Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Effect of the Intramolecular Hydrogen Bonding on the Photochromic Properties of the Hemiindigo Dye having a Pyrrole Ring

Masashi Ikegami [a] & Tatsuo Arai [a]

[a] Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki, Japan

Version of record first published: 31 Aug 2006

To cite this article: Masashi Ikegami & Tatsuo Arai (2005): Effect of the Intramolecular Hydrogen Bonding on the Photochromic Properties of the Hemiindigo Dye having a Pyrrole Ring, Molecular Crystals and Liquid Crystals, 431:1, 445-449

To link to this article: http://dx.doi.org/10.1080/15421400590947063

Mol. Cryst. Liq. Cryst., Vol. 431, pp. 145/[445]–149/[449], 2005

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590947063

Taylor & Francis
Taylor & Francis Group

Effect of the Intramolecular Hydrogen Bonding on the Photochromic Properties of the Hemiindigo Dye having a Pyrrole Ring

Masashi Ikegami
Tatsuo Arai
Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki, Japan

*Photochromism and fluorescence properties of 2-(2-pyrrolylidene)indolin-3-one (**1**) have been studied. The quantum yields of fluorescence emissions of both Z- and E-isomer were very small in protic solvents such as ethanol and water. However, the fluorescence intensity of E-**1** increased by addition of bovine serum albumin (BSA) in water, indicating that E-**1** should bind to the hydrophobic site of BSA.*

Keywords: fluorescence; hemiindigo; hydrogen bonding; photoisomerization

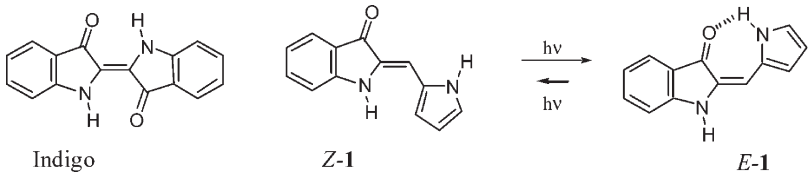
INTRODUCTION

Indigo is one of the important dyes in chemical industry, exhibiting deep blue color and excellent stability due to the intramolecular hydrogen bonding [1]. We have already reported the preparation of a hemiindigo dye having a pyrrole ring capable to form the intramolecular hydrogen bond in the *E*-isomer, 2-(2-pyrrolylidene)indolin-3-one (**1**) [2]. The compound **1** underwent photoisomerization mutually between the *Z*- and *E*- isomers and exhibited color change between greenish yellow and reddish orange in benzene [3–5]. The quantum yield of $E \rightarrow Z$ isomerization in benzene was lower than 0.01, while that of

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 417) and the 21st Century COE Program from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government, by Research Foundation for Opto-Science and Technology, by University of Tsukuba Research Projects, and by the Asahi Glass Foundation.

Address correspondence to Tatsuo Arai, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Tennodai 1-1-1, Tsukuba, Ibaraki 305-8571, Japan. E-mail: arai@chem.tsukuba.ac.jp

$Z \rightarrow E$ isomerization was 0.3. These results indicate that the intramolecular hydrogen bond suppresses the efficiency of $E \rightarrow Z$ isomerization in non-polar solvent.



Indigo *Z*-**1** *E*-**1**

SCHEME 1

In this paper, we will report the fluorescence and isomerization behavior of **1** in ethanol and in water. Especially, the absorption and fluorescence spectra were observed with changing temperature in ethanol. From the results, it was found that the non-radiative deactivation through hydrogen bonding strongly depends on temperature. In addition, we have found the effect of hydrophobic site of bovine serum albumin (BSA) on the photochemical properties of **1** in aqueous solution.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of *E*-**1** and *Z*-**1** in benzene, in ethanol and in water. The absorption maximum of *E*-**1** in ethanol (530 nm) and in water (532 nm) is similar to that in benzene (524 nm). On the other hand, the maximum of absorption spectrum of *Z*-**1** in ethanol (494 nm) and in water (498 nm) appeared at longer wavelength region by 25 nm than that in benzene (470 nm). These results indicate that *Z*-**1** is stabilized by intermolecular hydrogen bonding interaction with solvents in ethanol and water. The quantum yield of $E \rightarrow Z$ isomerization in ethanol was 0.05, which was 5 times larger than that in benzene, while the quantum yield of $Z \rightarrow E$ isomerization was the same in benzene and in ethanol, $\Phi_{Z \rightarrow E} = 0.3$.

