

# Structure Analysis of a Coloring and Decoloring Unsymmetrical Fluoran Dye by Carbon-13 Nuclear Magnetic Resonance Method

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Unsymmetrical fluoran dyes whose coloring-to-decoloring reversible reaction depends upon the acidity are used in heat-sensitive recording systems. The reversible reaction corresponds to open-to-closed forms of the lactone ring. We observed remarkable chemical shift differences in 4 species of <sup>13</sup>C NMR signals between open- and closed-forms of the lactone ring of an unsymmetrical fluoran dye, 3-diethylamino-6-methyl-7-chlorofluoran (DEAMCF) in CDCl<sub>3</sub>. According to the optimized molecular structure of DEAMCF by a semi-empirical molecular orbital (MO) Austin Model 1 (AM 1) method, the xanthene moiety in colorless form is folded at 166 degree around the C(spiro)-O(xanthene) axis, and the benzolactone moiety is almost perpendicular to the xanthene moiety. The moiety in color form for a molar DEAMCF/H<sub>2</sub>SO<sub>4</sub> ratio of 1/2.2 becomes almost planar and has canonical structure, while the lactone ring opens, according to NMR and MO analyses.

**Keywords** Fluoran dye, carbon-13 nuclear magnetic resonance, Austin Model 1 molecular orbital, coloring-to-decoloring mechanism

3-Diethylamino-6-methyl-7-chlorofluoran (DEAMCF) is one of the unsymmetrical fluoran dyes which are used in heat-sensitive recording systems;<sup>1</sup> facsimile, word-processors, POS systems and automatic ticket-checking machine. We studied DEAMCF in order to experimentally clarify the mechanism of coloring and decoloring of the unsymmetrical fluoran dyes. Despite the wide-spread use of the dyes in heat-sensitive recording materials, we believe that there has been no paper stating the structure dependency of coloring and decoloring of unsymmetrical fluoran dyes. By using the FTIR method, one can obtain the vibrational spectra of the CO group in either closed- or open-forms of the lactone ring. However, it is difficult to determine the change in the dye's molecular structure from the IR spectra. On the other hand, by using a UV spectral method, we can observe the absorption spectra while in the coloring state. However, the UV spectra are too simple for elucidating the coloring mechanism of the fluoran dye.

We demonstrate here that the structure analysis of coloring and decoloring DEAMCF dye can be clarified in terms of the <sup>13</sup>C NMR and semi-empirical molecular orbital (MO) Austin Model 1 (AM 1)<sup>2</sup> methods.

## Experimental

DEAMCF was purchased and recrystallized from CHCl<sub>3</sub>. We observed a UV absorption spectrum of the DEAMCF dye in a coloring CDCl<sub>3</sub> solution using a Shimadzu UV-3100 spectrophotometer at room temperature (25°C).

The <sup>13</sup>C NMR spectra were measured at 62.896 MHz with a Bruker AC 250 spectrometer. Between 100 and 1000 transients were accumulated using a 2 μs (40°) pulse; 32K data points were collected over a bandwidth of 4 kHz. These measurements were made at a temperature of 30°C. One-dimensional carbon and two-dimensional COSY and HETCOR (C-H correlation) spectra were obtained using pulse sequences available in the Bruker library.

## Results and Discussion

### <sup>13</sup>C NMR signal analysis of DEAMCF in CDCl<sub>3</sub>

Twenty-three species of <sup>13</sup>C NMR signals of the DEAMCF dye in CDCl<sub>3</sub> were assigned to the numbered carbons of the structural formula of the dye (see Fig. 1(a), Fig. 3(a,b,c) and Table 1) according to the <sup>13</sup>C INKA Data Bank<sup>3</sup>, as well as <sup>1</sup>H COSY and C-H correlation 2D pulse techniques. We found remarkable chemical shifts for some signals of the xanthene-ring carbons (the

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numbers 2, 4, 9 and 11 signals) between the closed- and open-forms of DEAMCF.

