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Trans→cis One-way Photoisomerization of an Olefin Substituted with an Indole and a Pyridine Ring. Effect of Intramolecular Hydrogen Bond

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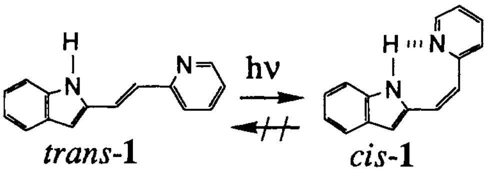
On direct irradiation in benzene 2-[2-(2-pyridyl)ethenyl]indole undegoes trans-to-cis one-way isomerization in the excited singlet state.

Recently we have revealed that the photochemical isomerization of unsaturated bonds can proceed through one-way mode solely from cis- to trans-isomers1) in addition to the traditional two-way mode occuring mutually between the two isomers,2) or through the dual mechanism of these two modes,3) depending on the electronic structure of the olefins.

As another factor to control the mode of isomerization, we wish to report the effect of intramolecular hydrogen bond4-6) between N-H group of indole and nitrogen of pyridine of an olefin **1**. The existence of an intramolecular hydrogen bond in *cis*-**1** has been clarified by IR and NMR data.5,7) On direct irradiation with 366 nm light in benzene *trans*-**1** undergoes isomerization to *cis*-**1**, while *cis*-**1** does not isomerize at all to *trans*-**1**. These facts show that intramolecular hydrogen bond in *cis*-**1** is still effective in the excited state to inhibit isomerization around C=C double bond.



The absorption, fluorescence, and fluorescence excitation spectra of **1** are shown in Fig. 1. The absorption maximum of *cis*-**1** appeared at longer wavelength than that of *trans*-**1** indicating that the intramolecular hydrogen bond loweres the excitation energy of *cis*-**1**. No fluorescence was observed on excitation of *cis*-**1**; on the contrary, *trans*-**1** exhibited broad fluorescence, which shows that the excitation is

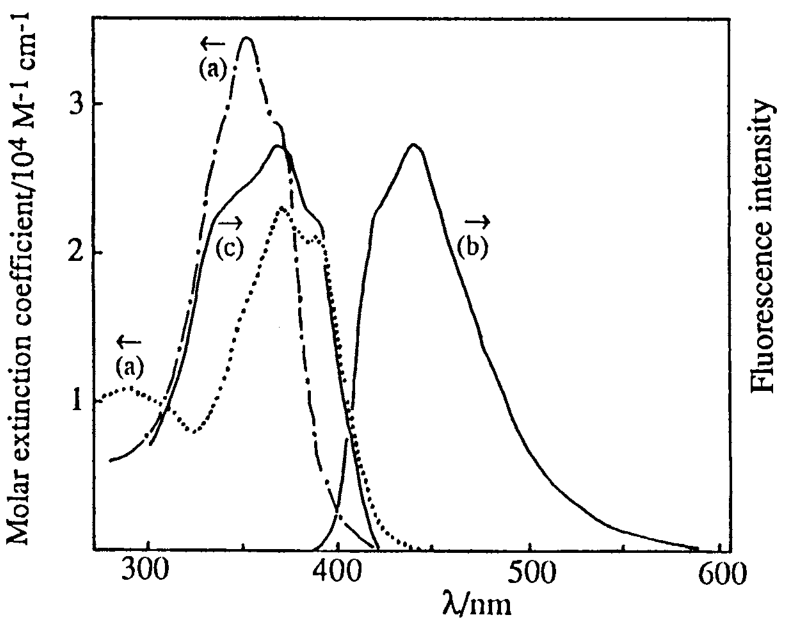


Fig. 1. Electronic spectra in benzene at room temperature. (a) Absorption spectra of cis (···) and trans (— · —), (b) fluorescence (excited at 400 nm), and (c) its excitation spectra (monitored at 450 nm) of trans (—).

accompanied by conformational change of *trans*-**1**. The quantum yield of fluorescence emission of *trans*-**1** was determined as 0.36 and 0.47, respectively, at the excitation wavelength of 300 and 400 nm under argon atmosphere.

The quantum yield of trans→cis isomerization on 366-nm excitation was determined at varying concentration of *trans*-**1** ((5.4-16.3)x10^{-4} M) as $\Phi_{t\rightarrow c}$=0.21±0.01 irrespective of the initial *trans*-**1** concentration under N_2. On the other hand, on biacetyl sensitization under N_2 **1** underwent mutual isomerization between the cis and trans isomers with quantum yields of 0.74 and 0.18 for cis→trans ([cis]=6.6x10^{-4} M) and trans→cis ([trans]=6.9x10^{-4} M) isomerization, respectively. Therefore, it is sure that the trans→cis isomerization of **1** under direct irradiation proceeds at the excited singlet state.

