

See discussions, stats, and author profiles for this publication at:  
<https://www.researchgate.net/publication/244286160>

# C-13 NMR chemical shifts and visible absorption spectra of unsymmetrical fluoran dye by MO calculations

ARTICLE *in* JOURNAL OF MOLECULAR STRUCTURE · JANUARY 2002

Impact Factor: 1.6 · DOI: 10.1016/S0022-2860(01)00700-1

---

CITATIONS

5

---

READS

10

6 AUTHORS, INCLUDING:



[Motohiro Mizuno](#)

Kanazawa University

90 PUBLICATIONS 1,108 CITATIONS

SEE PROFILE

# C-13 NMR chemical shifts and visible absorption spectra of unsymmetrical fluoran dye by MO calculations<sup>☆</sup>

T. Hoshiba<sup>a</sup>, T. Ida<sup>a</sup>, M. Mizuno<sup>a</sup>, T. Otsuka<sup>a</sup>, K. Takaoka<sup>b</sup>, K. Endo<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa, 920-1192 Japan

<sup>b</sup>Research Center, Mitsubishi Paper Mills Ltd. Tsukuba, 300-4247 Japan

Received 16 March 2001; accepted 30 March 2001

## Abstract

An unsymmetrical fluoran dye, 3-diethylamino-6-methyl-7-chlorofluoran (DEAMCF) is one of the leuco dyes which shows the coloring-to-decoloring reversible reaction with acidity. We calculated the <sup>13</sup>C chemical shieldings of the DEAMCF with the frame model compounds using ab initio gauge invariant atomic orbital methods, and compared it with the experimental shifts. The calculated values of the frame compounds are in good agreement with the experimental ones in the error range of -4.9-16.7 ppm. The calculated ones for the decolored-form of the DEAMCF reflected the observed ones, although the errors range from -13.4 to 23.1 ppm.

Furthermore, we analyzed the UV-Visible absorption spectra of the decolored and colored forms of DEAMCF by a semiempirical ZINDO MO method. For the colored form, the observed absorption peaks at 550 and 510 nm correspond to the excitation from  $\pi$ -bonding HOMO ( $\pi$ -electrons which conjugated in xanthene ring) and  $\pi$ -bonding nearest HOMO ( $\pi$ -electrons concentrated in benzene-ring with methyl and Cl groups of xanthene) to  $\pi^*$ -antibonding LUMO ( $\pi^*$ -electrons of xanthene), respectively. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Ab initio calculations; NMR chemical shift; UV-Visible absorption spectroscopy; Semiempirical ZINDO calculations; Fluoran dye

## 1. Introduction

3-Diethylamino-6-methyl-7-chlorofluoran (DEAMCF) is one of the leuco dyes that are used in heat sensitive recording system [1], such as facsimile, word-processors, and others. The coloring-to-decoloring reversible reaction of leuco dyes depends on the acidity, and corresponds to open-to-closed forms of the lactone ring. In Fig. 1, we show an example of the reversible reaction with acidity (the decolored

form (1a) when a lactone ring changes to a colorant (1b) with quinoid structure by protonation). We think that it would be a very useful step in the design of new materials in heat-sensitive recording systems to examine the electronic state of leuco dyes from theoretical and experimental viewpoints.

Studies of NMR properties in organic compounds contain a lot of valuable information concerning the nature of chemical bonds. Studies of the magnetic properties provide information about the roles of angular momentum of electrons in the chemical bonds. We are interested in theoretical and experimental studies on the <sup>13</sup>C NMR chemical shieldings in organic compounds of heat-sensitive recording systems. We think that the recent studies [2-5] on the ab initio calculations of <sup>13</sup>C chemical shifts for

<sup>☆</sup> Dedicated to Professor Graham A. Webb on the occasion of his 65th birthday.

\* Corresponding author. Tel.: +81-76-264-5924; fax: +81-76-264-5742.

E-mail address: endo@wiron1.s.kanazawa-u.ac.jp (K. Endo).

