

Control of the Photoisomerization Mode of Carbon–Carbon Double Bond by Intramolecular Hydrogen Bond; One-way Photoisomerization of 2'-Hydroxychalcone Induced by Adiabatic Intramolecular Hydrogen Atom Transfer

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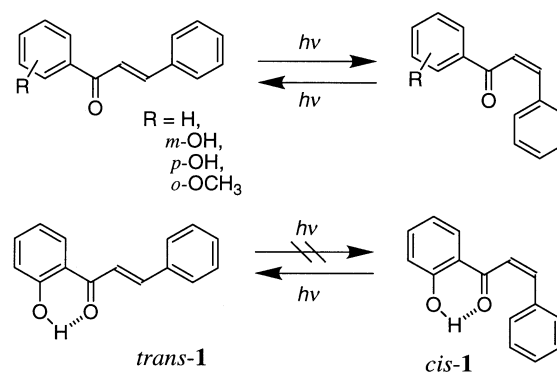
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To investigate the effect of intramolecular hydrogen bonding on the photoisomerization of carbon–carbon double bond, photoisomerization of 2'-hydroxychalcone has been studied. Based on the quantum yield measurements and laser flash photolysis studies, it was found that 2'-hydroxychalcone isomerized only from *cis*- to *trans*-isomer. The one-way *cis*-*trans* isomerization is induced by the adiabatic hydrogen atom transfer in the triplet state.

Intramolecular hydrogen bonding can affect the dynamic behavior of molecules in the excited state as well as in the ground state. In the excited state, it provides efficient deactivation pathways such as intramolecular hydrogen atom (proton) transfer or nonradiative internal conversion through the vibrational relaxation of the functional groups which participate in the hydrogen bonding. The intramolecular hydrogen atom transfer reaction in the excited singlet state has been well recognized.¹ However, only a few have been reported about the hydrogen atom transfer in the excited triplet state.² We have investigated the effect of N: H–N and O: H–N intramolecular hydrogen bonding on the photoisomerization of carbon–carbon double bond.^{3,4} As an example of O: H–O intramolecular hydrogen bonded compound, we have already reported the photochemical behavior of *trans*-2'-hydroxychalcone (*trans*-**1**);⁵ *trans*-**1** does not isomerize to the *cis*-**1** but *trans*-**1** exhibits intramolecular hydrogen atom transfer forming tautomer in the triplet state.

There are two possible mechanisms for the no isomerization of *trans*-to-*cis* direction in **1**. The deactivation from the excited state to the ground state of both *cis*- and *trans*-**1** may take place so fast that *trans*-to-*cis* isomerization would not be observed in the excited state of **1**. Otherwise, one-way isomerization may take place in the excited state from *cis*-to-*trans* direction induced by intramolecular hydrogen atom transfer. In order to make clear the reason why *trans*-to-*cis* isomerization cannot take place in the excited state of **1** we have synthesized *cis*-**1** and the mechanism of photoisomerization of **1** was studied by quantum yield measurement and laser flash photolysis. We wish to report here that **1** undergoes one-way photoisomerization from *cis*- to *trans*-isomers. Thus, the mode of photoisomerization of carbon–carbon double bond is controlled via intramolecular hydrogen atom transfer in the excited state.

Photoexcitation of *cis*-**1** gave *trans*-**1**, while *trans*-**1** does not isomerize to form *cis*-**1** in benzene, *n*-hexane, acetonitrile, and methanol. In contrast, chalcone,⁶ 3'-hydroxychalcone, 4'-hydroxychalcone, and 2'-methoxychalcone exhibit mutual photoisomerization between *cis*- and *trans*-isomers. The quantum yield of the photoisomerization of *cis*-**1** to *trans*-**1** (Φ_{ct}) was



0.05 on irradiation at 366 nm in benzene under Ar atmosphere. As the Φ_{ct} value was lowered by adding oxygen, the triplet state should be involved in the photoisomerization. In addition, the excitation of *cis*-**1** in benzene by a 308 nm laser pulse gave a transient absorption spectra shown in Figure 1(a). The transient

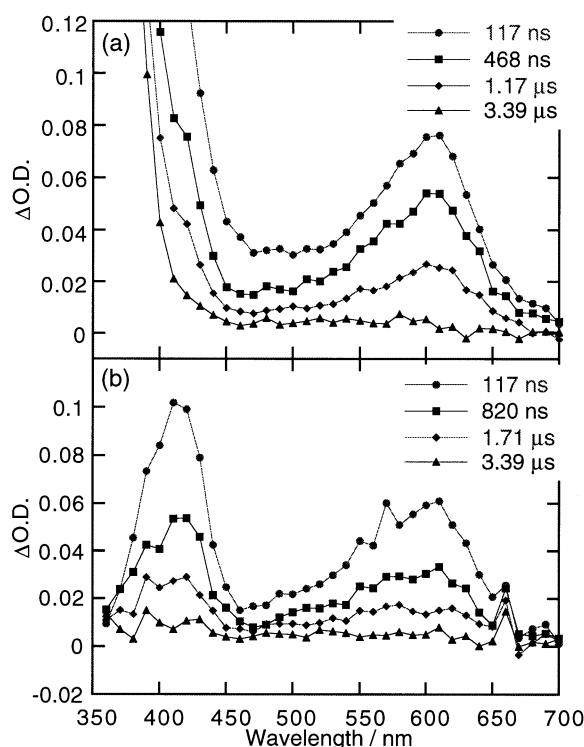


Figure 1. Transient absorption spectra of *cis*-**1** (a) and *trans*-**1** (b) observed on excitation at 308 nm in benzene. Time indicates the delay time after laser pulse.

