2766 *J. Phys. Chem. A* **2002,** *106,* 2766−2776

Photochemistry of 2′-Hydroxychalcone. One-Way Cis−Trans Photoisomerization Induced by Adiabatic Intramolecular Hydrogen Atom Transfer

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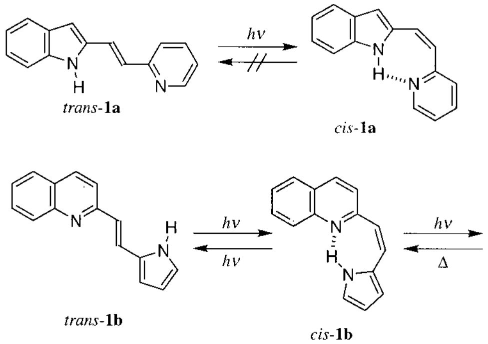
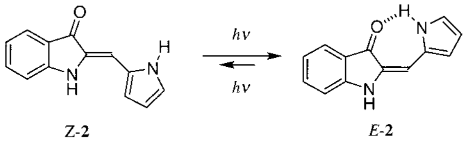
Received: August 27, 2001

Intramolecular hydrogen atom transfer and novel one-way photoisomerization of 2′-hydroxychalcone (**2HC**) were investigated by quantum yield measurements, transient absorption spectroscopy, and semiempirical calculations. The trans isomer of **2HC** (*trans*-**2HC**) did not give the cis isomer, while *cis*-**2HC** underwent one-way isomerization to give the *trans*-**2HC**. The triplet−triplet absorption spectra of *cis*- and *trans*-**2HC** were similar and were assigned to the tautomer produced via the intramolecular hydrogen atom transfer in the excited triplet state. The triplet energies of the normal form and the tautomer form of *trans*-**2HC** were estimated by quenching experiments to be 229 and 177.5 kJ mol^{-1}, respectively. Heats of formation, the frontier molecular orbital coefficients, and optimized structures of *trans*-**2HC** and *cis*-**2HC** in the ground, the excited singlet, and the excited triplet states were calculated by semiempirical (MOPAC93 PM3/4CI) calculations. These calculations agree well with the experimental observations. Based on the experimental observations and theoretical considerations, a novel mechanism and the potential energy surface for the one-way photoisomerization of **2HC** were proposed. The photoisomerization of **2HC** was induced by hydrogen atom transfer in the excited triplet state. Thus, **2HC** can be viewed as a molecule in which the mode of isomerization around the carbon−carbon double bond can be controlled by the remote intramolecular hydrogen bonding. Solvent affected the triplet lifetime without changing the mode of isomerization. On prolonged irradiation, *trans*-**2HC** gave flavanone by very low quantum yield ($\Phi = 1.9 \times 10^{-3}$ in benzene). The cyclization reaction to form flavanone was studied and the quantum yields were determined.

Introduction

Much attention has been paid to the effect of hydrogen bonding on the photochemical behaviors of ethylenic compounds.[1−14] Lewis and Arai et al. have studied the effect of hydrogen bonding on the photoisomerization behavior of olefins such as 2-[2-(2-pyridyl)ethenyl]indole[3,6] (**1a**) and 2-[2-(2-pyrrolyl)ethenyl]quinoline[5,7] (**1b**). In these compounds, only the cis isomer forms intramolecular hydrogen bonding as revealed by ^{1}H NMR spectroscopy. On photoirradiation *trans*-**1a** gave *cis*-**1a**, while *cis*-**1a** was stable and did not give any trans isomer.[3,6] However, in the case of **1b**, a mutual isomerization between cis and trans isomers was observed. In addition, *cis*-**1b** underwent hydrogen atom transfer through the intramolecular hydrogen bonding in the excited singlet state.[5] Recently, we have come to find a novel photochromic dye[14] (**2**), which exhibited the color change between red (*E*-**2**) and green (*Z*-**2**) on photoirradiation. The isomer ratio at the photostationary state could be controlled by selecting the exciting wavelength although the quantum yields of isomerizations showed almost one-way character. The photostability and the anomalous bathochromic shift of the absorption spectra of *E*-**2** were due to the intramolecular hydrogen bonding. In these compounds, it seems that the isomerization process competes with the deactivation via intramolecular hydrogen bond in the excited states.





It has been well recognized that various types of molecules, which form intramolecular hydrogen bonding, exhibit the intramolecular hydrogen atom transfer in the excited singlet state.[15−18] Although the intramolecular hydrogen atom transfer in the excited singlet state has been studied extensively, the hydrogen atom transfer in the triplet state has scarcely been reported.[19−24] Methyl salicylate (**MS**) is a well-known com-

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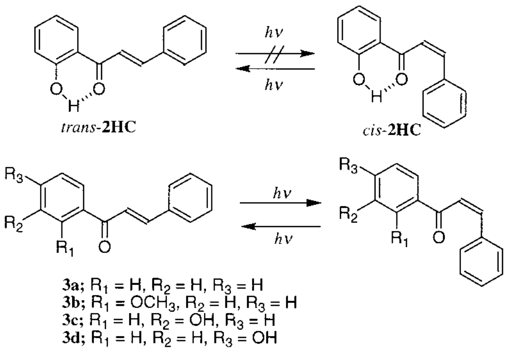
10.1021/jp0133081 CCC: $22.00

pound for the study of the intramolecular hydrogen atom transfer in the excited singlet state.[17] **MS** exhibits the fluorescence with a large Stokes shift and the emitting species is assigned to the tautomer form. We have investigated the behavior of **MS** in the excited triplet state by means of laser-flash photolysis[19] and revealed that **MS** undergoes the intramolecular hydrogen atom transfer in the triplet state to give the tautomer. We have extended our study of hydrogen atom transfer in the triplet state to N-salicylideneaniline[24] (**SA**), which has been well-known as photochromic and thermochromic compound. **SA** gave the tautomer in the excited triplet state as revealed by the observation of triplet tautomer by means of transient absorption spectroscopy. There are some difficulties in the study of the hydrogen atom transfer in the excited triplet state because of the limited method for the observation such as phosphorescence and transient absorption spectroscopies, while fluorescence spectroscopies are commonly applied to study the behavior of the excited singlet state in various atmospheres.

We should refer to using the term *intramolecular hydrogen atom transfer* instead of *intramolecular proton transfer*. In the study of methyl salicylate, the structure of the tautomer has been drawn as a "zwitterionic" structure since Weller had found the dual emission in the fluorescence spectrum of MS. However, recent extensive investigations on the structure of **MS** and related 2-hydroxy-benzoyl compounds have indicated that the final form has no zwitterion character.[25−28] Thus, this reaction can be viewed as tautomerization or intramolecular hydrogen atom transfer where the atomic bonds and electrons are redistributed in the time domain of the reaction.

