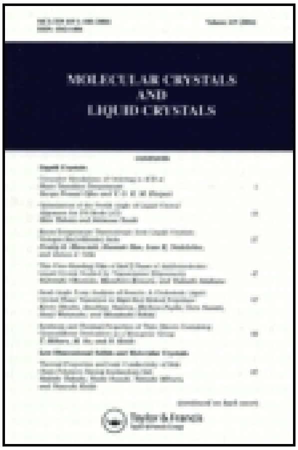


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photochromism of Hydrogen Bonded Compounds

Masashi Ikegami [a], Toshihide Suzuki [a], Yuji Kaneko [a] & Tatsuo Arai [a]

[a] Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki, 305-8571, Japan

To cite this article: Masashi Ikegami, Toshihide Suzuki, Yuji Kaneko & Tatsuo Arai (2000): Photochromism of Hydrogen Bonded Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 345:1, 113-118

To link to this article: http://dx.doi.org/10.1080/10587250008023904

Mol. Cryst. and Liq. Cryst., 2000, Vol. 345, pp. 113-118
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Photochromism of Hydrogen Bonded Compounds

MASASHI IKEGAMI, TOSHIHIDE SUZUKI, YUJI KANEKO
and TATSUO ARAI

Department of Chemistry, University of Tsukuba, Tsukuba,
Ibaraki 305–8571, Japan

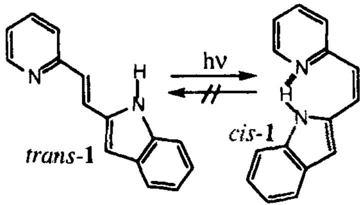
The effect of hydrogen bonding on the photochemical cis-trans isomerization is discussed on the basis of the results of absorption and fluorescence spectra as well as of the determination for the efficiencies of photochemical and photophysical processes.

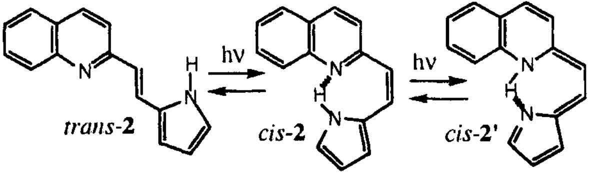
Keywords: Photoisomerization; hydrogen bonding; hydrogen atom transfer

INTRODUCTION

Photochemical cis-trans isomerization has extensively been studied and the relation between the isomerization mechanism and the molecular structure has been investigated [1]. In briefly, stilbene undergoes cis-trans isomerization mutually (two-way isomerization), while styrylanthracene undergoes only cis-to-trans isomerization (cis→trans one-way isomerization).

We have reported another type of one-way isomerization taking place only from trans-to-cis direction in an olefin with an indole ring and a pyridine ring (**1**): **1** exhibited one-way *trans*→*cis* isomerization due to the presence of an intramolecular hydrogen bonding [2-4]. The cis isomer did not undergo isomerization to the trans isomer on direct irradiation. Therefore, after prolonged irradiation the solution contained only cis isomer.





A compound with a quinoline ring and a pyrrole ring **2** underwent two-way isomerization giving a photostationary mixture of [c]/[t]=93.4:6.6 on irradiation at 399 nm [5]. The low composition of the *trans*-isomer at the photostationary state indicates that the deactivation through the hydrogen bonding is predominant also in compound **2**. In addition, *cis*-**2** gave a fluorescence spectrum at considerably longer wavelength region compared to the absorption spectrum. This spectrum is assigned to the tautomer (*cis*-**2'**) fluorescence produced by intramolecular hydrogen atom transfer in the excited singlet state.

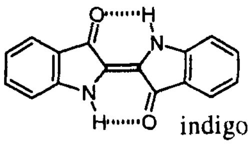
The cis isomer of an olefin with a pyrrole ring and a pyridine ring also underwent hydrogen atom transfer in the excited singlet state [6,7].

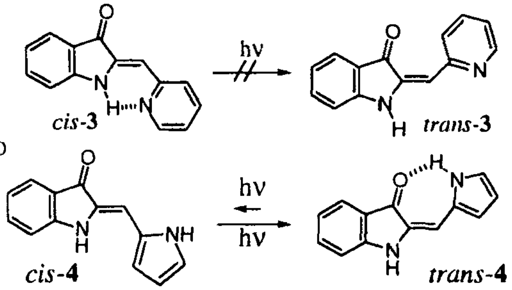
The photochromic properties of *N*-(2-hydroxybenzylidene)aniline and its derivatives have extensively been studied [8,9].

