzofuran), 7.51—7.64 (2H, *m*, isobenzofuran), 7.92 (1H, *d*, isobenzofuran). Mass spectrum: *M/Z* 533 (M$^+$). Found: C, 78.94; H, 6.75; N, 5.34%. Calcd for C$_{35}$H$_{36}$N$_2$O$_3$: C, 78.90; H, 6.81; N, 5.28%.

The solvents used for measuring the electronic absorption spectra were special-grade or equivalent.

Measurements. The NMR spectra of **1** were measured in chloroform-*d* (CDCl$_3$) at 25 °C and in phenol-d_6 at 50—140 °C. The signals were assigned by two-dimensional (2D) NMR techniques involving H,C-COSY (^{1}H, ^{13}C Chemical-shift Correlation Spectroscopy), COLOC (Correlated Spectroscopy by Long Range

Coupling) and 2D NOE [NOESY (Nuclear Overhauser Effect Spectroscopy)]. The concentrations of **1** employed were 0.2 M. The solid state ^{13}C NMR spectrum, i.e., CP/MAS (Cross Polarization Magic-Angle Spinning) with TOSS (Total Suppression of Sidebands) of the crystal powder of **1** was also measured at a spinning speed of 3500 rpm. The NMR spectrometer used was a Bruker AMX 400 (proton resonance frequency, 400 MHz).

The electronic absorption spectra of **1** in various solvents involving several phenols and alcohols were recorded with a Shimadzu UV-2200 spectrophotometer using a quartz cell (1 cm × 1 cm). To determine the thermodynamic parameters for the equilibrium of **1** in phenolic solvents, the absorption spectra of **1** were obtained from 20 to 110 °C at 15 °C intervals. The changes in the concentrations of

1 by solvent expansion with increasing temperature were corrected using solvent densities which were experimentally determined with a densitometer manufactured by Toyoseiki. The concentrations of 1 in the working solutions were 4.0×10^{-5} M or 7.5×10^{-5} M. In all cases, the absorption spectra satisfied Lambert–Beer's law.

Results and Discussion

^{13}C NMR Spectra of the Lactone and the Zwitterion of 1.

The fluoran compound 1 appeared to have no color in aprotic solvents such as chloroform, benzene, 1,4-dioxane, and acetonitrile, while in protic solvents, such as phenol-related compounds and alcohols, 1 showed visible absorption. The absorption spectra of 1 in chloroform at 25 °C and phenol at 50 °C are shown in Fig. 1. In phenol 1 formed absorption bands of substantially equal ε (apparent molar absorptivity) values near 450 nm and near 600 nm, which are the wavelengths of the complementary color. This absorption mode appears black to the naked eye. The appearance of the two visible bands in 1 instead of the usual one found with the rhodamines has been well accounted for by PPP MO calculations.[17]

It is generally accepted that the colorless and colored species of 1 can be ascribed to the lactone (L) and the zwitterion (Z) forms of 1, respectively.[4—9] However, no NMR spectroscopic evidence for their structures has been provided so far. In order to obtain more accurate insight into the molecular structure and equilibrium between L and Z, ^{13}C NMR spectra were measured in CDCl₃ and phenol-d_6. The spectra are illustrated in Fig. 2 and the chemical-shift (δ, ppm from Me₄Si) values of each carbon atom are listed in Table 1. In CDCl₃, the signal of the spiro carbon in 1 ($\delta = 84.2$) appeared in the typical C (sp³, quaternary)–O region [$\delta = 75$—85],[18] indicating that 1 substantially exists as L. The signal of the
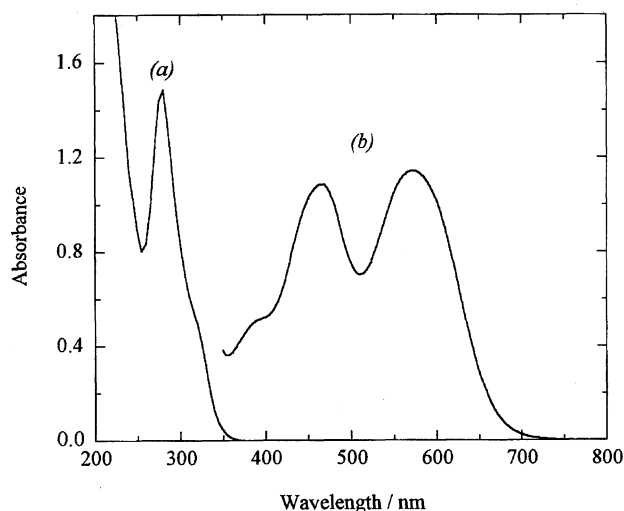