2′-Hydroxychalcone (**2HC**) has an intramolecular hydrogen bonding between the carbonyl oxygen and the hydroxy group. It should be noted that both cis and trans isomer form the intramolecular hydrogen bond, while only cis isomers form the intramolecular hydrogen bond in **1** and **2**. It was previously reported that the trans isomer of **2HC** (*trans*-**2HC**) did not undergo *trans*-cis isomerization on photoirradiation,[29] while it has been known that chalcone undergoes the mutual isomerization.[30] Chou et al. reported that *trans*-**2HC** exhibited very weak fluorescence maximum at 635 nm in nonpolar solvent.[15] The emitting species with a very large Stokes shift has been assigned to the tautomer form of *trans*-**2HC** produced via hydrogen atom transfer in the excited singlet state. The photocyclization reactions from *trans*-**2HC** to flavanone[31,32] and 3-hydroxyflavone[15] have been reported. Chou et al. reported that 3-hydroxyflavone was formed with 355 nm laser irradiation of *trans*-**2HC** in aerated *n*-hexane.[15] Matsushima et al. reported that the photoirradiation of *trans*-**2HC** gave flavanone and they proposed that the formation of the tautomer via intramolecular hydrogen atom transfer is necessary for the cyclization.[31,32] The quantum efficiencies for these cyclization processes seem to be very small. Due to the very low quantum yield of the tautomer fluorescence[15] and of the cyclization reactions,[15,31,32] not much information about the behavior of 2′-hydroxychalcone in the excited states have been known. In addition, behavior of 2′-hydroxychalcone in the excited triplet manifold has not been reported, and the photochemical behavior of cis isomer of **2HC** (*cis*-**2HC**) has been unknown. We have found that **2HC** underwent one-way cis−trans isomerization and have reported preliminary results as communications.[13]



trans-**2HC**

cis-**2HC**

3a; $R_1 = H, R_2 = H, R_3 = H$
3b; $R_1 = OCH_3, R_2 = H, R_3 = H$
3c; $R_1 = H, R_2 = OH, R_3 = H$
3d; $R_1 = H, R_2 = H, R_3 = OH$

In the present paper, we report the photochemistry of *trans*- and *cis*-2′-hydroxychalcone studied by means of the quantum yield measurements, laser-flash photolysis, and semiempirical (MOPAC93 PM3/4CI) calculations. Our main interest is the effect of intramolecular hydrogen bonding on the photoisomerization behavior of **2HC** where the intramolecular hydrogen bond exists in both trans and cis isomers, in contrast to the compounds where only cis isomers are capable to form the hydrogen bond such as **1** and **2**. **2HC** underwent intramolecular hydrogen atom transfer in the excited triplet state as revealed by the observation of the tautomer triplet. **2HC** exhibited one-way isomerization only from the cis isomer to the trans isomer. This one-way isomerization is induced by the adiabatic hydrogen atom transfer in the triplet state. The potential energy surface of the isomerization and the hydrogen atom transfer are discussed. The cyclization reaction to form flavanone is also studied.

Results

Ground-State Properties. Both *trans*- and *cis*-**2HC** form O−H:O intramolecular hydrogen bonding. The hydroxyl proton signals were observed by ^{1}H NMR in chloroform-*d* at 12.8 and 12.3 ppm for *trans*- and *cis*-**2HC**, respectively. These downfield shifts were indicative of the intramolecular hydrogen bonding. The semiempirical calculations indicated that the hydrogen-bonded conformers are the most stable for both *trans*- and *cis*-**2HC**. The optimized structures of the two isomers by PM3 calculation indicate that they have planar structure so that there are conjugation between styryl and benzoyl moieties. The rotation around the single bond between the carbonyl α-carbon and the benzene ring which possesses the hydroxyl group in *trans*-**2HC** was studied by using PM3 calculation. Two rotational isomers around the single bond, *trans-s-trans* and *trans-s-cis* forms can be equilibrated with each other. However, the heat of formation (ΔH_f) calculated for *trans-s-trans* and *trans-s-cis* forms indicated that the *trans-s-cis* form is more stable than the *trans-s-trans* form. These results are in good agreement with the previous study by the AM1 calculation.[33]

UV and Fluorescence Spectra. The absorption spectra of *trans*-**2HC** in various solvents are shown in Figure 1. *trans*-**2HC** has its absorption maxima around 315 nm and a shoulder about 350 nm in benzene. The shoulder becomes a peak in cyclohexane ($\lambda_{max} = 352$ nm). The electronic transition corresponding to the peak and the shoulder are both likely to have the π,π^* character because they have comparatively large molar extinction coefficients ($\epsilon \sim 10^4$ M^{-1} cm^{-1}). The PM3 calculation (C.I. = 4) supported that the S_1 state of *trans*-**2HC** has π,π^* character. Not much shift of the absorption maximum was observed by changing the solvents. Similarly, *trans*-**3b** (Figure 1) exhibits its maximum at 304 nm with π,π^* character and very weak absorption band from 345 to 400 nm with n,π^* character in benzene.

The molar extinction coefficient of *cis*-**2HC** is smaller than that of *trans*-**2HC**, indicating that there should be a distortion of conjugation due to the steric hindrance between the carbonyl group and the benzene ring as implied by the PM3 calculation.

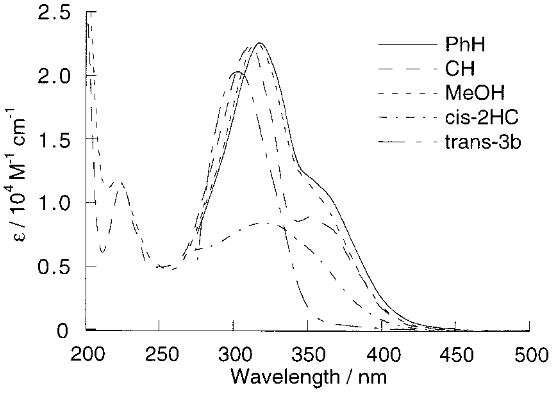


Figure 1. Absorption spectra of *trans*-**2HC** in benzene (PhH), cyclohexane (CH), methanol (MeOH), *cis*-**2HC** in benzene, and *trans*-**3b** in benzene.

TABLE 1: Triplet Lifetimes (τ_T), Quantum Yields of Dissappearance of *trans*-2HC (Φ_{Dis}), and Quantum Yields of Formation of Flavanone (Φ_{Fla}) in Various Solvents under Ar and Oxygen

		Φ_{dis}		Φ_{fla}			
solvent	τ_T/ns	Ar	O_2	Ar	O_2	$^1\Phi_0$[a]	$^3\Phi_0$[a]
benzene	1200	0.0020	0.0017	0.0019	0.0016	0.0016	0.0003
hexane	1100	0.0014	0.0012	0.0012	0.0010	0.0010	0.0002
acetonitrile	420	0.0103	0.0063	0.0102	0.0056	0.0053	0.0049
ethyl acetate	210	0.0029	0.0016	0.0018	0.0009	0.0018	0.0009
methanol	140	0.0030	0.0023	0.0021	0.0004	0.0001	0.0020
methanol-*d₁*	150	0.0037	0.0027	0.0021	0.0005	0.0001	0.0020

[a] $\Phi_{fla}{}^{Ar} = {}^1\Phi_0 + {}^3\Phi_0$. ${}^1\Phi_0 = (\tau_T{}^{Ar}\Phi_{fla}{}^{O2} - \tau_T{}^{O_2}\Phi_{fla}{}^{Ar})/(\tau_T{}^{Ar} - \tau_T{}^{O2})$.