By considering a molecular model of DEAMCF using the MO method, we can determine the structure of the dye in closed form. In Fig. 1(b), we show an optimized molecular structure determined by a semi-empirical MO AM 1 method.<sup>2</sup> The xanthene moiety was found to be folded at 166 degrees around the C(spiro)-O(xanthene) axis (C(9)-O(10) in Fig. 1(b)); the benzolactone moiety is almost perpendicular to the xanthene. Especially, the bond length of C(9)-O(8) at the lactone ring in Fig. 1 was

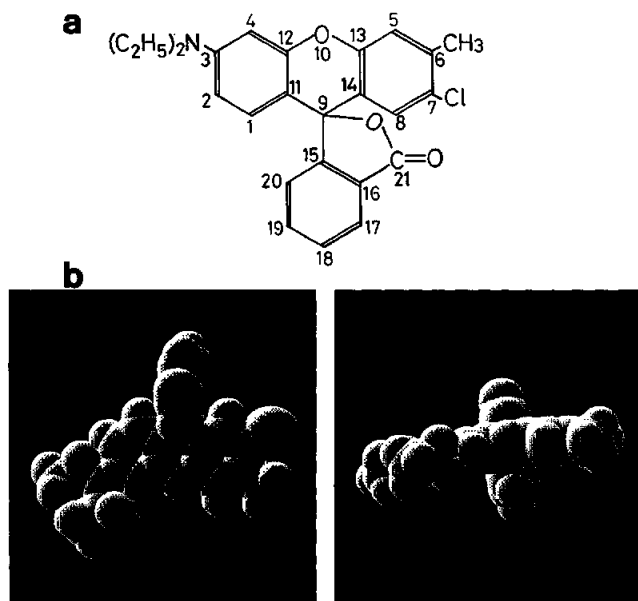


Fig. 1 Molecular structure of DEAMCF dye in closed form: (a) structural formula, and (b) optimized molecular models by the AM 1 MO method.

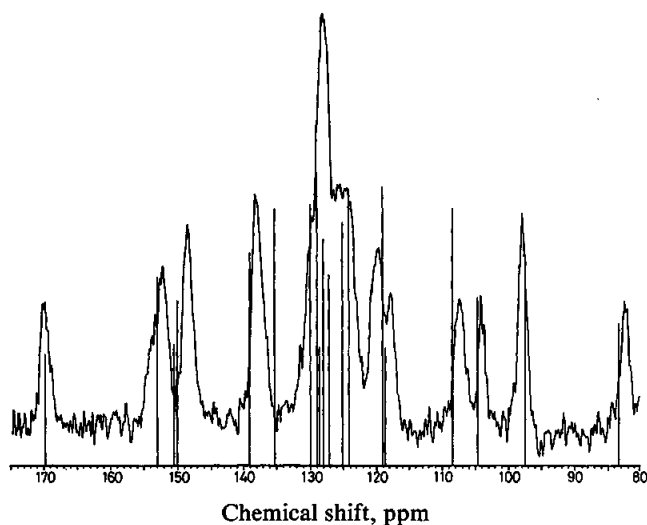


Fig. 2 <sup>13</sup>C CPMAS spectra in a DEAMCF solid compared with those (line spectra) in a CDCl<sub>3</sub> solution over the range 80 to 175 ppm.

calculated to be 1.48 Å, which is longer than the normal C(sp<sup>3</sup>)-O bond length (1.43 Å). This means that the opening of the lactone ring occurs here. These results are in good accordance with an X-ray diffraction analysis<sup>4</sup> of a fluoran dye (such as DEAMCF).

In Fig. 2, the observed <sup>13</sup>C CPMAS NMR spectra in DEAMCF crystal are compared with the <sup>13</sup>C spectra of DEAMCF in a CDCl<sub>3</sub> solution over the chemical shift range of 80 to 175 ppm. The good accordance of the spectra in a solid state with that in a CDCl<sub>3</sub> solution implies that the structure of DEAMCF in a CDCl<sub>3</sub> solution corresponds considerably well to that of a DEAMCF solid in closed-form of the lactone ring. We can thus consider that the coloring mechanism of DEAMCF can be elucidated from an analysis of the <sup>13</sup>C NMR spectra in a CDCl<sub>3</sub> solution.