Fig. 1. Electronic absorption spectra of 1 in chloroform at 25 °C (a) and in phenol at 50 °C (b). [1]: (a) 4.0×10^{-5} M, (b) 7.5×10^{-5} M. Light-path length: 1 cm.

spiro carbon could be easily assigned by the COLOC technique. The solid state ^{13}C NMR spectrum (CP/MAS) of 1 was also measured (Fig. 3). The signal of the spiro carbon in the CP/MAS spectrum appeared at $\delta = 83.7$ ppm (from the external reference of the carbonyl carbon in glycine, $\delta = 176.0$), which is almost consistent with the δ value observed in CDCl₃. Because the lactone structure of 1 in the single crystal was already confirmed by the X-ray crystallographic method,[14] the similarity of the ^{13}C NMR signals of 1 in CDCl₃ with those in the solid state strongly supports the belief that 1 really exists as L in CDCl₃. In L, π electrons localized in each phenyl ring, and no visible absorption occurred.
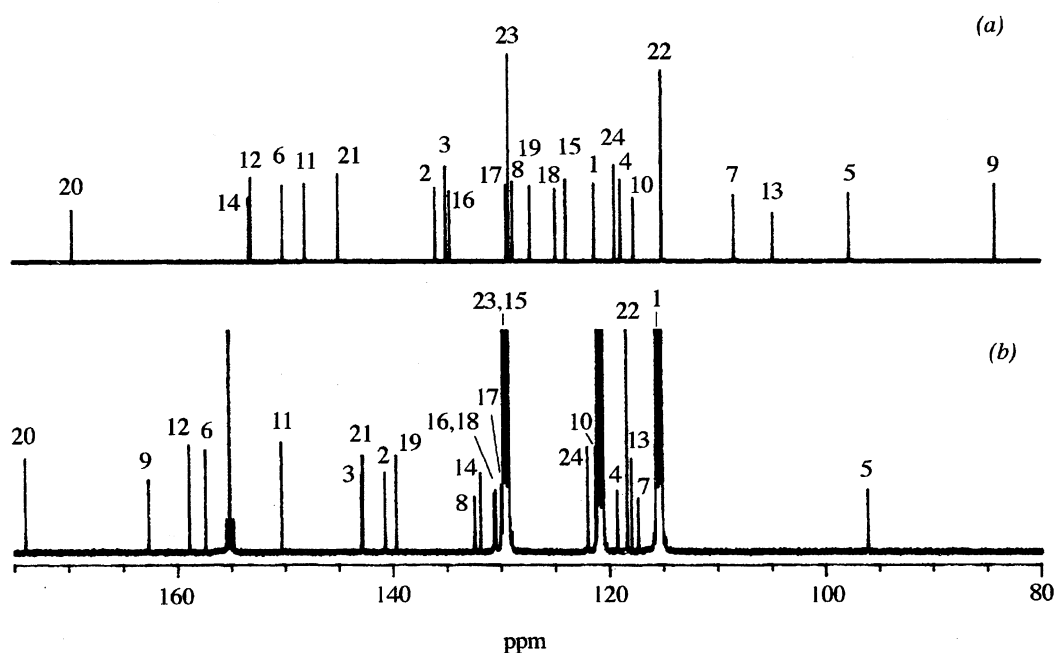