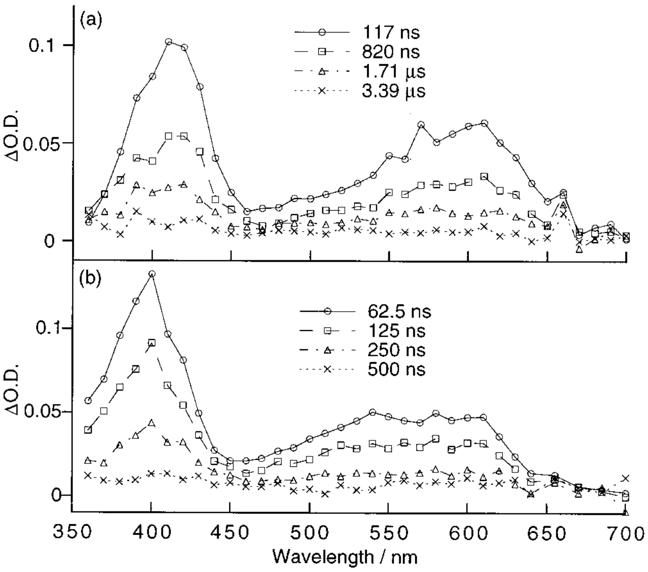


Figure 2. Transient absorption spectra of *trans*-**2HC** observed on excitation at 308 nm in benzene (a) and methanol (b). Time indicates the delay time after laser pulse.

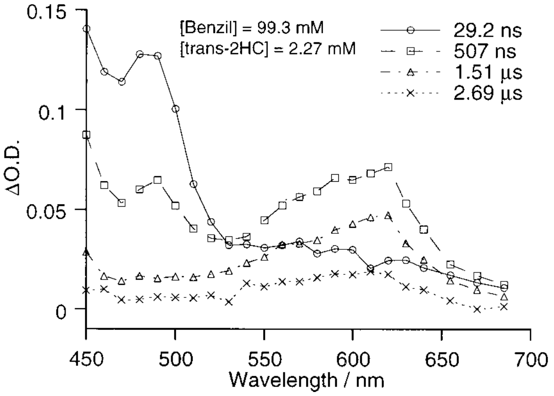


Figure 3. Transient absorption spectra observed benzil-sensitized laser excitation of *trans*-**2HC** in benzene. The excitation wavelength was 425 nm.

It has been reported that *trans*-**2HC** exhibits fluorescence at 635 nm.[15] The large Stokes shifted fluorescence is attributed to the formation of the tautomer in the excited singlet state. The quantum yield of the emission is very low (~10^{-5}). No fluorescence has been detected in the region of the normal emission (450−500 nm). It must be due to the ultrafast intramolecular hydrogen atom transfer and/or ultrafast deactivation processes such as intersystem crossing and internal conversion through the hydrogen bonding.

Photoirradiation. *trans*-**2HC** did not isomerize to the cis isomer on photoirradiation at 366 or 300 nm in benzene, hexane, acetonitrile, or methanol. On prolonged irradiation, *trans*-**2HC** cyclized to give flavanone instead of forming the cis isomer. The quantum yields of disappearance of *trans*-**2HC** (Φ_{dis}) and formation of flavanone (Φ_{fla}) are listed in Table 1. There are no distinguishable differences among the quantum yields Φ_{fla} in nonpolar solvents (1.9×10^{-3} in benzene and 1.2×10^{-3} in hexane), protic polar solvents (2.1×10^{-3} in methanol), and aprotic polar solvent (1.8×10^{-3} in ethyl acetate), except for relatively high yield in acetonitrile (1.02×10^{-2}). Thus, Φ_{dis} and Φ_{fla} values were very low in all solvents examined except for acetonitrile. In all solvents, molecular oxygen decreased the quantum yields. The Φ_{dis} values are in fair agreement with the Φ_{fla} values indicating that consumption of *trans*-**2HC** does not lead to the formation of *cis*-**2HC** but flavanone.

On the other hand, *cis*-**2HC** isomerized to form the *trans*-**2HC** on photoirradiation at 366 nm in benzene, acetonitrile, and methanol. The quantum yield of the photoisomerization from *cis*-**2HC** to *trans*-**2HC** was 0.05 on irradiation at 366 nm in benzene under Ar atmosphere. In contrast, **3a−d** isomerized mutually between trans and cis isomers on photoirradiation. The quantum yield for *cis*-to-trans isomerization of chalcone in cyclohexane was reported to be 0.23[30] which is almost five times as large as that of **2HC**. It is noteworthy that the quantum yield of isomerization of **2HC** is smaller than that of two-way isomerizing chalcones **3a−d**. These results indicate that the intramolecular hydrogen bonding influences the photoisomerization mechanism of **2HC** and imply that the character of the electronic state of *trans*-**2HC** might be different from those of **3a−d**.

Transient Absorption Spectra of *trans*-2HC. The transient absorption spectra of *trans*-**2HC** on excitation at 308 nm in benzene and methanol are shown in Figure 2 and their observed lifetimes are listed in Table 1. In benzene, *trans*-**2HC** gave the transient absorption spectrum peaked at 410 and ca. 600 nm. The both bands have the same lifetime (1.2 μs under argon) and were assigned to the same transient. The triplet to triplet (T−T) absorption spectrum observed on benzil-sensitized excitation of *trans*-**2HC** in benzene is shown in Figure 3. These transient spectra, observed on direct and sensitized excitation, exhibited similar spectral profile especially at 600 nm and were both quenched by oxygen with the rate constant of 2.4×10^9 M^{-1} s^{-1}. Thus, both transients observed were assigned to the triplet state.

Similar T−T absorption spectra were observed in all solvents examined. However, there was a considerably large solvent dependence on the lifetime of the triplet transients (Table 1). In methanol, for example, the T−T spectra was observed at

390 nm and around 550−600 nm. Both bands decayed with the lifetime of 140 ns, which was almost 1/9 of the lifetime in benzene. The shortest lifetime (78 ns) was observed in pyridine. Attempts to fit the correlation between the observed triplet lifetime and various physical parameter of solvents, such as dielectric constants (ϵ), acidity (pK_a), viscosity (η) and empirical value for solvatochromizm (E_T(30)),[34] were unsuccessful. Those plots did not exhibit any correlation between solvent properties and observed triplet lifetimes. Thus, there should be other factor(s) which govern the deactivation process from the observed triplet state. These solvent effects on the triplet lifetime of *trans*-**2HC** are discussed in the later section.