In order to draw the potential energy surface of one-way trans→cis isomerization of **1**, the energy difference between the cis and trans isomers in the ground state was determined by differential scanning calorimetry (DSC). The DSC thermograms at a rising rate of temperature of 2.5-7 °C min^{-1} showed that in the ground state ^{1}t is 6.9 kcal mol^{-1} higher in energy than ^{1}c. Taking into account the usually assumed energy difference between ^{1}c and ^{1}t where ^{1}c has a higher energy than ^{1}t by ca. 5 kcal mol^{-1}, the intramolecular hydrogen bond must stabilize ^{1}c as high as 6.9+5 ≈ 12 kcal mol^{-1}. This stabilization energy is considerably larger than that for intermolecular hydrogen bond between indole and pyridine (the standard enthalpy change for the formation of intermolecular hydrogen bond, ΔH^0 = -3.6 kcal mol^{-1} in CCl_4).[8] The red shift of

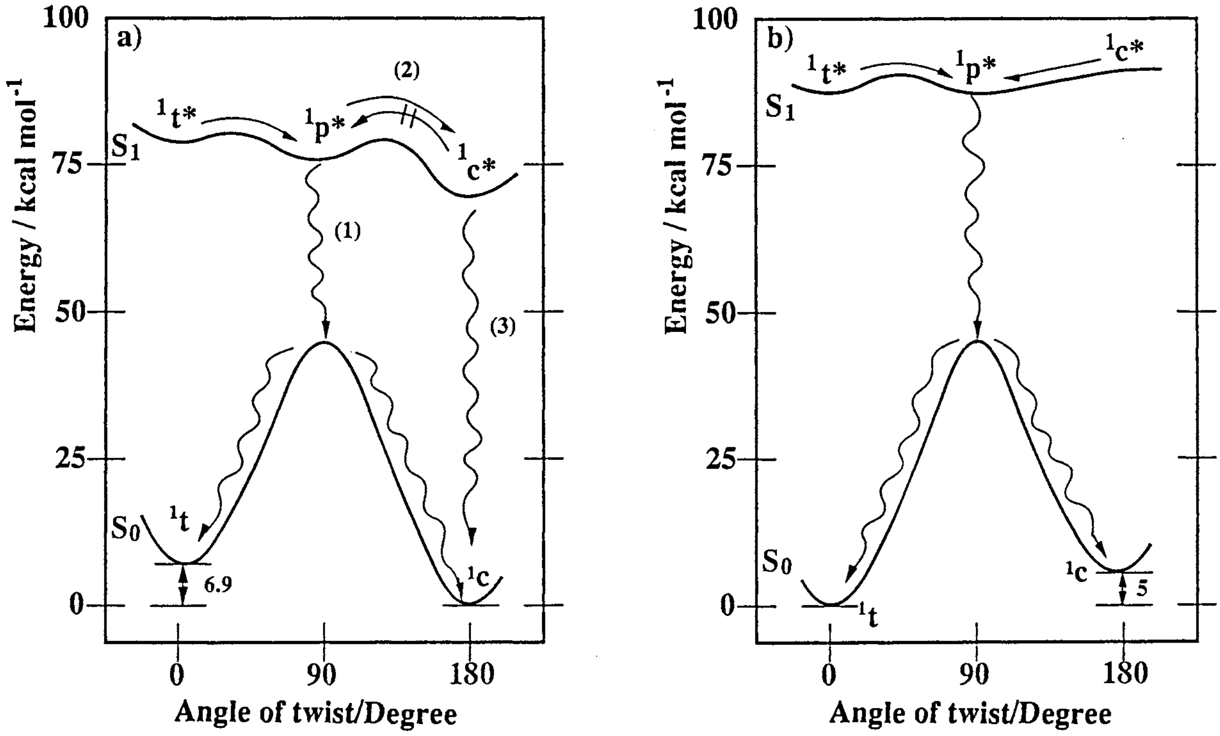


Fig. 2. (a) Potential energy surfaces of trans→cis one-way isomerization of **1** and (b) two-way isomerization of stilbene in the excited singlet state.

the absorption spectra of *cis*-**1** compared to *trans*-**1** suggests that the intramolecular hydrogen bond becomes stronger in the excited singlet state.[9] The intramolecular hydrogen bond will accelerate the deactivation of the excited singlet, $^1c^*$, to the ground state as previously proposed for 2-aminoanthraquinone[10] suppressing the fluorescence emission or the isomerization around the double bond. The singlet excitation energies of ^1t and ^1c are estimated as ca. 72 and 70 kcal mol^{-1}, respectively, from their absorption and fluorescence spectra. Fig. 2 depicts the potential energy surface of one-way trans→cis isomerization of **1** based on the above data and, for comparison, that of cis-trans two-way isomerization of stilbene[11] in the excited singlet state.

Since $^1c^*$ does not give any detectable fluorescence, it is not possible to distinguish whether the trans→cis isomerization takes place through a diabatic process via deactivation at the perpendicular excited singlet state ($^1p^*$) (process (1) in Fig. 2a) or through adiabatic conversion[12] of $^1t^* \rightarrow {}^1c^*$ followed by deactivation to the ground state cis isomer (process (2) and (3) in Fig. 2a).

The present findings indicate that the intramolecular hydrogen bond changes not only the relative energy of ^1c and ^1t but also that of $^1c^*$ and $^1t^*$ and, accordingly, controls the mode as well as the direction of isomerization, which is in contrast to the recently discovered one-way isomerization taking place from cis to trans isomers in the excited state through an adiabatic process.$^{1,12)}$

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7) ^{1}H NMR studies in $CDCl_3$ revealed a remarkable downfield shift of an indole N-H proton of *cis*-**1** (δ=13.95) compared to that of *trans*-**1** (δ=8.35), which indicates the presence of intramolecular hydrogen bond for *cis*-**1**.

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