#### Coloring-to-decoloring reversible reaction of DEAMCF in CDCl<sub>3</sub> solution

In order to compare the coloring state of the DEAMCF dye in CDCl<sub>3</sub> with the state of DEAMCF with Bisphenol A (BPA) in a heat-sensitive recording system, we used a UV absorption spectral method. We observed the absorption spectra in two species of colored states for the DEAMCF dye. The double peaks (around 500 and 530 nm) in CDCl<sub>3</sub> correspond well to the reflection spectrum of a coloring heat-sensitive sample comprising dispersed particles of DEAMCF and BPA in polyvinylalcohol (PVA) layer on an aluminum plate. We then confirmed that the coloring state in CDCl<sub>3</sub> is similar to that in the PVA layer.

We now examine how the <sup>13</sup>C NMR spectra of DEAMCF in CDCl<sub>3</sub> change as a small amount of concentrated H<sub>2</sub>SO<sub>4</sub> is added, and the reddish-orange color deepens. In Fig. 3(a)–(c) we show the <sup>13</sup>C spectra over the range 80 to 175 ppm for molar DEAMCF/H<sub>2</sub>SO<sub>4</sub> ratios of 1/0.26, 1/0.54 and 1/2.2, respectively. An inspection of (a) to (c) in this figure indicates that some signals of the xanthene ring shift considerably as H<sub>2</sub>SO<sub>4</sub> is added: the assigned signals of numbers 2, 4, 9 and 11 move to a lower field, while the signals of 12 and 15 shift to a higher field. These results are tabulated in Table 1. In the deepened-reddish orange CDCl<sub>3</sub> solution, most of the <sup>13</sup>C NMR signals of the xanthene ring exist in the shift range of the normal benzene-ring carbons of about 110–150 ppm. This may mean that the xanthene ring becomes almost planar and has a canonical structure in Fig. 4(a). On the other hand, after 4.5 mol NaOH (*versus* 1 mol DEAMCF) was added to the sample for a molar DEAMCF/H<sub>2</sub>SO<sub>4</sub> ratio of 1/2.2, the coloring sample gradually became decolorized, the decoloring sample showed the same spectra as did the closed form in Table 1. We have confirmed the reversible coloring-to-decoloring reaction three times, indicating that the reversible reaction of DEAMCF depends on the acidity, and corresponds to the open-to-closed form of the lactone ring.