The observed triplet state would be a planar trans triplet (^{3}t*), a planar cis triplet (^{3}c*), or a perpendicular triplet (^{3}p*) in which the carbon−carbon double bond is twisted by 90°. The planar cis triplet (^{3}c*) is precluded because no cis isomer is detected as a photoproduct, since the planar cis triplet should deactivate to give the ground-state cis isomer as a photoproduct. The perpendicular triplet is also excluded since it must deactivate to the ground state to give the trans and the cis isomers in a certain ratio. The observed triplet was quenched by oxygen with a rate constant of $k_q^{O_2} = 2.4 \times 10^9$ M^{-1} s^{-1}, which is nearly 1/9 of the diffusion controlled rate constant in benzene ($k_{dif} = (2-3) \times 10^{10}$ M^{-1} s^{-1})[35] and strongly indicates that the triplet is the planar geometry. In addition, the triplet lifetime of *trans*-**2HC** (1.2 μs in benzene) is much longer than those of chalcone (**3a**), 2′-methoxychalcone (**3b**), 3′- (**3c**), and 4′-hydroxychalcone (**3d**); their triplet lifetimes are ∼20 ns and have been assigned to the perpendicular triplet state.[36,37] In addition, the absorption maxima of these perpendicular triplets were around 430 nm and no T−T absorption was observed around 600 nm. Thus, the observed triplet for *trans*-**2HC** was assigned to a planar triplet. However, there are still two possible forms for the planar triplet; the normal form or the tautomer form. Taking account of **3b** as a model compound for the normal form of *trans*-**2HC**, the most stable conformer of **3b** in the excited triplet state should be the perpendicular form as mentioned above. Therefore, from T−T absorption, triplet lifetimes, and quenching rate constant by oxygen we may assign the observed triplet to the triplet state of enol tautomer (^{3}(*trans*-**2HC′**)*). To make clear the assignment of the triplet state which was observed by the transient absorption, the triplet excitation energy of the normal form of *trans*-**2HC** and that of the observed triplet were estimated. Details of the estimations are described in the following sections.

Triplet Excitation Energy of *trans*-2HC. To estimate the triplet excitation energies of *trans*-**2HC**, triplet quenching experiments were carried out in benzene, since we could not observe the phosphorescence of *trans*-**2HC** in glass forming solvents at 77 K. On laser excitation of benzil at 425 nm, a T−T absorption spectrum of benzil was observed peaked at 490 nm.

The pseudo-first-order decay rate constant (k_{obs}) of the benzil triplet increased with increasing *trans*-**2HC** concentration. The slope of eq 1

$$k_{obs} = k_q[\textit{trans}\text{-}\mathbf{2HC}] + k_d \tag{1}$$

gives the rate constant ($k_q = 5.0 \times 10^8$ M^{-1} s^{-1}) for the triplet energy transfer from the benzil triplet to *trans*-**2HC**. The value of $k_q = 5.0 \times 10^8$ M^{-1} s^{-1} is lower than the diffusion controlled rate constant ($k_{dif} = 6.3 \times 10^9$ M^{-1} s^{-1}),[38] and indicates that the quenching process of benzil triplet by *trans*-**2HC** should be endothermic. The difference of the triplet energies (ΔE_a) between triplet sensitizer (benzil) and quencher (*trans*-**2HC**) is calculated to be 6.0 kJ mol^{-1} by eq 2.[39]

$$k_q = k_{dif}\frac{\exp(-\Delta E_a/RT)}{1 + \exp(-\Delta E_a/RT)} \tag{2}$$

Thus, the triplet energy of *trans*-**2HC** is 6 kJ mol^{-1} higher than the triplet state of benzil. Since the triplet energy of benzil is 223 kJ mol^{-1},[40] we can estimate the triplet energy of *trans*-**2HC** to be 229 kJ mol^{-1}.

Triplet Energy of the Relaxed Triplet of *tran*s-2HC Observed by Transient Absorption Spectra. The triplet energy of the transient observed on laser-flash photolysis was estimated by the similar quenching experiments. In benzene, the T−T absorption spectra of *trans*-**2HC** on benzil sensitization by 425 nm laser excitation were quenched by several quenchers (**Q**) with varying triplet energies (eqs 3, 4 and 5).

$${}^3(\textit{trans}\text{-}\mathbf{2HC})^* \xrightarrow{k_r} {}^3(\textit{trans}\text{-}\mathbf{2HC'})^* \tag{3}$$

$${}^3(\textit{trans}\text{-}\mathbf{2HC'})^* + \mathbf{Q} \xrightarrow{k_q'} \textit{trans}\text{-}\mathbf{2HC} + {}^3\mathbf{Q}^* \tag{4}$$

$${}^3(\textit{trans}\text{-}\mathbf{2HC'})^* \xrightarrow{k_d'} \textit{trans}\text{-}\mathbf{2HC} \tag{5}$$

The concentration of *trans*-**2HC** (10 mM) was carefully chosen so that the sensitization of *trans*-**2HC** by benzil was achieved immediately after the laser pulse. The lifetime of the observed triplet is decreased with increasing the concentration of anthracene as a quencher. A reciprocal plot of the triplet lifetime of **2HC** vs the concentration of anthracene gave the straight line (eq 6)

$$k_{obs} = k_q'[\mathrm{Q}] + k_d' \tag{6}$$

and the quenching rate constant by anthracene was determined. Thus, anthracene quenches the observed triplet of **2HC** with the rate constant of $k_q' = 1.7 \times 10^9$ M^{-1} s^{-1}. The process (eq 4) is slightly endothermic as calculated to be 2.5 kJ mol^{-1} from eq 2. Since the triplet energy of anthracene is 178 kJ mol^{-1},[40] the triplet energy of the observed transient is estimated to be 175.5 kJ mol^{-1}.

The similar quenching experiment was carried out using pyrene (E_T = 203 kJ mol^{-1})[40] instead of anthracene as a quencher in benzene. Pyrene did not quench the triplet state of **2HC** up to the concentration of pyrene at 3.8×10^{-3} M. Therefore, the triplet energy of the observed triplet is much lower than that of pyrene and is lower than that of anthracene by 2.5 kJ mol^{-1}.

If the observed triplet is assigned to the triplet state of the starting geometry, that is, *trans*-**2HC**, these quenching experiments should give similar triplet energies. However, the energy transfer from benzil triplet to *trans*-**2HC** gave the triplet energy of 229 kJ mol^{-1}, while the energy transfer from the triplet state of **2HC** to anthracene gave the triplet energy of 175.5 kJ mol^{-1}. Therefore, the observation of the long-lived planar triplet and the difference in triplet energies from quenching experiments strongly indicate the formation of the tautomer (*trans*-**2HC′**) in the triplet state.

Transient Absorption Spectra of *cis*-2HC. As mentioned above, *cis*-**2HC** exhibited the one-way photoisomerization to *trans*-**2HC**. Absorbance from 270 to 430 nm increased upon photoirradiation and finally the spectra becomes identical to that of *trans*-**2HC**. Figure 4 shows the transient absorption spectra observed on excitation of *cis*-**2HC** in benzene by a 308 nm laser pulse under Ar atmosphere. The transient spectra peaked

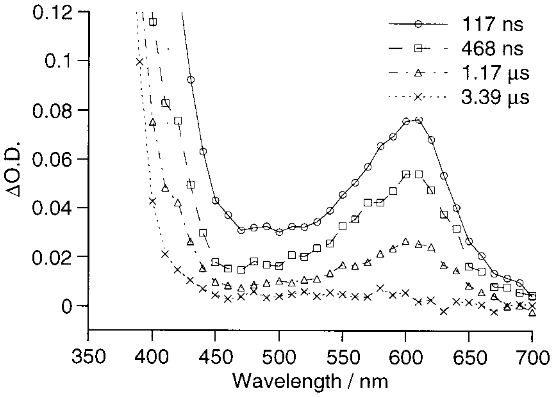


Figure 4. Transient absorption spectra of *cis*-**2HC** observed on excitation at 308 nm in benzene.