spectra peaked at 610 nm was assigned to the triplet state (T–T absorption spectrum) since it was quenched by oxygen. The T–T absorption spectrum is very similar to that of *trans*-**1** observed on excitation with a 308 nm laser pulse ($\lambda_{\text{max}} = 610$ nm and 410 nm, Figure 1(b)), which has been assigned to the triplet tautomer of *trans*-**1**.⁵ Since they both have absorption peaked at 610 nm and have lifetime of 1.2 μs , we can assign that they are the same triplet state and both are the triplet tautomer of *trans*-**1**. The quantum yield of intersystem crossing from $^1(\text{trans-1})^*$ to $^3(\text{trans-1}')^*$ on excitation of *trans*-**1** at 308 nm was 0.09 in benzene. The quantum yield of intersystem crossing in *cis*-**1** was determined to be 0.06 and is very close to the quantum yield of photoisomerization (0.05). These results indicate that the photoisomerization proceeds in the excited triplet state and photoirradiation of *cis*-**1** forms the triplet tautomer of *trans*-**1**.

From these experimental results, we have proposed a novel mechanism for the photoisomerization of **1** as shown in Figure 2. The photoexcitation of *cis*-**1** gives the triplet tautomer of *cis*-**1** either via intramolecular hydrogen atom transfer in the singlet state and subsequent intersystem crossing, or via intersystem crossing followed by intramolecular hydrogen atom transfer in the triplet state. The triplet tautomer of *cis*-**1** ($^3(\text{cis-1}')^*$) isomerizes adiabatically to give the triplet tautomer of *trans*-**1** ($^3(\text{trans-1}')^*$), which has sufficient lifetime to be detected by the laser flash photolysis. Such one-way characteristics from $^3(\text{cis-1}')^*$ to $^3(\text{trans-1}')^*$ can be explained by the very low triplet energies of these tautomers. The tautomer has a conjugation of tetraenone structure and therefore, the planar *trans* triplet $^3(\text{trans-1}')^*$ should be the most stable conformation in the excited triplet state. Actually, the triplet energy of *trans*-**1'** was estimated to be 173 kJ mol⁻¹, which is much lower than the triplet energy of *trans*-**1** (229 kJ mol⁻¹). Thus, in the excited triplet state of **1**, the tautomer ($^3(\text{cis-1}')^*$) formed by intramolecular hydrogen atom transfer in the excited state undergoes twisting around the double bond to give the perpendicular triplet state ($^3\text{p}^*$), but the perpendicular geometry is no longer a funnel for the deactivation to the ground state and the deactivation takes place solely at $^3(\text{trans-1}')^*$.

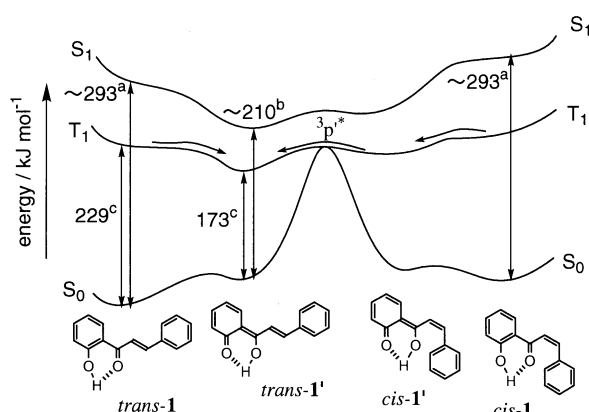


Figure 2. Potential energy surfaces of intramolecular hydrogen atom transfer and isomerization around double bond of **1**. a) Calculated from absorption spectra. b) Calculated from fluorescence spectra in Ref. 1b. c) From Ref. 5.

We have performed semiempirical calculations (PM3 / 4CI)^{7,8} in order to study the potential energy surface of the photoisomerization and hydrogen atom transfer in the ground, the excited singlet, and the excited triplet states. The results agree well to the experimental results. For example, there is no potential minimum at $^3(\text{cis-1})^*$ and the heat of formation (ΔH_f) of $^3(\text{cis-1})^*$ is 18.7 kJ mol⁻¹ higher than that of $^3(\text{cis-1}')^*$; it indicates the occurrence of adiabatic hydrogen atom transfer of *cis*-**1** in the excited triplet state.

We have reported various types of photochemical isomerization of arylenes.⁹ In these cases the mode of isomerization as well as the potential energy surfaces of isomerization was understood by the effect of aryl group on the triplet energies of planar *trans* and perpendicular geometries. The present findings of the one-way isomerization open a novel mechanism of highly specific isomerization induced by the remote hydrogen atom transfer where two adiabatic photochemical processes, hydrogen atom transfer and *cis*-*trans* isomerization takes place by the absorption of only one photon. We are now extending these findings to apply the intramolecular multi adiabatic photochemical reactions.

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