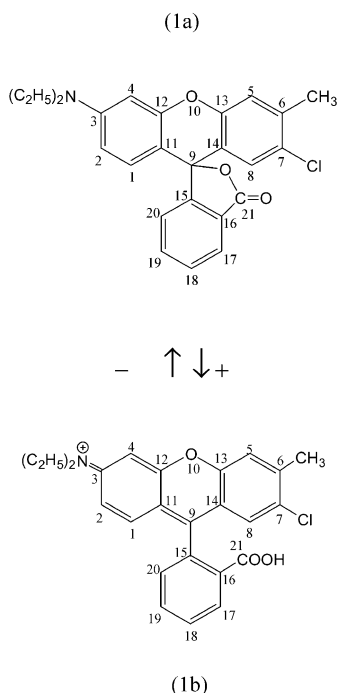


Fig. 1. Reversible reaction of DEAMCF by protonation ((1a) and (1b) show decolorized and colored types, respectively).

substituted aromatic compounds to lignin reflect considerably reasonable values in experiments. In a previous work [6], we demonstrated the structural analysis of coloring and decoloring of DEAMCF dye by  $^{13}\text{C}$  NMR and semiempirical Austin Model 1 (AM 1) [7,8] methods. One of our aim is, then, to reproduce and predict the experimental data for  $^{13}\text{C}$  chemical shifts of the leuco dyes from ab initio MO calculations.

Recently, Pearl and co-workers [9] analyzed the UV–Visible absorption spectra of benzene, pyridine, pyrimidine, and pyridazine in the configuration interaction (CI) calculation using a semiempirical ZINDO method [10]. The ZINDO calculations of the vacuous spectra for mono-substituted benzenes are used to predict the maximum absorption frequency in water with linear correlation coefficient square of 0.941, although the difference between the observed and predicted maximum is not a constant: the linear relation is given by  $\nu_{\text{obsd}}(\text{nm}) = 17.893 + 0.8524\nu_{\text{calc}}(\text{nm})$ , where  $\nu_{\text{obsd}}(\text{nm})$  and  $\nu_{\text{calc}}(\text{nm})$  denote the observed and calculated maxima of absorption frequencies in nm, respec-

tively. For example, the value of 287 nm for the calculated maximum of nitrobenzene becomes 262.5 nm as the observed value in water. Here we use a ZINDO method to clarify the electronic state of transitions for visible spectra of the leuco dye.

In this paper, we calculate the  $^{13}\text{C}$  chemical shieldings of the DEAMCF molecule with the frame model compounds using an ab initio GAUSSIAN 94 program [11] with double- $\zeta$  basis set after the optimization of geometry by a semiempirical AM1 method and compare with the experimental shifts. We also analyze the UV–Visible absorption spectra of the decolorized and colored forms of DEAMCF by a semiempirical ZINDO MO method.

## 2. Calculation

The  $^{13}\text{C}$  chemical shieldings of DEAMCF and the frame model (A–E) molecules were obtained from calculations of the finite perturbation method in GAUSSIAN 94 program using double- $\zeta$  basis set for all atoms after the optimization of geometry by semiempirical AM1 method. These calculations produce absolute shielding values that are converted into chemical shifts by subtraction from the shielding value for TMS [12]. The ab initio MO calculations were performed on a DEC VT-Alpha 533 workstation.

We obtained the UV–Visible absorption spectra of DEAMCF by ZINDO method, after the geometry optimization of the molecule with a semiempirical AM1 method. For the comparison between calculations for the molecules in vacuum and experiments in solution, we must shift each computed energy value  $E_k'$  by a quantity  $\sigma$  as  $E_k = E_k' - \sigma$  due to solvent effect. The intensity of UV–Visible absorption spectra was obtained from the transition probability of each transition energy by the CI method in the ZINDO program.

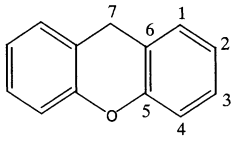
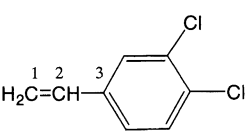
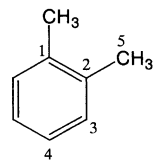
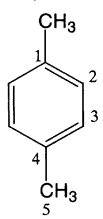
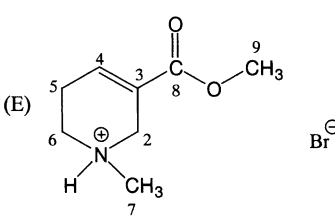
The UV–Visible absorption spectra were simulated by the superposition of a peak centered on the shifted energy values,  $E_k$ . The peak shape is represented by a Gaussian lineshape function:

$$F(x) = A(k) \exp\{-B(k)(x - E_k)^2\} \quad (1)$$

where the intensity,  $A(k)$ , is estimated from the transition probabilities. For  $B(k)$ , we used a constant line width of 0.20 eV.