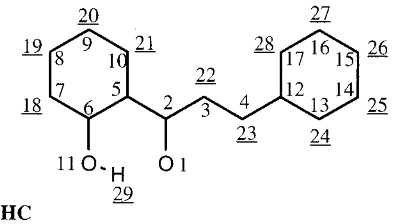
at 610 nm and was assigned to the excited triplet state. The lifetime of the triplet was 1.2 μs. The permanent absorption in the shorter wavelength region (λ < 450 nm) is due to the ground state of *trans*-**2HC** as a photoproduct. The T−T absorption spectrum is very similar to that of *trans*-**2HC** with the absorption maxima at 610 nm and the lifetime of 1.2 μs (Figure 2a), which has been assigned to the triplet state of the tautomer of *trans*-**2HC** (^{3}(*trans*-**2HC′**)*). Therefore, we can assign the observed T−T absorption spectra for *cis*-**2HC** to the tautomer of *trans*-**2HC** (^{3}(*trans*-**2HC′**)*). Thus, based on the photochemical studies and laser-flash photolysis experiments, we can propose that the tautomer of *trans*-**2HC** (^{3}(*trans*-**2HC′**)*) is formed on direct irradiation of *cis*-**2HC** and the twist of the carbon−carbon double bond takes place from ^{3}(*cis*-**2HC′**)* to ^{3}(*trans*-**2HC′**)*.

Quantum Yield for Formation of ^{3}(*trans*-2HC′)*. The quantum yield of intersystem crossing from ^{1}(*trans*-**2HC**)* to ^{3}(*trans*-**2HC′**)* in benzene on 308 nm excitation was 0.09, which was measured by comparing the intensities of T−T absorption of *trans*-**2HC** and anthracene as a standard. The quantum yield of intersystem crossing from ^{1}(*cis*-**2HC**)* to ^{3}(*trans*-**2HC′**)* was 0.06, which was determined by comparing the intensities of T−T absorption of *trans*-**2HC** and *cis*-**2HC** on 308 nm excitation, since the transients observed on excitation of *trans*-**2HC** and *cis*-**2HC** are the same triplet (^{3}(*trans*-**2HC′**)*). The quantum yield of intersystem crossing of *cis*-**2HC** (0.06) is very close to the quantum yield of cis−trans photoisomerization (0.05). These results indicate that the photoisomerization proceeds in the excited triplet state.

Theoretical Considerations. Optimized Structures. Numbering of atoms that were used in the calculation is shown in Figure 5. These numbers are used for the expression of the structure and bond orders.

Molecular structures of each conformation of **2HC** (*trans*-**2HC**, *trans*-**2HC′**, *cis*-**2HC**, and *cis*-**2HC′**) in the ground, the excited singlet, and the excited triplet states were optimized by MOPAC93 (PM3) calculation. Bond lengths, bond angles, and dihedral angles are listed in Tables 2 (*trans*-**2HC** and *trans*-**2HC′**) and 3 (*cis*-**2HC**, and *cis*-**2HC′**). As mentioned above, the stable geometries of both *trans*-**2HC** and *cis*-**2HC** in the ground state are planar. The planarity holds for each electronic state of *trans*-**2HC**, *trans*-**2HC′**, and *cis*-**2HC**. However, ^{3}(*cis*-**2HC**)* was not stable and could not be optimized. This indicates that there is no potential minimum in ^{3}(*cis*-**2HC**)*. All the electronic states of *cis*-**2HC′** were not planar in geometry. The single bond between the olefinic carbon and the benzene ring (C_4−C_{12}) is twisted by ca. 30° and the single bond between the carbonyl α-carbon and the olefinic carbon (C_2−C_3) is twisted by 25−44°.

(a) *trans*-**2HC**



(b) *cis*-**2HC**

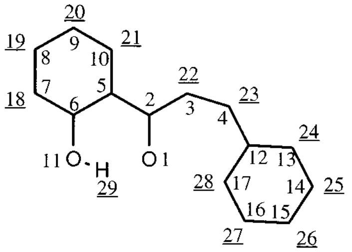


Figure 5. Numbering of atoms for the calculation of *trans*-**2HC** (a) and *cis*-**2HC** (b). Underlined numbers indicate hydrogen atoms.

Heats of Formation (ΔH_f). The estimated heats of formation (ΔH_f) of each optimized conformation of **2HC** in the ground, the excited singlet, and the excited triplet states of *trans*-**2HC**, *trans*-**2HC′**, *cis*-**2HC,** and *cis*-**2HC′** forms are shown in Figure 6. In the ground state, the normal forms (*cis*- and *trans*-**2HC**) are more stable than the corresponding tautomer forms (*trans*-**2HC′** and *cis*-**2HC′**). The differences of ΔH_f between the normal and the tautomer forms are ca. 55 kJ mol^{-1} for both cis and trans isomers. These values are lower than those of salicylic acid[18] (78−98 kJ mol^{-1}) and methyl salicylate[17] (74 kJ mol^{-1}), while higher than those of *o*-hydroxyacetophenone[17] (47.4 kJ mol^{-1}). In the excited state of planar trans and cis forms of **2HC**, all the ΔH_f values of the tautomers are lower than those of corresponding normal forms. These results are indicative of the occurrence of the intramolecular hydrogen transfer in the triplet state as well as the singlet state.

Bond Orders. Table 4 shows the bond orders of each optimized conformation of *trans*-**2HC** and *trans*-**2HC′** in the ground, the excited singlet, and the excited triplet states. It is noteworthy that the bond orders of C═C double bond (C_3−C_4) increase by tautomerization in the excited states. In the normal forms, the values of the bond order are 1.136 and 1.301 for ^{3}(*trans*-**2HC**)* and ^{1}(*trans*-**2HC**)*, respectively. However, in the tautomer forms, the bond orders are 1.478 and 1.511 for ^{3}(*trans*-**2HC′**)* and ^{1}(*trans*-**2HC′**)*, respectively. Generally, a bond order of a C═C double bond decreases in the excited states and it leads to isomerization. In the present case, the increase of the bond orders by tautomerization indicates that the twisting of the C_3−C_4 bond in ^{3}(*trans*-**2HC′**)* might have a higher energy barrier than that in ^{3}(*trans*-**2HC**)*. Another notable result is concerned with the bond order of the single bond between the phenyl and carbonyl groups (C_2−C_5 bond). In the ground state, it increases from 0.986 to 1.485 by tautomerization, while it increases slightly in the excited triplet and singlet states. These values indicate that the C_2−C_5 bond still has a single bond character in the excited states, rather than a double bond character.