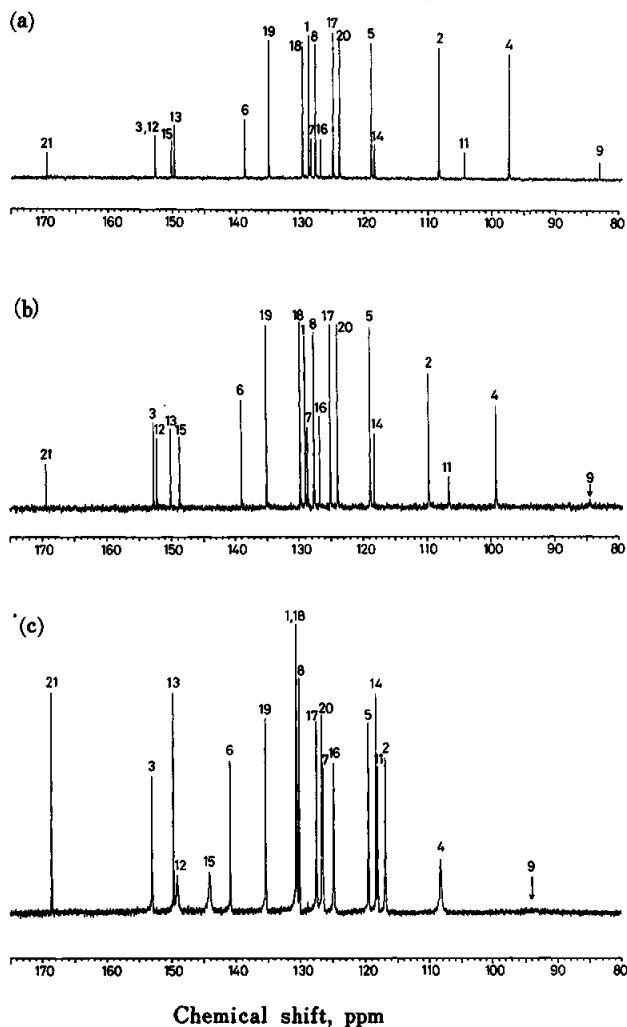


Fig. 3  $^{13}\text{C}$  spectra of DEAMCF over the range 80 to 175 ppm for three molar DEAMCF/ $\text{H}_2\text{SO}_4$  ratios ((a), (b) and (c), corresponding to ratios of 1/0.26, 1/0.54 and 1/2.2, respectively).

#### Structure of DEAMCF in coloring state

It is very interesting to discuss the correlation between the remarkable chemical shifts for some signals and the canonical and steric structures in the coloring form. In Table 1, large shift differences between the open and closed form of the lactone ring appear to exist in the diethylaniline ring of the xanthene moiety. The large shift differences in the diethylaniline ring correspond well to the canonical structure in Fig. 4(a). In Table 2, we compare the  $^{13}\text{C}$  chemical shifts in the signals of the diethylaniline ring in DEAMCF with those of the diethylaniline (DEA) and diethylaniline ring in Rhodamine B (Fig. 5). These comparisons show that the xanthene moiety of DEAMCF in the coloring form is almost planar, and has canonical structures; this is because the shifts of the diethylaniline ring in the coloring form are in good agreement with those of DEA and the ring in Rhodamine B of Fig. 5.

In Fig. 4(b), we show an optimized molecular structure

Table 1  $^{13}\text{C}$  NMR chemical shieldings for DEAMCF in  $\text{CDCl}_3$  solution

	Closed-form shift, ppm	Open-form shift, ppm	Difference, ppm
1	128.8	130.5	-1.7
2	108.5	116.8	-8.3
3	152.7	153.0	-0.3
4	97.5	108.2	-10.7
5	119.0	119.4	-0.4
6	138.7	140.8	-2.1
7	128.5	126.5	2.0
8	127.8	130.1	-2.3
9 (spiro)	83.5	94.0	-10.5
11	104.6	118.0	-13.4
12	152.8	149.0	3.8
13	149.7	149.7	0.0
14	118.5	118.3	0.2
15	150.2	144.0	6.2
16	127.0	124.8	2.2
17	125.0	127.5	-1.5
18	129.7	130.5	-0.8
19	135.0	135.3	-0.3
20	124.0	126.6	-2.6
21 (=CO)	169.4	168.5	0.9
-N=(CH <sub>2</sub> ) <sub>2</sub>	44.5	51.8	-7.3
-CH <sub>2</sub> -CH <sub>3</sub>	12.5	11.1	1.4
-CH <sub>3</sub>	20.2	20.2	0.0

The chemical shifts were referred to TMS carbon.

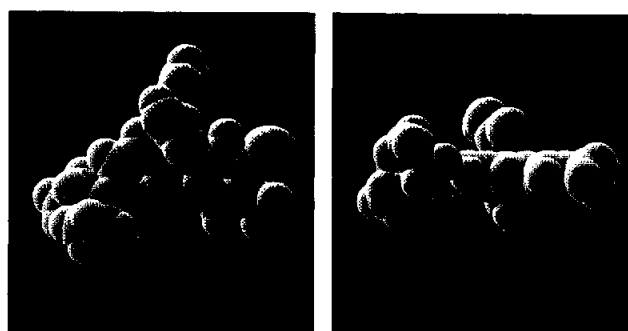
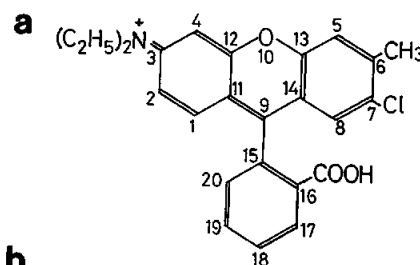