Fig. 2. Partial ^{13}C NMR spectra of 1 in CDCl₃ at 25 °C (a) and in phenol-d_6 at 50 °C (b). [1]: 0.2 M. Numbers attached to the signals: see Table 1.
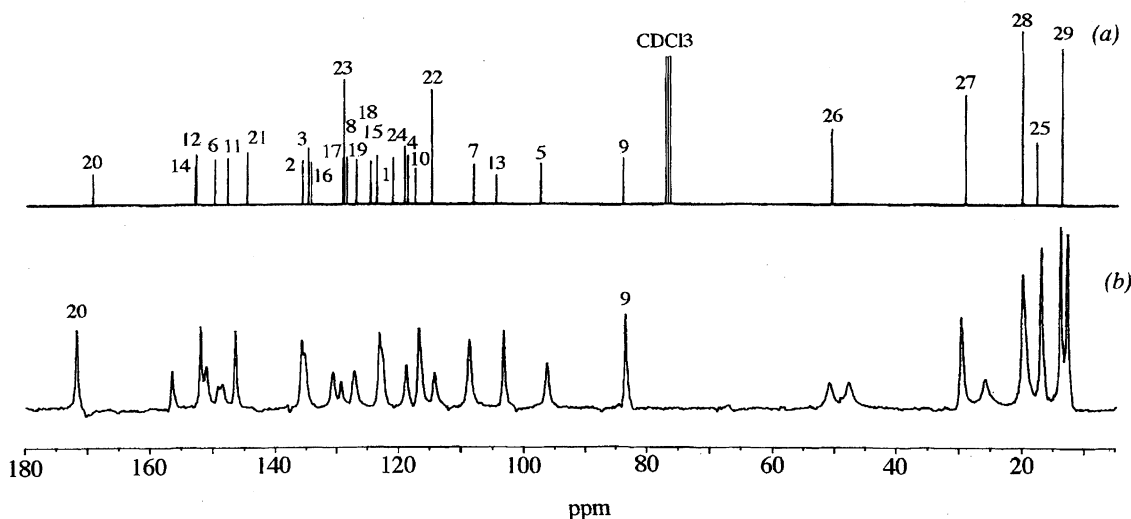
Fig. 3. ^{13}C NMR spectra of **1** in CDCl₃ at 25 °C (*a*) and in the solid state (CP/MASS) at 25 °C (*b*). Numbers attached to the signals: see Table 1.

On the other hand, in phenol-d_6 at 50 °C, the signal of the spiro carbon in **1** significantly shifted to a lower magnetic field (relative chemical shift ($\Delta\delta$) values from the corresponding signals observed in CDCl₃, $\delta = 78.5$) and appeared in the sp²-hybridization region ($\delta = 162.7$). A remarkable upfield shift was also produced in an ortho carbon atom of the lactone ring (No. 14 in Table 1) which is linked to the spiro carbon. In addition to these changes, relatively large shifts ($\delta = 1 > 3$ ppm) in the δ values were observed for most of the fluoran carbons. These results support the view that, in phenol-d_6, a cleavage of the C(spiro)–O bond in the lactone ring takes place and the conjugation system of the xanthene ring significantly changes. The X-ray structure for the colored species of a fluoran–cadmium(II) chelate has been reported, and the lactone ring-opened zwitterionic structure of the fluoran skeleton was confirmed.[15] Furthermore, the

signal of the carbon atom corresponding to the spiro carbon of this chelate in CD₂Cl₂ appeared at $\delta = 162.25$.[15] This δ value is almost consistent with that of **1** observed in phenol-d_6. Thus, the colored species of **1** formed in phenol-d_6 would be the zwitterion (**Z**), which would be stabilized in phenol-d_6 by a hydrogen-bonding interaction between the solute (**Z**, acceptor) and the solvent (phenol-d_6, donor).[19–21]