Frontier Molecular Orbitals and CI Contributions. Frontier molecular orbitals and the weight of each electronic configuration derived from the PM3 calculation are shown in Figure 7. It is noteworthy that in the LUMO, the phase of C_2−C_5 bond has a bonding character in either *trans*-**2HC** or *cis*-**2HC**, while it has an antibonding character in either *trans*-**2HC′** or *cis*-**2HC′**. Those LUMO orbitals reflect the decrease in the

TABLE 2: Bond Lengths, Bond Angles, and Dihedral Angles of Each Conformer of *trans*-2HC Calculated by PM3/CI4

	trans-**2HC**	*trans*-**2HC′**	^{3}(*trans*-**2HC**)*	^{3}(*trans*-**2HC′**)*	^{1}(*trans*-**2HC**)*	^{1}(*trans*-**2HC′**)*
			Bond Length			
O_1-C_2	1.232	1.340	1.235	1.350	1.236	1.354
C_2-C_3	1.474	1.460	1.455	1.414	1.473	1.415
C_3-C_4	1.343	1.346	1.447	1.365	1.396	1.380
C_4-C_{12}	1.456	1.455	1.362	1.451	1.395	1.439
C_2-C_5	1.482	1.390	1.484	1.457	1.476	1.422
C_5-C_6	1.413	1.471	1.412	1.483	1.410	1.483
C_6-O_{11}	1.352	1.240	1.353	1.237	1.354	1.233
$O_{11}-H_{29}$	0.963	1.763	0.963	1.793	0.961	1.788
O_1-H_{29}	1.792	0.968	1.795	0.961	1.809	0.963
			Bond Angles			
$C_2-C_3-C_4$	123.4	125.1	122.3	125.1	123.3	124.9
$C_3-C_4-C_{12}$	122.5	122.2	121.7	122.2	122.0	122.2
$C_3-C_2-C_5$	118.7	122.4	118.6	121.3	118.7	122.6
			Dihedral Angles			
$O_1-C_2-C_3-C_4$	2.2	0.4	−0.5	−0.1	1.9	−1.1
$C_2-C_3-C_4-C_{12}$	−179.7	179.7	−177.2	179.8	−178.0	180.0
$O_1-C_2-C_5-C_6$	−0.7	0.1	0.3	0.1	−2.5	0.0
$C_3-C_4-C_{12}-C_{13}$	−179.0	−179.9	179.9	−179.8	178.7	179.5
$C_5-C_6-O_{11}-H_{29}$	0.6		−0.3		0.4	
$C_3-C_2-O_1-H_{29}$		179.8		179.7		−179.7

TABLE 3: Bond Lengths, Bond Angles, and Dihedral Angles of Each Conformer of *cis*-2HC Calculated by PM3/CI4

	cis-**2HC**	*cis*-**2HC′**	^{3}(*cis*-**2HC**)*[a]	^{3}(*cis*-**2HC′**)*	^{1}(*cis*-**2HC**)*	^{1}(*cis*-**2HC′**)*
			Bond Length			
O_1-C_2	1.234	1.339		1.348	1.236	1.350
C_2-C_3	1.472	1.464		1.428	1.467	1.447
C_3-C_4	1.344	1.340		1.352	1.403	1.341
C_4-C_{12}	1.451	1.455		1.454	1.389	1.456
C_2-C_5	1.487	1.388		1.456	1.491	1.427
C_5-C_6	1.414	1.470		1.485	1.403	1.479
C_6-O_{11}	1.352	1.240		1.237	1.357	1.239
$O_{11}-H_{29}$	0.962	1.765		1.785	0.958	1.777
O_1-H_{29}	1.781	0.970		0.962	1.801	0.967
			Bond Angles			
$C_2-C_3-C_4$	132.7	131.2		132.6	133.2	131.7
$C_3-C_4-C_{12}$	134.1	130.9		131.8	132.6	130.0
$C_3-C_2-C_5$	118.4	121.2		120.8	118.3	120.2
			Dihedral Angles			
$O_1-C_2-C_3-C_4$	5.8	43.7		24.5	5.1	43.1
$C_2-C_3-C_4-C_{12}$	0.4	0.4		1.9	−0.0	0.1
$O_1-C_2-C_5-C_6$	−0.3	−4.0		−8.1	0.6	−3.9
$C_3-C_4-C_{12}-C_{13}$	−176.9	149.3		148.9	178.0	146.3
$C_5-C_6-O_{11}-H_{29}$	0.5				0.9	
$C_3-C_2-O_1-H_{29}$		180.0		−175.1		-179.6

[a] ^{3}(*cis*-**2HC**)* was not stable and could not be optimized.

bond order of C_2-C_5 bond of the excited-state tautomers. The results of CI contributions indicate that the main electronic transitions occurs from HOMO to LUMO. These molecular orbitals and CI contributions indicate that both S_1 and T_1 have π,π^* character, since the n orbital is calculated in lower energy level than HOMO by 1.713 eV for *trans*-**2HC**.

Discussion

Intramolecular Hydrogen Atom Transfer of *trans*-2HC. Laser flash photolysis of *trans*-**2HC** gave the T−T absorption spectra with maxima at 410 and 610 nm. The quenching experiments indicated the formation of the triplet tautomer (^{3}(*trans*-**2HC′**)*) with the triplet energy of 175.5 kJ mol^{-1} over the ground state, while the triplet energy of the normal form was 229 kJ mol^{-1}.

On direct irradiation, the excited singlet state of *trans*-**2HC** follows two possible pathways to form the triplet tautomer (^{3}(*trans*-**2HC′**)*); via intramolecular hydrogen atom transfer in the singlet state and subsequent intersystem crossing (eqs 7, 8, and 9),

$$trans\text{-}\mathbf{2HC} \xrightarrow{h\nu} {}^1(trans\text{-}\mathbf{2HC})^* \tag{7}$$

$${}^1(trans\text{-}\mathbf{2HC})^* \xrightarrow{\text{hydrogen atom transfer}} {}^1(trans\text{-}\mathbf{2HC'})^* \tag{8}$$

$${}^1(trans\text{-}\mathbf{2HC'})^* \xrightarrow{\text{ISC}} {}^3(trans\text{-}\mathbf{2HC'})^* \tag{9}$$

or via intersystem crossing followed by intramolecular hydrogen atom transfer in the triplet state (eqs 7, 10, and 11).

$${}^1(trans\text{-}\mathbf{2HC})^* \xrightarrow{\text{ISC}} {}^3(trans\text{-}\mathbf{2HC})^* \tag{10}$$

$${}^3(trans\text{-}\mathbf{2HC})^* \xrightarrow{\text{hydrogen atom transfer}} {}^3(trans\text{-}\mathbf{2HC'})^* \tag{11}$$

Chou et al. reported that the weak fluorescence at 635 nm should be attributed to the emission from *trans*-**2HC′**.[15] It indicates

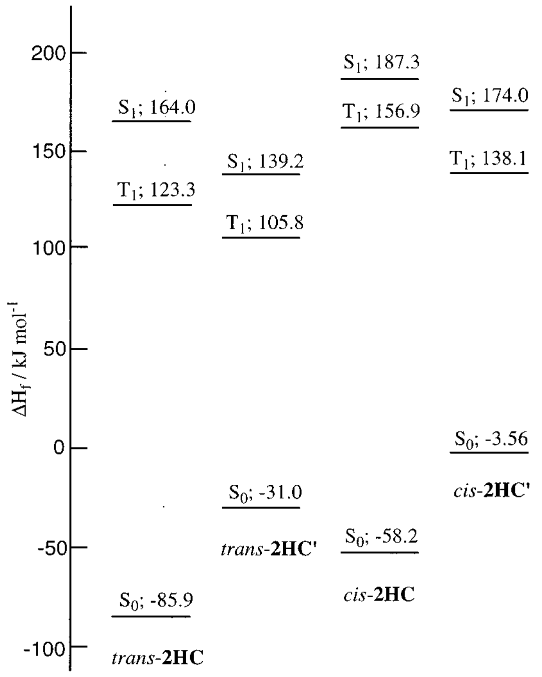


Figure 6. Heats of formation (ΔH_f) of **2HC** in the ground, the excited triplet and the excited singlet states calculated by PM3. Each ΔH_f value is calculated by using totally optimized molecular geometries in each state.

that on direct irradiation, the triplet state of the tautomer form (^{3}(*trans*-**2HC′**)*) is produced by the hydrogen atom transfer in the excited singlet state to give ^{1}(*trans*-**2HC′**)* followed by intersystem crossing (eqs 7, 8, and 9). However, since the rates of intersystem crossings of carbonyl compounds are usually very fast ($k_{ISC} \sim 10^{10}$ s^{-1}) and this process can compete with the intramolecular hydrogen atom transfer, the intersystem crossing might take place from the normal form ^{1}(*trans*-**2HC**)* (eqs 7, 10, and 11).