Table 1

Calculated and experimental chemical shifts (ppm) for frame models (A–E) of DEAMCF

Carbon	Calculated	Experimental	Error	
1	139.2	128.9	10.3	(A) 
2	129.5	123.0	6.5	
3	137.8	127.7	10.1	
4	126.6	116.6	10.0	
5	159.5	152.1	7.4	
6	124.8	120.8	4.0	
7	23.0	27.9	–4.9	
1	122.5	115.0	7.5	(B) 
2	139.1	132.6	6.5	
3	142.9	137.8	5.1	
1	142.8	136.4	6.4	(C) 
2	141.1	136.4	4.7	
3	137.7	129.9	7.8	
4	133.6	126.1	7.5	
5	23.2	19.6	3.6	
1	142.0	134.5	7.5	(D) 
2	136.5	129.1	7.4	
3	137.3	129.1	8.2	
4	142.0	134.5	7.5	
5	22.3	20.9	1.4	
2	52.7	50.5	2.2	(E) 
3	122.3	124.1	–1.8	
4	155.7	139.0	16.7	
5	23.5	23.5	0.0	
6	53.4	51.5	1.9	
7	46.2	43.4	2.8	
8	178.9	169.8	9.1	
9	58.2	53.7	4.5	

### 3. Results and discussion

In Table 1, we show the calculated and experimental chemical shifts, along with the error for five frame (A–E) compounds of DEAMCF and each carbon. These compounds were selected to reflect the major structures in DEAMCF based on xanthene ring, ortho- and meta-xylenes, and others. The calculated shifts of the frame compounds are in a considerably good agreement with the experimental ones in the error range of –4.9–16.7 ppm. A least squares fit of all data, as shown in Fig. 2, gives a strong linear relationship with an *R*-square value of 0.993–0.998.

Let us consider the structure of the decolorized-form (closed form of the lactone ring) for DEAMCF by the semiempirical AM1 method. In Fig. 1, the xanthene moiety was found to be folded at 166° around the C(spiro)–O(xanthene) axis (C(9)–O(10)); 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 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 the X-ray diffraction analysis of a fluoran dye [13] (such as DEAMCF).