Effects of Solvents and Temperature on the Lactone–Zwitterion Equilibrium.   In order to investigate the effects of solvents on the equilibrium between **L** and **Z**, the electronic absorption spectra of **1** in various phenols and alcohols were measured; the absorption characteristics (λ_{max} and ε) are summarized in Table 2. As mentioned above, the fluoran **1** showed no visible absorption in aprotic solvents, such as chloroform and acetonitrile. Among the phenol-related solvents examined, a remarkable decrease in the ε

Table 2.   Electronic Absorption Maxima (λ_{max}) and Apparent Molar Absorptivities (ε at λ_{max}) of **1** in Various Solvents at 25 °C

Solvent	Dielectric constant of solvent[a]	pK_a of solvent[b]	λ_{1max}	ε at λ_{1max}[c]	λ_{2max}	ε at λ_{2max}[c]
m-Cresol	11.8	10.1	579	1.45	467	1.43
o-Cresol	11.5	10.3	563	1.51	466	1.49
m-Methoxyphenol	—	9.7	576	1.52	467	1.40
o-Methoxyphenol	11.7	9.9	562	0.05	462	0.05
o-Chlorophenol	6.3	8.3	565	1.55	468	1.46
o-Hydroxyacetophenone	—	—	ND[d]	—	ND	—
Methanol	32.7	15.5	571	0.13	458	0.14
Ethanol	24.6	15.9	ND	—	ND	—
2,2,2-Trifluoroethanol	27	12.3	554	1.75	448	1.55
(CH₃)₂CHOH[e]	—	9.3	549	1.81	449	1.43
Methanol–HCl (0.2 M)	—	—	589	1.67	451	1.67
Chloroform	4.8	—	ND	—	ND	—
Benzene	2.3	—	ND	—	ND	—
1,4-Dioxane	2.1	—	ND	—	ND	—
Acetonitrile	37.5	—	ND	—	ND	—

a) at 25 °C, Ref. 23.   b) In water at 25 °C, Ref. 25.   c) $10^4\ \mathrm{M^{-1}\,cm^{-1}}$.   d) Not detected.   e) 1,1,1,3,3,3-Hexafluoro-2-propanol.

value was observed in o-methoxyphenol and o-hydroxyace-tophenone, indicating that in these solvents the formation of **Z** was strongly inhibited. It is considered that the formation of the zwitterion of a fluoran compound in phenol solvents is promoted by hydrogen-bonding interactions between the fluoran (at the charged–COO⁻ group) and the phenolic OH.[19–21] The interaction should be inhibited when the hydrogens in the phenolic OH groups become unavailable through ortho chelation (formation of an intramolecular hydrogen bond) and/or steric effects. Because no decrease in the ε values of **1** was observed in o-cresol and o-chlorophenol at 25 °C, the steric effects of the substituent groups at the ortho position in o-methoxyphenol and o-hydroxyace-tophenone may be negligible, and the ortho chelation effects are a dominant factor for decreasing the formation of **Z** in these solvents. Similar phenomena were reported in the case of rhodamine B.[22]

As for alcoholic solvents, methanol, being a weak hydrogen-bonding donor compared with phenols, developed only ca. 10% or less **Z**, judging from the ε value, and almost 100% of **1** exists as **L** in ethanol. The difference in the position of the equilibrium of **1** in methanol and ethanol would be ascribed to the electrostatic factor of the solvents[19] (dielectric constant at 25 °C, 32.7 for methanol and 24.6 for ethanol).[23] In contrast, almost full color development occurred in 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP), which are known to be strong hydrogen-bonding donors.[20,21,24] The pK_a values of these fluoro alcohols are almost consistent with those of phenols (pK_a in water, 12.3 for TFE, 9.3 for HFP, 10.1 for m-cresol).[25] The predominant formation of **Z** in TFE is not attributed to the dielectric constant (27 for TFE),[21] which is close to that of ethanol. In a strongly acidic methanol solution containing 0.2 M hydrochloric acid, a cation form of **1** in which a proton is attached to the charged–COO⁻ group in **Z** may be produced, because a similar case was reported for the rhodamine.[20,21]