Quantum yields of fluorescence emission of *E*-**1** and *Z*-**1** were determined to be 6×10^{-3} and 0.02, respectively in benzene, and 6×10^{-4} and 6×10^{-4}, respectively in ethanol. However, neither *E*-**1** nor *Z*-**1** exhibited fluorescence emission in water. These results indicate that the non-radiative deactivation from the singlet excited state of **1** is accelerated in protic and polar solvents.

The fluorescence intensities of both *E*-**1** and *Z*-**1** in ethanol increased with decreasing temperature with changing spectral profile as shown in Figure 2. The quantum yield of fluorescence emission (Φ_f)

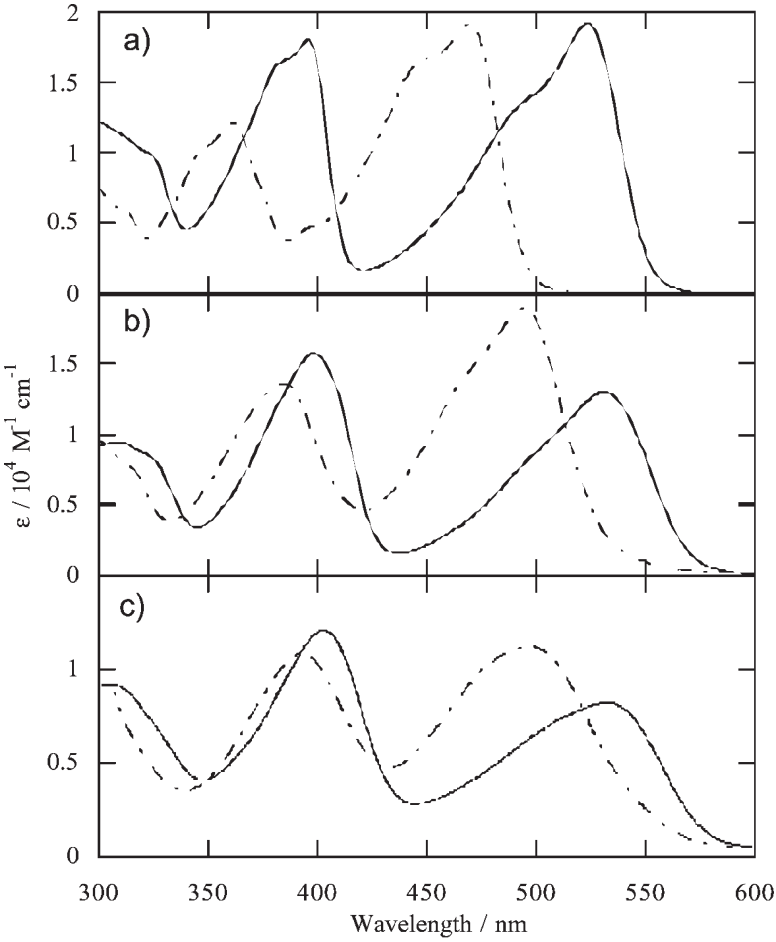


FIGURE 1 Absorption spectra of *Z*-**1** (broken line) and *E*-**1** (solid line) in benzene (a), in ethanol (b), and in water (c).

at 77 K was determined to be 0.1 for both *Z*-**1** and *E*-**1**. The maximum wavelength of fluorescence spectrum (λ_{fm}) of *Z*-**1** at 77 K was similar to that at room temperature. On the other hand, the λ_{fm} of *E*-**1** was shifted from 578 nm to 565 nm with decreasing temperature from 165 K to 77 K, while λ_{fm} at 165 K was identical to that at 295 K. The shift of the maximum of fluorescence emission of *E*-**1** indicates the existence of two emissive states (S_1 and S_1') in the singlet excited state and the existence of activation barrier for deactivation pathway through the intramolecular hydrogen bonding from S_1 to S_1'. *E*-**1**