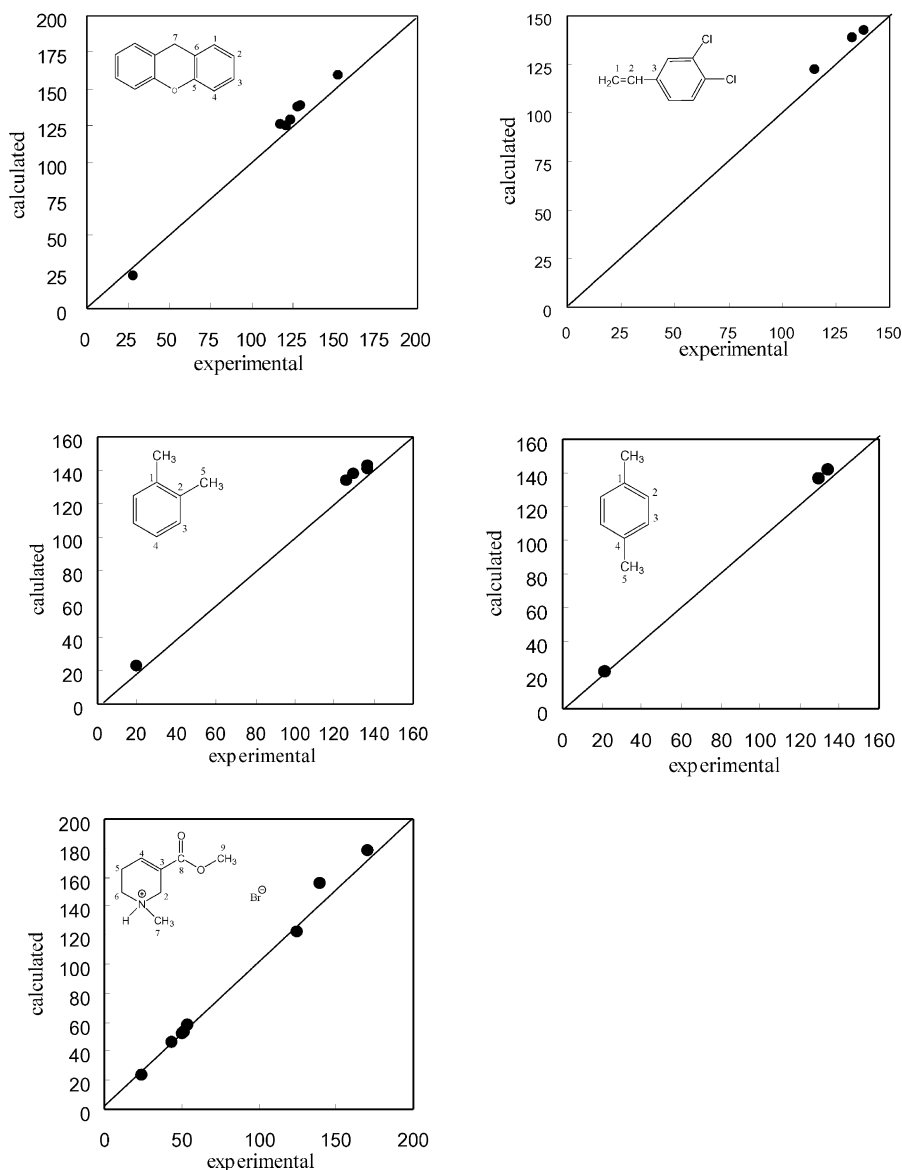
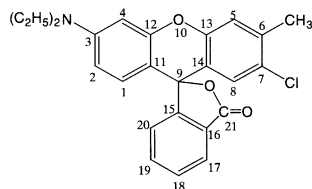


Fig. 2. Plots of data for comparison between calculated and experimental values (in ppm) for  $^{13}\text{C}$  chemical shifts of the frame compounds of DEAMCF.

In Table 2, we summarize the calculated and experimental chemical shifts with the error for the decolored form of DEAMCF and each carbon. The calculated ones for the decolored-form of the DEAMCF reflected the observed ones, as shown in Fig. 3(a), although the errors range from  $-13.4$  to  $23.1$  ppm. The least squares fit of all data for the

decolored DEAMCF molecule, as shown in Fig. 4, shows a considerably good linear relationship with an  $R$ -square value of  $0.954$ . However, for the colored-form of DEAMCF, we were unable to obtain a good agreement of calculated shifts with the experimental ones, as seen in Fig. 3(b) (we omit the table for the calculated and experimental shifts of DEAMCF in

Table 2  
Calculated and experimental chemical shifts (in ppm) for DEAMCF



DEAMCF

Closed form

	Calculated	Experimental	Error
1	142.8	128.8	14.0
2	115.4	108.5	6.9
3	162.8	152.7	10.1
4	107.7	97.5	10.2
5	126.0	119.0	7.0
6	150.0	138.7	11.3
7	136.3	128.5	7.8
8	143.3	127.8	15.5
9	70.1	83.5	– 13.4
11	111.6	104.6	7.0
12	162.7	152.8	9.9
13	160.1	149.7	10.4
14	126.7	118.5	8.2
15	173.3	150.2	23.1
16	127.4	127.0	0.4
17	138.2	125.0	13.2
18	133.6	129.7	3.9
19	146.6	135.0	11.6
20	128.4	124.0	4.4
21	186.3	169.4	16.9

the colored form). We found large differences between the calculated and observed values especially for the C(9) of the colored-form. This is still an unsolved point.