When a phenol solution of **1** was heated, a hypochromic

effect was observed in the absorption spectra, indicating that a shift in the equilibrium from **Z** to **L** occurs with increasing temperature. On the other hand, in the ¹³C NMR spectra of **1** in phenol-d_6, a large upfield shift and a large downfield shift were observed for the C(9) and C(14), respectively, as the temperature increased (Table 3). These phenomena correspond to a shift in the equilibrium toward **L**. Only one signal was observed for each carbon atom at any temperature, suggesting that the equilibrium occurs much faster than the NMR time scale. The observed δ values thus reflect the ratio of the two isomers (**L** and **Z**) in equilibrium. Because the lowering of the δ value of C(9) with decreasing temperature is almost saturated at 50 °C, almost 100% of **1** could be postulated to exist as **Z** at this temperature in phenol-d_6.

Although the ε values of **1** in o-cresol and o-chlorophenol were almost equivalent to those in m-cresol at 25 °C (Table 2), substituent-group effects on the position of the **L–Z** equilibrium occurred with increasing temperature. Figure 4 shows the absorption spectra of **1** in m-cresol and o-cresol at various temperatures; the absorption characteristics of **1** in m-cresol, o-cresol and o-chlorophenol at various temperature are given in Table 4. The hypochromic effects of **1** in o-cresol and o-chlorophenol were more significant than that observed in m-cresol. In order to determine the **L** : **Z** ratio, the intrinsic molar absorptivities (ε_0) of **Z** in each solvent

Table 3.   ¹³C NMR Chemical Shifts (δ in ppm from SiMe₄) of C(9) and C(14) in **1** at Various Temperatures in Phenol-d_6[a]

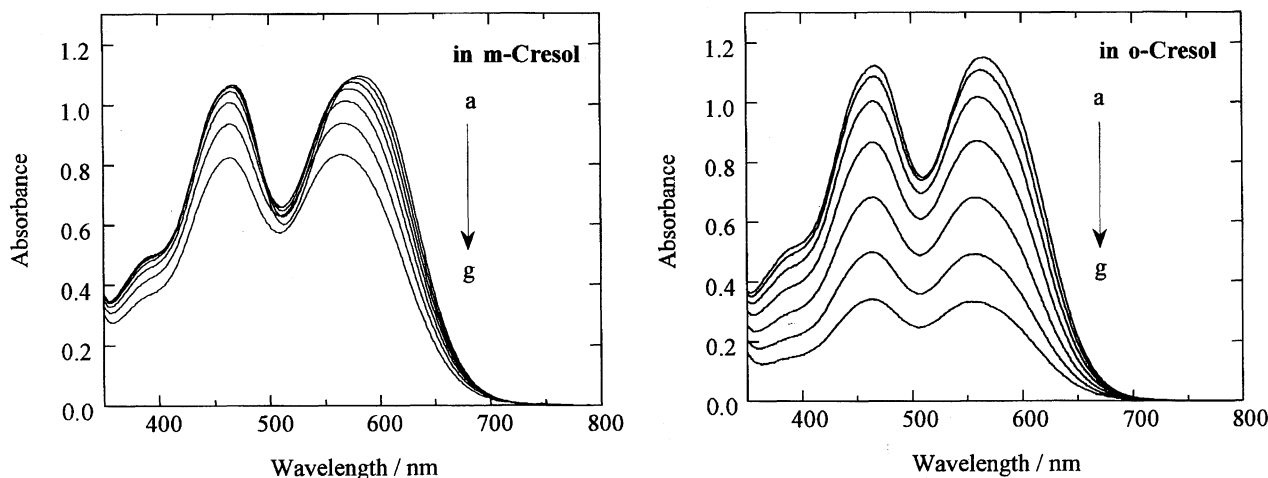| Temperature/°C	δ of C(9)	δ of C(14)
40	162.8	131.8
50	162.7	132.0
80	160.6	132.9
110	148.5	136.7
125	137.8	139.7
140	125.6	143.3

a) C(9) and C(14): reference to Table 1.