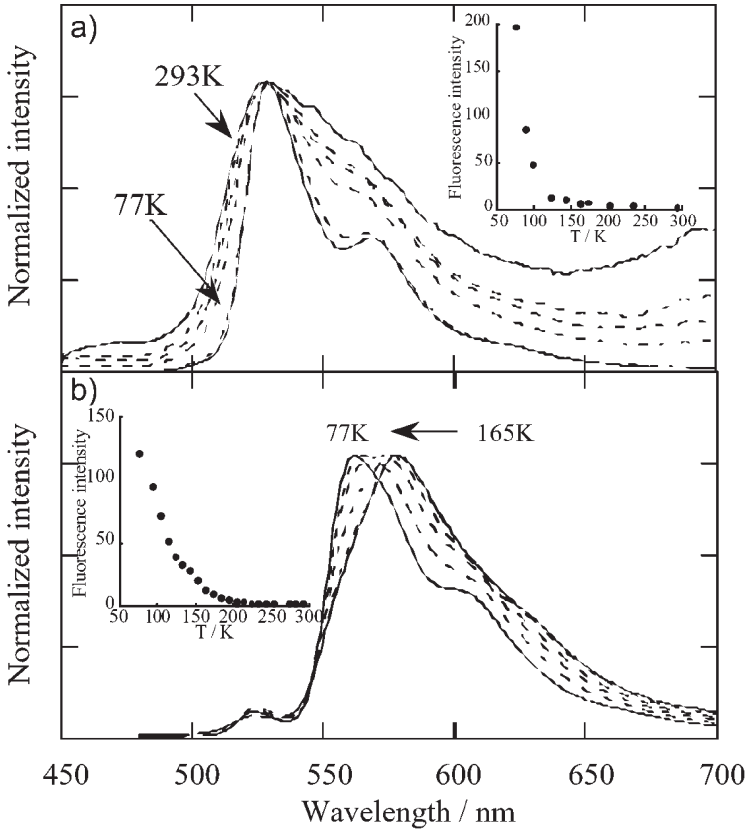


FIGURE 2 Normalized fluorescence spectra of *Z*-**1** (a) and *E*-**1** (b) at different temperatures in ethanol. Inset shows temperature dependence of the fluorescence intensity.

underwent deactivation from S_1 to the relaxed singlet excited state S_1' and exhibited fluorescence emission with the maximum of 578 nm at temperature higher than 165 K. However, the conversion from S_1 to S_1' was suppressed at low temperatures, and *E*-**1** exhibited fluorescence emission from S_1 with a maximum of 565 nm at 77 K.

Compound **1** underwent photoisomerization mutually between *Z*-isomer and *E*-isomer exhibiting a color change. As mentioned above, both *E*-**1** and *Z*-**1** did not exhibit fluorescence emission in water. However, the fluorescence intensity of *E*-**1** in phosphate buffer increased with increasing in the concentration of BSA by incorporation of *E*-**1** into the hydrophobic site of BSA. The suppression of non-radiative deactivation pathway from the singlet excited state to the ground state

of *E*-**1** in hydrophobic site of BSA may increase the fluorescence intensity of *E*-**1**. *Z*-**1** did not exhibit fluorescence emission in the presence or in the absence of BSA. Since *Z*-**1** has three hydrophilic group capable to form intermolecular hydrogen bonding with water, *Z*-**1** should mainly exist in bulk water rather than in BSA.

CONCLUSION

The fluorescence emission of *E*-**1** strongly depends on temperature and solvent. The quantum yields of fluorescence emission of *E*-**1** and *Z*-**1** in protic solvent are smaller than in aprotic solvent due to the intermolecular hydrogen bonding, and those of both *E*-**1** and *Z*-**1** are 6×10^{-4} in ethanol. The fluorescence emission was not observed in aqueous solution. BSA can incorporate *E*-**1** at the hydrophobic site to increase the fluorescence intensity of *E*-**1**.

REFERENCES

[1] Giuliano, C. R., Hess, L. D., & Margerum, J. D. (1968). *J. Am. Chem. Soc.*, *90*, 587.
[2] Katritzky, A. R., Li, Q. L., & Fan, W. Q. (1988). *J. Heterocyclic Chem.*, *25*, 1287.
[3] Ikegami, M. & Arai, T. (2003). *Bull. Chem. Soc. Jpn.*, *76*, 1783.
[4] Ikegami, M., Suzuki, T., Kaneko, Y., & Arai, T. (2000). *Mol. Cryst. Liq. Cryst.*, *345*, 437.
[5] Arai, T. & Ikegami, M. (1999). *Chem. Lett.*, 965.