In order to simulate the UV–Visible absorption spectrum of DEAMCF, we used the method of CI for DEAMCF by ZINDO method. In Fig. 5(a) and (b), we show the calculated and observed spectra for both cases, decolored and colored forms. The energies at high intensities on such forms were selected from the output of the calculation. For a best fit of the simulated spectra with the observed ones, we shifted the energy levels with 0.3 and 0.1 eV for the decolored and colored type, respectively. The simulation results seem to reflect the experimental ones. Thus, we

show the MO diagram of the transitions for the absorption spectra of DEAMCF in Fig. 6 to clarify the orbital nature.

In the case of the decolored form, we assumed that the absorption shoulder at around 320 nm is due to the transition between the  $\pi$ -bonding HOMO ( $N,N'$ -diethylaniline unit) and  $\pi^*$ -antibonding LUMO ( $\pi^*$ -electrons of lactone involving phenyl ring). For the colored form, the experimental absorption peak at around 550 nm results from the excitation between the  $\pi$ -bonding HOMO ( $\pi$ -electrons which conjugated in xanthene ring) and  $\pi^*$ -antibonding LUMO ( $\pi^*$ -electrons of xanthene ring). The absorption peak and shoulder at 510 and 480 nm seem to correspond to the transition from the  $\pi$ -bonding nearest HOMO ( $\pi$ -electrons concentrated in benzene ring with methyl and Cl groups of xanthene) and the  $\pi$ -bonding MOs under HOMO ( $\pi$ -electrons of phenyl ring with methyl and carboxyl group) to  $\pi^*$ -antibonding LUMO ( $\pi^*$ -electrons of xanthene ring) for the simulated shoulder and intermediate peak at around 480 and 460 nm, respectively.

#### 4. Conclusions

We calculated the  $^{13}\text{C}$  chemical shieldings of an unsymmetrical fluoran dye 3-diethylamino-6-methyl-7-chlorofluoran with the frame model compounds from calculations of the finite perturbation method in GAUSSIAN 94 program using double- $\zeta$  basis set for all atoms after the optimization of the geometry by semiempirical AM1 method, and compared it with the experimental shifts. The calculated values of the frame compounds are in a considerably good agreement with the experimental ones in the error range of  $-4.9$ – $16.7$  ppm. The calculated ones for the decolored form of the DEAMCF reflected the observed ones, although the errors range from  $-13.4$  to  $23.1$  ppm.

We also analyzed the UV–Visible absorption spectra of the decolored and colored forms of DEAMCF by semiempirical ZINDO MO method. For the colored form, the observed absorption peaks at 550 and 510 nm correspond to the excitation from  $\pi$ -bonding HOMO ( $\pi$ -electrons which conjugated in xanthene ring) and  $\pi$ -bonding nearest HOMO ( $\pi$ -electrons concentrated in benzene ring with methyl