Fig. 4.   Electronic absorption spectra of **1** (7.5×10^{-5} M) in m-cresol and in o-cresol at various temperatures. The changes in the concentrations of **1** by solvent expansion with increasing temperature were corrected. Temperature: a, 20; b, 35; c, 50; d, 65; e, 80; f, 95; g, 110 °C. Light-path length: 1 cm.

Table 4. Electronic Absorption Characteristics of **1** at Various Temperatures in *m*-Cresol, *o*-Cresol, and *o*-Chlorophenol[a]

Temperature	in *m*-Cresol				in *o*-Cresol				in *o*-Chlorophenol			
°C	λ_{1max}/nm	$\varepsilon^{b,c}$	**Z**/%	$K=[\mathbf{Z}]/[\mathbf{L}]$	λ_{1max}/nm	$\varepsilon^{b,c}$	**Z**/%	$K=[\mathbf{Z}]/[\mathbf{L}]$	λ_{1max}/nm	$\varepsilon^{b,c}$	**Z**/%	$K=[\mathbf{Z}]/[\mathbf{L}]$
10	580	1.47	100	—	—[d]	—	—	—	568	1.58	99.4	166
20	579	1.46	99.3	142	567	1.54	98.1	51.6	565	1.57	98.7	75.9
35	578	1.45	98.6	70.4	563	1.48	94.3	16.5	564	1.53	96.2	25.3
50	576	1.43	97.3	36.0	562	1.36	86.6	6.46	563	1.46	91.8	11.2
65	572	1.40	95.2	19.8	561	1.16	73.9	2.83	562	1.30	81.8	4.49
80	570	1.35	91.8	11.2	558	0.907	57.8	1.37	561	1.06	66.7	2.00
95	568	1.25	85.0	5.67	558	0.653	41.6	0.712	561	0.775	48.7	0.949
110	565	1.11	75.5	3.08	555	0.442	28.2	0.393	560	0.521	32.8	0.488

a) The concentration of **1** employed was 7.50×10^{-5} M. b) Apparent molar absorptivity, 10^4 M^{-1} cm^{-1} at λ_{1max}. The changes in the concentration of **1** by solvent expansion with increasing temperature were corrected. c) Intrinsic molar absorptivities (ε_0) of **Z**: 1.47×10^4 M^{-1} cm^{-1} in *m*-cresol, 1.57×10^4 M^{-1} cm^{-1} in *o*-cresol, 1.59×10^4 M^{-1} cm^{-1} in *o*-chlorophenol. The ε_0 values of **Z** in each solvent were estimated by extrapolation of the ε vs. temperature plots. d) Did not measured because the solvent solidified.

were estimated by extrapolation of the ε vs. temperature plots (ε_0 values of **Z**: 1.47×10^4 M^{-1} cm^{-1}, 1.57×10^4 M^{-1}, 1.59×10^4 M^{-1} cm^{-1} in *m*-cresol, *o*-cresol and *o*-chlorophenol, respectively). As can be seen in Table 4, more than 98% of **1** exists as **Z** in these three phenolic solvents at 20 °C, whereas at 110 °C the ratio of **Z** is about 75% in *m*-cresol, and only about 28 and 33% in *o*-cresol and *o*-chlorophenol, respectively.

The standard Gibbs-energy change ($\Delta G°$) for the **L–Z** equilibrium is

$$\Delta G° = -RT\ln K,$$

where R is the gas constant, T is the temperature in kelvins and K is the equilibrium constant between **L** and **Z** ($K=$ [**Z**]/[**L**]). The enthalpy and entropy changes from the dependence of $\ln K$ on the inverse temperature are determined from