On triplet sensitization, the triplet state of the normal form (^{3}(*trans*-**2HC**)*) is initially formed. However, according to the transient absorption spectra and the quenching experiments, the triplet observed by the laser-flash photolysis is assigned to ^{3}(*trans*-**2HC′**)*. These results indicate that the intramolecular hydrogen atom transfer occurs so fast in the excited triplet state that the normal form (^{3}(*trans*-**2HC**)*) could not be detected upon sensitized excitation.

Intramolecular Hydrogen Atom Transfer in the Excited Triplet State. As mentioned in the Introduction, there are a lot of extensive studies of the intramolecular hydrogen atom transfer in the excited singlet state for various type of compounds.[15−18] However, only a few molecules have been reported about the intramolecular hydrogen atom transfer in the excited triplet state.[19−24] For example, there is an equilibrium between the normal and the tautomer form in the triplet state of 1-(acylamino)anthraquinone derivatives[22] which possess O:H−N intramolecular hydrogen bond. The equilibrium depends on substituents and solvents. In O:H−O intramolecular hydrogen bonded system, 3-hydroxyflavone[23] and methyl salicylate[19] have been reported. We have estimated the triplet energies of the normal and the tautomer forms of methyl salicylate (**MS**) and concluded that **MS** gives the tautomer form in the excited triplet state in benzene at room temperature.[19] No evidence of the establishment of the equilibrium between the normal and the tautomer form has been reported in O:H−O intramolecular hydrogen bonded systems. In *trans*-**2HC**, it is concluded that there is no equilibrium between the normal (^{3}(*trans*-**2HC**)*) and the tautomer (^{3}(*trans*-**2HC′**)*) forms in the excited triplet state because there was no temperature or solvent dependence upon the T−T absorption spectra. Although a blue shift of the T−T spectra was observed with increasing the polarity of solvent, it is not attributable to the shift of the equilibrium in the triplet state because the same decay rate constant was observed at any monitoring wavelength in each solvent. In addition, the spectra did not exhibit temperature dependence in methanol (180−324 K) or in benzene (280−323 K). Thus, the blue shift of the T−T absorption spectra by solvent is attributed to the stabilization of the triplet tautomer (^{3}(*trans*-**2HC′**)*). Therefore, the T−T spectra was assigned to one species i.e., the triplet tautomer (^{3}(*trans*-**2HC′**)*). The heats of formation (ΔH_f) derived from PM3 calculations support the formation of ^{3}(*trans*-**2HC′**)*. As can be seen in Figure 6, *trans*-**2HC′** is the most stable conformer in the excited triplet state. The difference of ΔH_f value between ^{3}(*trans*-**2HC**)* and ^{3}(*trans*-**2HC′**)* is 17.5 kJ mol^{-1} indicating that the hydrogen atom transfer proceeds adiabatically.

Attempts to observe the ground-state tautomer (*trans*-**2HC′**) were unsuccessful. It was not detected by transient absorption spectroscopy. However, the results are in good agreement with the previous studies of O:H−O intramolecular hydrogen bonded systems. In methyl salicylate (**MS**), the ground-state energy gap between the normal and the tautomer forms is as high as 74 kJ mol^{-1} which indicates the ground-state tautomer is very unstable.[17] Furthermore, some groups have pointed out that there is no potential minimum at the ground-state tautomer in O:H−O intramolecular hydrogen bonded systems.[17,18] Although it is still a controversial point whether there is a minimum or not, there is no doubt that the ground-state tautomer is very short-lived. Since the triplet tautomer (^{3}(*trans*-**2HC′**)*) has a longer lifetime than that of the ground-state tautomer, the ground-state tautomer could not be detected by the transient absorption.

Photoisomerization Mechanism. From quantum yield measurements, laser flash photolysis and PM3 calculations, a novel mechanism for one-way photoisomerization of **2HC** as shown in Figure 8 is proposed. On direct excitation *cis*-**2HC** gives the triplet tautomer of *cis*-**2HC** (^{3}(*cis*-**2HC′**)*) either via intramolecular hydrogen atom transfer in the singlet state and subsequent intersystem crossing (eqs 12, 13, and 14),

$$cis\text{-}\mathbf{2HC} \xrightarrow{h\nu} {}^1(cis\text{-}\mathbf{2HC})^* \qquad (12)$$

$$^1(cis\text{-}\mathbf{2HC})^* \xrightarrow[\text{transfer}]{\text{hydrogen atom}} {}^1(cis\text{-}\mathbf{2HC'})^* \qquad (13)$$

$$^1(cis\text{-}\mathbf{2HC'})^* \xrightarrow{\text{ISC}} {}^3(cis\text{-}\mathbf{2HC'})^* \qquad (14)$$

or via intersystem crossing followed by intramolecular hydrogen atom transfer in the triplet state (eqs 12, 15, and 16).

$$^1(cis\text{-}\mathbf{2HC})^* \xrightarrow{\text{ISC}} {}^3(cis\text{-}\mathbf{2HC})^* \qquad (15)$$

$$^3(cis\text{-}\mathbf{2HC})^* \xrightarrow[\text{transfer}]{\text{hydrogen atom}} {}^3(cis\text{-}\mathbf{2HC'})^* \qquad (16)$$

It should be noted that ^{3}(*cis*-**2HC**)* was not stable and could not be optimized in the PM3 calculation, indicative of very fast hydrogen atom transfer in eq 16. The triplet tautomer of *cis*-**2HC** (^{3}(*cis*-**2HC′**)*) isomerizes adiabatically to give the triplet tautomer of *trans*-**2HC** (^{3}(*trans*-**2HC′**)*) (eq 17),

$$^3(cis\text{-}\mathbf{2HC'})^* \xrightarrow{\text{isomerization}} 3(trans\text{-}\mathbf{2HC'})^* \qquad (17)$$

which has sufficient lifetime to be detected by the nanosecond

TABLE 4: Bond Orders of Each Conformer of *trans*-2HC Calculated by PM3/CI4

	trans-**2HC**	*trans*-**2HC′**	^{3}(*trans*-**2HC**)*	^{3}(*trans*-**2HC′**)*	^{1}(*trans*-**2HC**)*	^{1}(*trans*-**2HC′**)*
O_1-C_2	1.786	1.173	1.699	1.108	1.705	1.105
C_2-C_3	0.990	1.049	1.092	1.339	1.054	1.257
C_3-C_4	1.833	1.802	1.136	1.478	1.301	1.511
C_4-C_{12}	1.044	1.051	1.553	1.133	1.366	1.127
C_2-C_5	0.986	1.485	0.981	1.081	0.985	1.165
C_5-C_6	1.331	1.025	1.332	0.987	1.341	1.016
C_6-O_{11}	1.118	1.712	1.117	1.730	1.116	1.692
$O_{11}-H_{29}$	0.874	0.041	0.872	0.034	0.876	0.053
O_1-H_{29}	0.043	0.845	0.045	0.889	0.042	0.853