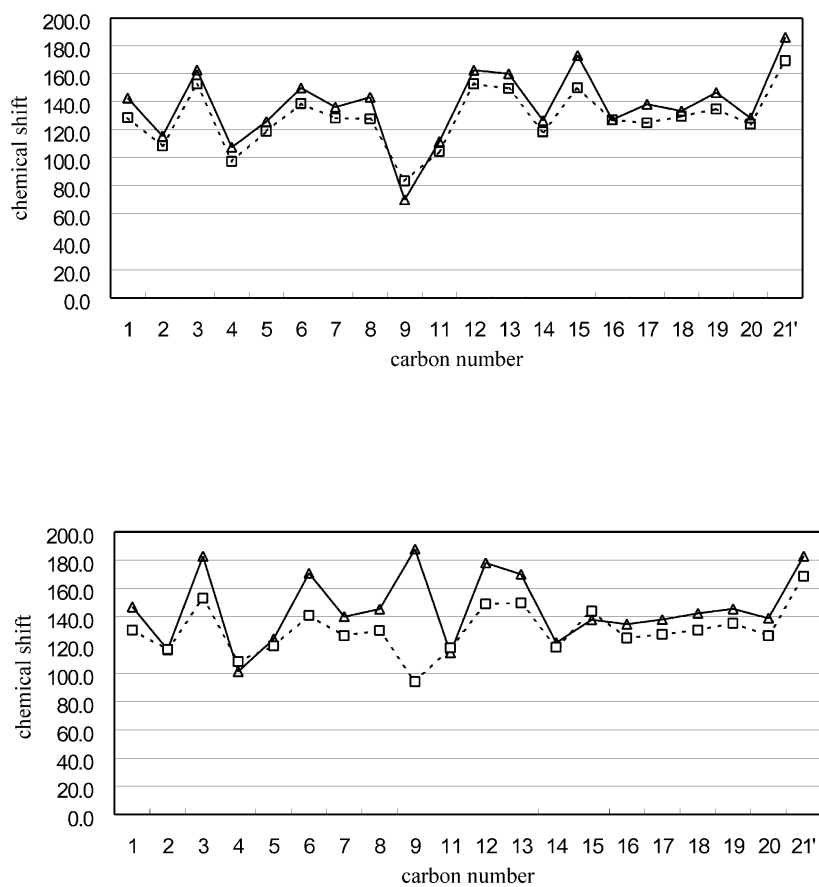


Fig. 3. Plot of data for comparison between calculated and experimental values (in ppm) for  $^{13}\text{C}$  chemical shifts of DEAMCF in each carbon. (a) Decolored DEAMCF; (b) colored DEAMCF.

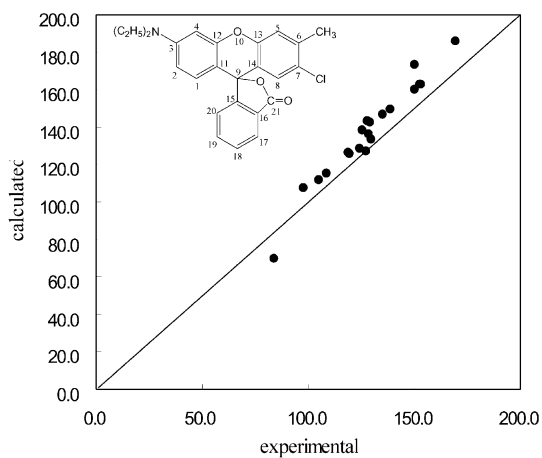


Fig. 4. Plot of data for comparison between calculated and experimental values (in ppm) for  $^{13}\text{C}$  chemical shifts of decolored DEAMCF.

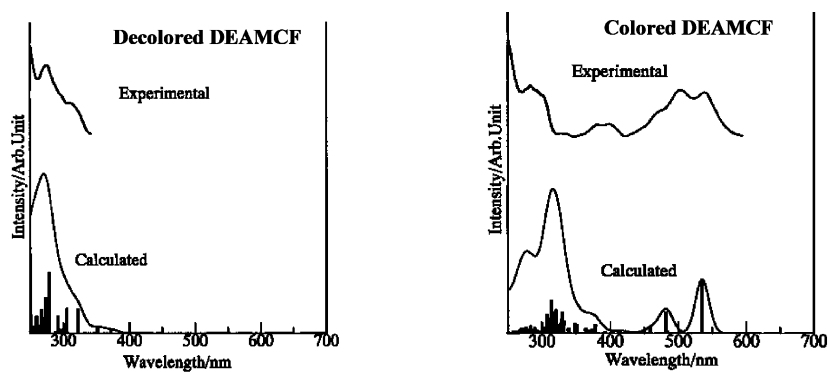


Fig. 5. UV–Visible spectra of DEAMCF with simulated spectra of single molecule. (a) Decolored DEAMCF; (b) colored DEAMCF.

