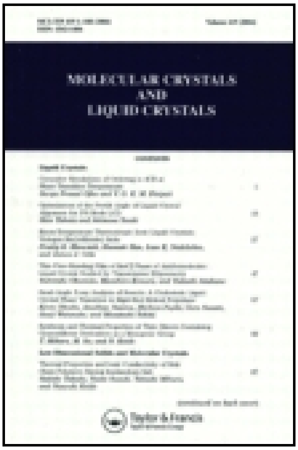
This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 18 February 2013, At: 13:24
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



# 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 by the Way of Intramolecular Hydrogen Transfer in -N-H :N- Bond

Katsumi Tokumaru [a] , Tatsuo Arai [a] & Masaya Moriyama [a]
[a] Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki, 305, Japan

Version of record first published: 24 Sep 2006.

To cite this article: Katsumi Tokumaru , Tatsuo Arai & Masaya Moriyama (1994): Photochromism by the Way of Intramolecular Hydrogen Transfer in -N-H :N- Bond, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 147-149

To link to this article: http://dx.doi.org/10.1080/10587259408037803

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:24 18 February 2013

*Mol. Cryst. Liq. Cryst.* 1994, Vol. 246, pp. 147–149
Reprints available directly from the publisher
Photocopying permitted by license only
© 1994 Gordon and Breach Science Publishers S.A.
Printed in the United States of America

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:24 18 February 2013

# PHOTOCHROMISM BY THE WAY OF INTRAMOLECULAR HYDROGEN TRANSFER IN -N-H :N- BOND

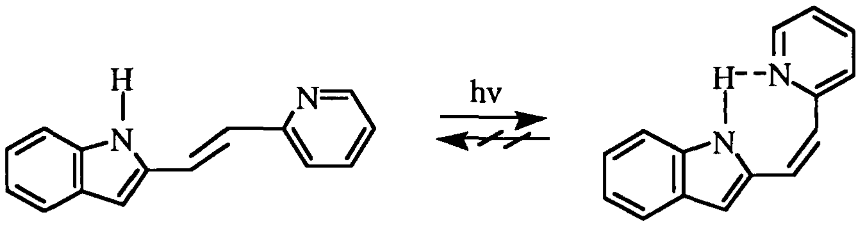
KATSUMI TOKUMARU, TATSUO ARAI, AND
MASAYA MORIYAMA
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki
305 Japan

Abstract The intramolecular hydrogen bonding N-H···N between two heterocycles substituted on an ethylenyl linkage brought about photochromic behavior in a transient way exhibiting ground state transient absorption of the resulting tautomeric form.

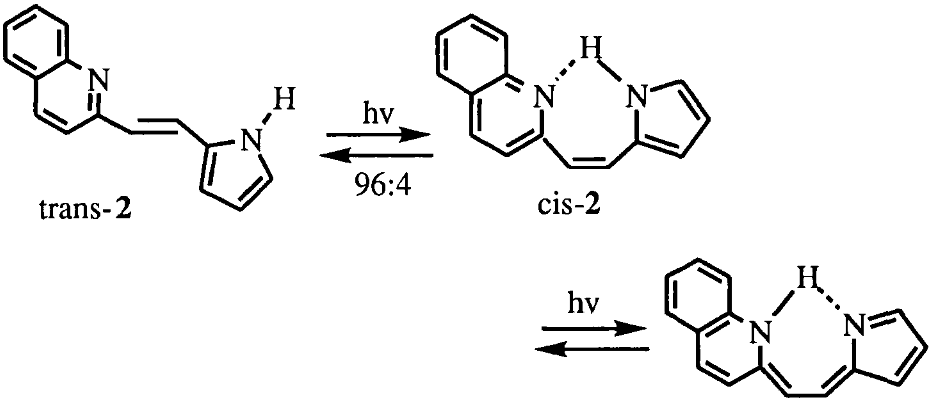
Photoinduced enolization is often accompanied by transient photochromic phenomena as observed on irradiation of 2-methylbenzophenone, which was known to undergo intramolecular hydrogen transfer from 2-methyl group to triplet excited carbonyl oxygen giving an enol ($\lambda_{max}$=405 nm) reverting to the starting molecule with a lifetime of nearly 10 s at ambient temperature.[1] We now examine a possible photochromic reaction taking place between -N-H and N-bond between two nitrogen heterocycles substituted on an unsaturated bond.