Indigo has a absorption spectrum at visible region and is a photochemically stable compound due to the intramolecular hydrogen bonding. In order to explore the photochromic dye [8,9] having absorption maximum at visible region, we prepared and studied indoline derivatives **3** and **4** which have similar structure to indigo [10,11].

RESULTS AND DISCUSSION

The intramolecular hydrogen bonding is present in the *cis*-**3** and *trans*-**4** as revealed by ^{1}H NMR spectroscopy.





On direct irradiation in benzene *cis*-**3** did not isomerize to the *trans*-**3**, while **4** underwent two-way isomerization between cis and trans isomers.

The cis isomer of **3** did not undergo isomerization to give the trans isomer in methanol as well as in benzene on irradiation at 366 nm. In addition, *cis*-**3** was stable on iradition at the edge of the absorption spectrum (λ=525 and 535 nm in benzene and in methanol, respectively). Therefore, we could not observe an absorption spectrum of *trans*-**3**. The absorption spectrum of the cis isomer is shown in Figure 1a. No fluorescence spectrum was detected at room temperature. Thus, *cis*-**4** undergoes ultra fast deactivation from the excited singlet state through the intramolecular hydrogen bonding. However, at 77 K in ethanol glass the fluorescence spectrum with the fluorescence maximum at λ_{max}=520 nm and the lifetime of ca. 8 ns was observed. This result indicates that the deactivation through the intramolecular hydrogen bonding is suppressed with lowering of the temperature.

The absorption maximum of *trans*-**4** appeared at longer wavelength (λ_{max} = 530 nm) than that of *cis*-**4** (λ_{max} = 480 nm) in benzene due to the presence of intramolecular hydrogen bonding in *trans*-**4** (Figure 1b). On irradiation with 366 nm light, **4** gave photostationary isomer mixture with a very high ratio of trans isomer (($[\text{trans}]/[\text{cis}])_{\text{pss}}$= 99 /1) in benzene. Although the $([\text{trans}]/[\text{cis}])_{\text{pss}}$ value decreased in polar and protic solvent and is 95 / 5 and 90 / 10 in acetonitrile and methanol, respectively, the efficiency for trans-to-cis isomerization is still smaller than that for cis-to-trans isomerization. These results indicate that an intramolecular hydrogen bonding in *trans*-**4** still plays an important role in the deactivation from the excited singlet state even in polar protic solvent.

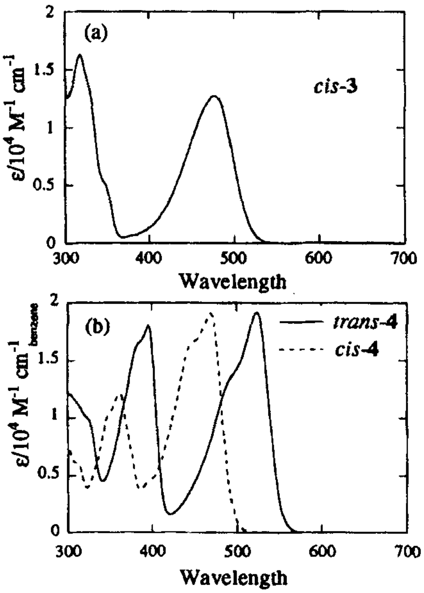


FIGURE 1 Absorption spectra of *cis*-**3** (a) and *cis*- and *trans*-**4** (b) in benzene.

The fluorescence spectrum of *trans*-**4** was observed in various solvents: the fluorescence maximum appeared at 554, 560, 574 nm, in benzene, methanol, and acetonitrile, respectively. The Stokes shift is only 1000-1500 cm^{-1} in these solvents which is similar to that of *cis*-**4**. Typical examples of the fluorescenc spectra of *trans*- and *cis*-**4** in benzene are shown in Figure 2. The quantum yield of fluorescence emission of *trans*-**4** is less than 0.01 in all the solvent examined and is slightly lower than that of *cis*-**4** in non-polar solvent, but is comparable in polar solvent. Since the fluorescence spectrum was observed only at the normal region, the excited state intramolecular hydrogen atom transfer is not efficient in *trans*-**4**. Otherwise, if the hydrogen atom transfer takes place in the excited singlet state, the produced tautomer form scarcely gives fluorescence emission but undergoes radiationless deactivation to the ground state .