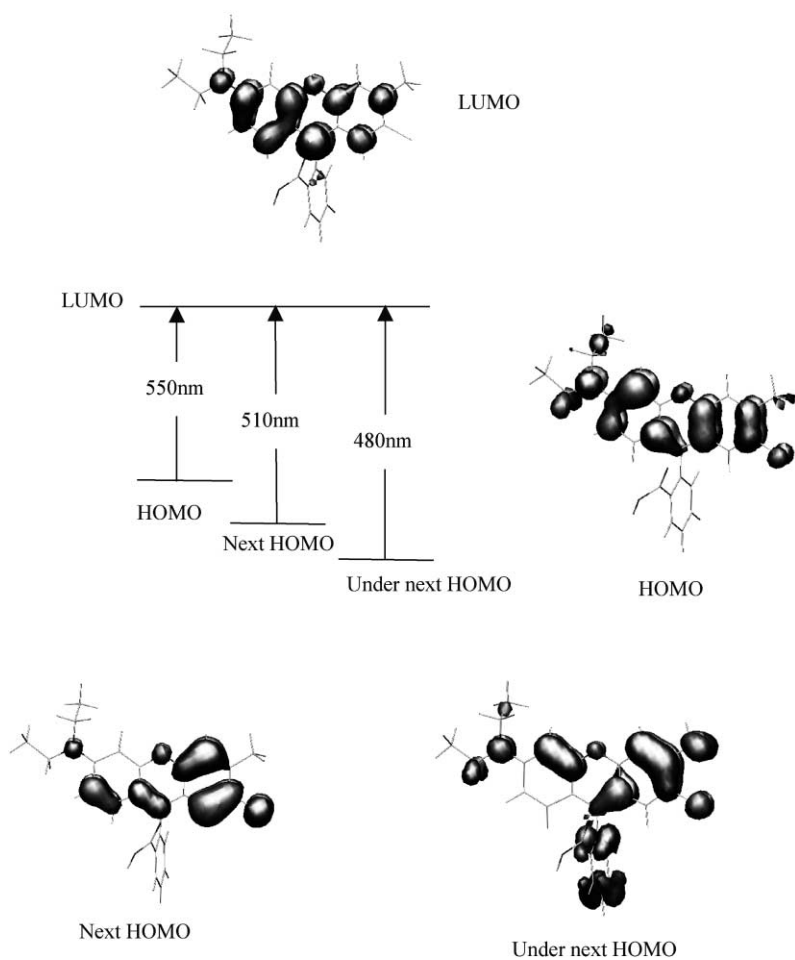


Fig. 6. MO diagram of the transitions for the absorption spectra of DEAMCF in colored type using CI method for single molecule by ZINDO method.



and Cl groups of xanthene) to  $\pi^*$ -antibonding LUMO ( $\pi^*$ -electrons of xanthene), respectively.

## References

- [1] Z. Yoshida, K. Kitao, in: 'Chemistry of Functional Dyes' International Symposium in Osaka as the 70th Anniversary of the Founding Proceeding, Mita Press, Tokyo, Kinki Chemical Society, 1989.
- [2] H.-U. Siehl, F.-P. Kaufmann, K. Hori, J. Am. Chem. Soc. 114 (1995) 9343.
- [3] J.C. Facelli, A. Orendt, Y.J. Jiang, R.J. Pugmire, D.M. Grant, J. Phys. Chem. 100 (1996) 8268.
- [4] G. Zheng, J. Hu, X. Zhang, L. Shen, C. Ye, G.A. Webb, Chem. Phys. Lett. 266 (1997) 533.
- [5] T. Elder, J. Mol. Struct. 505 (2000) 257.
- [6] K. Endo, I. Fujita, N. Kobayashi, Anal. Sci. 7 (1991) 785.
- [7] M.J.S. Dewar, E.G. Zebisch, Theochem 180 (1988) 1.
- [8] M.J.S. Dewar, E.G. Zebisch, E.F. Healy, J.J.P. Stewart, J. Am. Chem. Soc. 107 (1985) 3902.
- [9] G.M. Peary, M.C. Zerner, A. Broo, J. Mckelvey, J. Comput. Chem. 19 (1998) 781.
- [10] ZINDO, A semiempirical quantum chemistry program by M.C. Zerner and co-workers, University of Florida, Gainesville, FL, distributed by MSI Technologies, San Diego, CA, www.msi.com.
- [11] M.J. Frisch, G.M. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Ceeseman, T.A. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacomb, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Address, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. DeFrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN 94, Revision C. 2, Gaussian, Pittsburgh, PA, 1995.
- [12] J. Foresman, A. Frisch, Exploring Chemistry with Electronic Structure Calculations, vol. 2, Gaussian Inc., Pittsburgh, PA, 1993.
- [13] K. Kubata, H. Yoshida, K. Nakatsu, H. Matsumoto, Y. Sato, Ref. 1, pp. 223–225.