$$\ln K = -\Delta H°/RT + \Delta S°/R.$$

The $\ln K$ vs. $1/T$ plots of **1** in *m*-cresol, *o*-cresol, and *o*-chlorophenol are shown in Fig. 5. Linear relationships between $\ln K$ and $1/T$ were obtained over the temperature range from 50 to 110 °C with correlation coefficients of 0.9970,
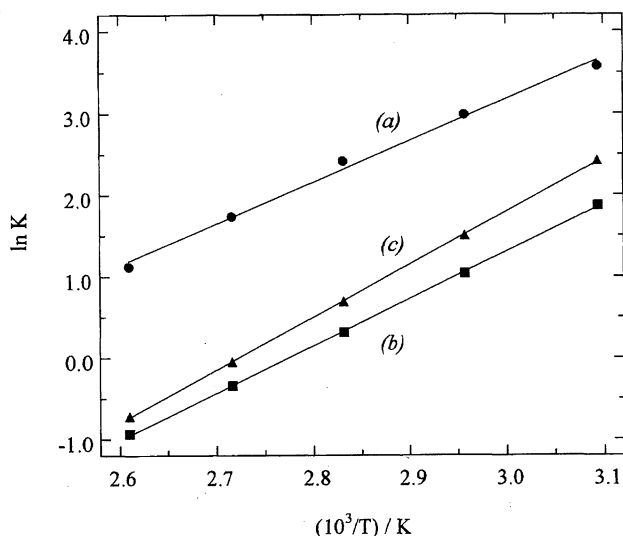
0.9999, and 0.9999 in *m*-cresol *o*-cresol and *o*-chlorophenol, respectively. The resulting thermodynamic parameters for the **L–Z** equilibrium are given in Table 5. Both the $\Delta H°$ and $\Delta S°$ values become more negative in the following order: *m*-cresol > *o*-cresol > *o*-chlorophenol. From the point of view of enthalpy changes, although *o*-chlorophenol is rather favorable for producing **Z**, the most negative value of the entropy change in this solvent makes the $\Delta G°$ value less negative compared with that in *m*-cresol. On the contrary, $\Delta G°$ showed the most negative value in *m*-cresol due to its least negative entropy change in spite of the least negative enthalpy change. The entropy term, thus, tends to dominate the **L–Z** equilibrium in these three phenols. As pointed out by Hinckley et al. in rhodamine–alcohol systems,[20,21] the observed thermodynamic changes reflect not only the donating ability of the solvent in solute (**Z**)–solvent hydrogen bonds, but also the degree of self-association of the solvent itself. $\Delta S°$ should have its least negative values in solvents which are highly associated and its most negative values in less associated solvents.[20,21] It would be considered that the situation in the **L–Z** equilibrium in phenols is similar to that in the rhodamine–alcohol systems. *o*-Chlorophenol would be less associated compared with *m*-cresol due to an intramolecular interaction between the phenolic OH group and the chloro substituent at the ortho position. The methyl group in *o*-cresol should also disturb the self-association, though the degree would be less significant compared with that of *o*-chlorophenol.

Fig. 5. Plots of $\ln K$ vs. $1/T$ for the equilibrium between **L** and **Z**.

Table 5. Thermodynamic Values for the Equilibrium between **L** and **Z** in *m*-Cresol, *o*-Cresol, and *o*-Chlorophenol

Solvent	$\Delta G°$ [a] kJ mol^{-1}	$\Delta H°$ [b] kJ mol^{-1}	$\Delta S°$ [b] J mol^{-1} K^{-1}
m-Cresol	−12.3	−42.3	−100
o-Cresol	−8.32	−48.1	−133
o-Chlorophenol	−10.1	−53.9	−147

a) at 25 °C. b) Average values for the range 50—110 °C, ±5%.

Conclusions

Although the fluoran compound **1** has been widely used as a black color former in pressure and thermosensitive recording systems, there have been few studies concerning the chemical and physical properties of **1** from a fundamental point of view. In this report we have described a study of the equilibrium between the colorless lactone (**L**) and the colored zwitterion (**Z**) forms of **1** by ^{13}C NMR and electronic absorption spectroscopies. The NMR data showed us a clear-cut description of the structural and electronic changes in **1** accompanying the equilibrium reaction between **L** and **Z**. The effects of solvents and temperature were also revealed and the thermodynamic parameters for the equilibrium in the phenolic solvents were estimated. This information would be important to understand the characteristics of **1** as a color former.

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