Similar to the temperature effect on the fluorescence emission in **3**, temperature affected the fluorescence intensity and the lifetime in **4**. The fluorescence lifetime of *trans*-**4** increased with decreasing of temperature from 0.21 ns (at 295K) to 2.86 ns (at 185 K) in toluene. One can propose that the deactivation from the excited singlet state through intramolecular hydrogen bonding should overcome some activation barrier.

On 308 nm laser irradiation, no transient spectrum was observed for **3** and **4**, except the permanent change of the absorption spectrum due to the cis→trans isomerization in *cis*-**4**. These results exclude the intervention of the triplet state in the photochemical reactions on direct irradiation of **3** and **4**.

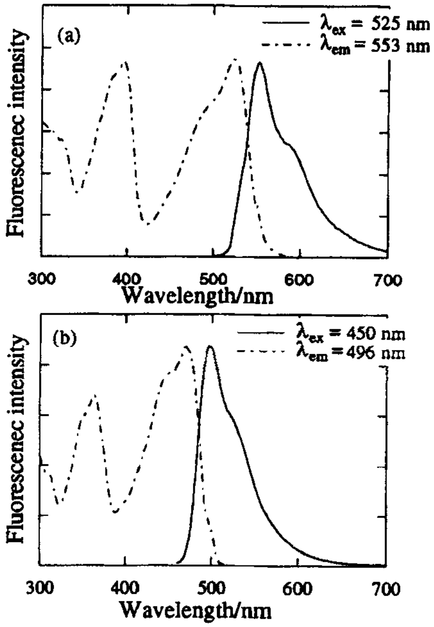


FIGURE 2 Fluorescence and fluorescence excitation spectra of *trans*- (a) and *cis*-**4** (b) in benzene.

CONCLUSION

The hydrogen bonding affected the behavior of excited singlet state in **3** to result in the ultra fast deactivation from the excited state without giving any fluorescence as well as isomerization around the double bond. However, **4** underwent photochromic behavior giving the isomer mixture at the photostationary state depending on the solvent properties.

Acknowledgments
This work was supported by a Grant-in-Aid for Scientific Research (No. 10440166) and a Grant-in-Aid for Priority Areas (No. 10146103) from the Ministry of Education, Science, Sports and Culture, Japan and by Research Foundation for Opto-Science and Technology.

References

[1] T. Arai and K. Tokumaru, *Chem. Rev.*, **93,** 23–39 (1993).
[2] T. Arai, T. Iwasaki, and K. Tokumaru, *Chem. Lett.*, **1993,** 691–694.
[3] F. D. Lewis, B. A. Yoon, T. Arai, T. Iwasaki, and K. Tokumaru, *J. Am. Chem. Soc.*, **117,** 3029–3036 (1995).
[4] T. Arai, M. Obi, T. Iwasaki, K. Tokumaru, and F. D. Lewis, *J. Photochem. Photobiol. A:Chem.*, **96,** 65–69 (1996).
[5] T. Arai, M. Moriyama, and K. Tokumaru, *J. Am. Chem. Soc.*, **116,** 3171–3172 (1994).
[6] M. Obi, H. Sakuragi, and T. Arai, *Chem. Lett.*, 1998, 169.
[7] T. Arai and Y. Hozumi, *Chem. Lett.*, **1998,** 1153.
[8] "Organic Photochromic and Thermochromic Compounds," Vols. 1,2, ed by J. C. Crano and R. Guglielmetti, Kluwer Academic / Plenum Press, New York (1999).
[9] "Photochromism: Molucules and Systems," ed by H. Durr and H. Bouas-Laurent, Elsevier, Amsterdam (1990).
[10] A. R. Katritzky, Q. L. Li, and W. Q. Fan, *J. Heterocyclic Chem.*, 25, 1287 (1988).
[11] T. Arai and M. Ikegami, *Chem. Lett.*, **1999,** 965–966.