On direct excitation of olefin **1**, presence of intramolecular hydrogen bonding between indole and pyridine rings led to solely trans to cis one-way isomerization, whereas mutual isomerization between cis- and trans-**1** took place on triplet sensitization.[2] The behavior of **1** is contrasted with the cis to trans one-way adiabatic isomerization of unsaturated bonds substituted with aryl groups of low triplet excitation energies.[3] trans-**1** showed fluorescence ($\lambda_{max}$=450 nm) in benzene, however cis-**1** did not fluoresce at all, which means that the intramolecular hydrogen bonding serves to acceleration of deactivation of the singlet excited state of cis-**1** to the ground state.

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:24 18 February 2013



trans-1 cis-1



trans-2 cis-2

cis-2'

Replacement of indole and pyridine in **1** by quinoline and pyrrole changed the behavior of the unsaturated molecule, 1-(2-pyrrolyl)-2-(2-quinolyl)ethene, **2**. Direct irradiation in benzene led to isomerization between cis- and trans-**2** with a photostationary state much shifted to cis. Both trans- and cis-**2** exhibited fluorescence with $\lambda_{max}$=440 and 600 nm, respectively. Accordingly, the intramolecular hydrogen bonding in the singlet excited state between quinoline and pyrrole rings are weaker than that between indole and pyridine rings to allow the fluorescence emission and isomerization of the double bond. Moreover, laser excitation gave rise to an absorption at $\lambda_{max}$=580 nm, different from the triplet state but attributable to the enolic form (cis-**2'**), which decayed with a lifetime of a few hundreds nanoseconds.[4]

The above results indicate that the intramolecular hydrogen bonding between -N-H···N- in cis-**2** may lead the molecule to exhibiting photochromic behavior in a transient way.

Generally, the -X-H···X- system may be photolabile, however, the resulting system may facilely revert over an activation barrier. Therefore, to accomplish ordinary photochromic system it is necessary to do another approach to molecular design to increase the amount of the activation energy of the reversion, however, it may be worthwhile to search procedures to use the transient property of this system for applied purpose such as transient diffraction.[5,6]

$$\begin{tikzcd}
(\text{cis-}\mathbf{2})^* \arrow[r] & (\text{cis-}\mathbf{2}')^* \arrow[d, "h\nu_f\ 600\ \text{nm}"', "\approx 100\ \text{ps}"] \\
\text{cis-}\mathbf{2} \arrow[u, "h\nu\ 400\ \text{nm}"] & \text{cis-}\mathbf{2}' \arrow[l, "\approx 300\ \text{ns}"']
\end{tikzcd}$$

The authors thank the Ministry of Education, Science and Culture for the Grant-in-Aid for Specially Promoted Research No. 03101004.

## REFERENCES

1. For example, N. J. Turro, Modern Molecular Photochemistry (The Benjamin/Cumming, California, 1978), p. 371.
2. T. Arai, T. Iwasaki and K. Tokumaru, Chem. Lett., 691 (1993).
3. T. Arai and K. Tokumaru, Chem. Rev., 93, 23 (1993).
4. M. Moriyama, T. Arai and K. Tokumaru, Abstracts for Symposium on Photochemistry, Sapporo, Japan (1993).
5. S. Ishizaka, T. Urano and K. Tokumaru, Chem. Lett., 1705 (1984). T. Urano, K. Tokumaru and S. Ishizaka, J. Photog. Sci., 34, 143 (1986).
6. L. Léger, H. Hervet and F. Rondlez, Macromolecules, 14, 1732 (1981).

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:24 18 February 2013