Fig. 4 Molecular structure of the cation of the DEAMCF dye in open form: (a) structural formula, and (b) optimized molecular models by the AM 1 MO method.

in the open form of the cation of DEAMCF by the semi-empirical MO AM 1 method. In this figure the xanthene can be seen as having become planar. In

Table 2  $^{13}\text{C}$  NMR chemical shieldings for diethylaniline-ring moiety of DEAMCF compared with those of diethylaniline (DEA) and diethylaniline-ring moiety of Rhodamine B

Assigned number	Chemical shift, ppm			
	DEAMCF		Rhodamine B	DEA
	Colorless	Coloring		
1	128.8	130.5	131.6	130.1(3)
2	108.5	116.8	113.9	113.4(2)
3	152.7	153.0	155.3	148.6(1)
4	97.5	108.2	96.0	113.4(2)
11	104.6	118.0	113.7	
12	152.8	149.0	152.8	

The  $^{13}\text{C}$  shifts were referred to TMS carbon. The assignment of Rhodamine B carbon was performed by our study.

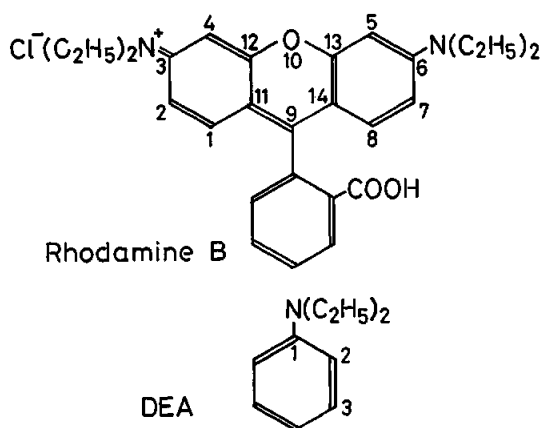


Fig. 5 Structural formulas of Rhodamine B and DEA.

Fig. 6, the bond-order is shown in closed and open forms for an optimized structure using the MO method. In the open form, the diethylaniline ring of the xanthene has a quinoid structure: DEAMCF has a canonical structure.

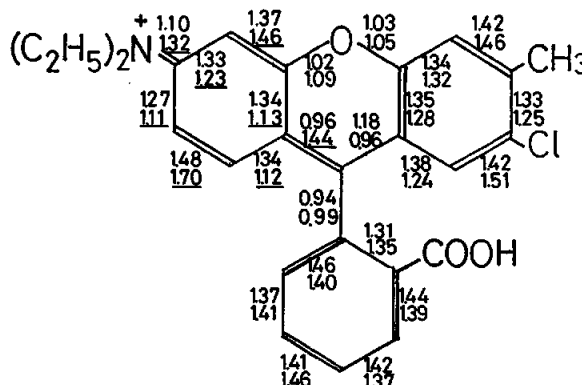


Fig. 6 Optimized molecular structural formula of the cation of DEAMCF dye with bond-order in both closed and open forms by the AM 1 MO method. The upper values denote the closed form, and the lower values the open form.

These results reflect well informations obtained from NMR.

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## References

1. Z. Yoshida and T. Kitao, "Chemistry of Functional Dyes", International Symposium in Osaka as the 70th Anniversary of the Founding Proceeding, Kinki Chemical Society, 1989, Mita Press, Tokyo.
2. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).
3. Estimated  $^{13}\text{C}$  chemical shifts for DEAMCF were obtained from  $\text{C}13$  NMR/IR (INKA, DAT);  $^{13}\text{C}$  NMR Data Bank in Karlsruhe in Germany.
4. K. Kubata, H. Yoshida, K. Nakatsu, H. Matsumoto and Y. Sato, ref. 1, pp. 223 - 225.

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