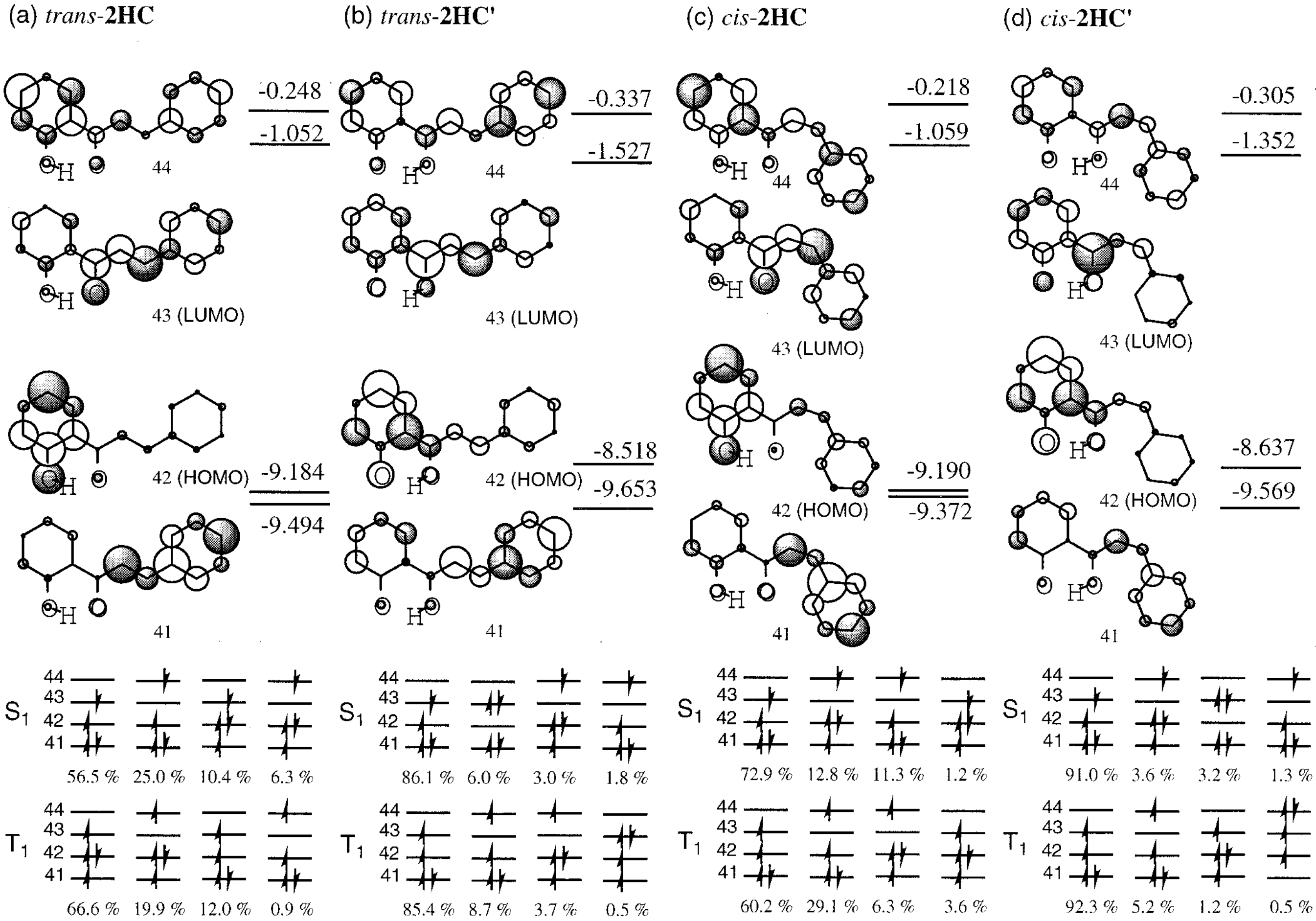


Figure 7. Frontier molecular orbitals, its energies (eV), and descriptions of the excited triplet and singlet states for *trans*-**2HC** (a), *trans*-**2HC′** (b), *cis*-**2HC** (c), and *cis*-**2HC′** (d) as optimized by PM3/CI4. Geometry optimized in the ground state using the PM3 Hamiltonian.

laser flash photolysis. The triplet tautomer of *trans*-**2HC** (^{3}(*trans*-**2HC′**)*) is more stable than the perpendicular triplet state (^{3}p′*); deactivation from the triplet state takes place only from ^{3}(*trans*-**2HC′**)*. If the perpendicular triplet state (^{3}p′*) is more stable than ^{3}(*trans*-**2HC′**)* or there is an equilibrium between ^{3}p′* and ^{3}(*trans*-**2HC′**)*, the deactivation from ^{3}p′* takes place to give the mixture of *trans*-**2HC** and *cis*-**2HC**. However, the excited state *trans*-**2HC** does not give the cis isomer, while the excited state *cis*-**2HC** gives the *trans*-**2HC**. Thus, the deactivation of triplet state does not take place from the perpendicular conformation (^{3}p′*).

Such one-way properties from ^{3}(*cis*-**2HC′**)* to ^{3}(*trans*-**2HC′**)* can be explained by the very low triplet energies of these tautomers. These tautomers have conjugation of tetraenone structure and therefore the planar trans triplet should be the most stable conformation in the triplet state. Actually, the estimated triplet energy of *trans*-**2HC′** is 175.5 kJ mol^{-1} and is much lower than the triplet energy of *trans*-**2HC** (229 kJ mol^{-1}). Photochemical isomerization of arylethenes[41] are reported and the mode of isomerization as well as the potential energy surfaces of isomerization are well understood by the effect of aryl group on the triplet energies of planar and perpendicular geometries. For example, the triplet energies of trans isomers of one-way isomerizing olefins such as 2-anthrylethenes were estimated to be ca. 180 kJ mol^{-1}. Thus, in the excited triplet state of **2HC**, the tautomer of *cis*-**2HC** (^{3}(*cis*-**2HC′**)*) formed by the intramolecular hydrogen atom transfer undergoes twisting around the double bond to give the perpendicular triplet state (^{3}p′*), but ^{3}p′* is no longer the funnel for the deactivation to the ground state state and the deactivation takes place solely at ^{3}(*trans*-**2HC′**)*.

Solvent Effect on the Lifetime of ^{3}(*trans*-2HC′)*. As shown in Table 1, the lifetime of the triplet (τ_T) observed on excitation of *trans*-**2HC** varies with solvents. It is longer in nonpolar solvents such as benzene, hexane, and methylcyclohexane, while shorter in protic or aprotic polar solvents. As described above, the plot of the ln(1/τ_T) against dielectric constant, E_T(30), or other parameters of solvents did not exhibit any correlation.

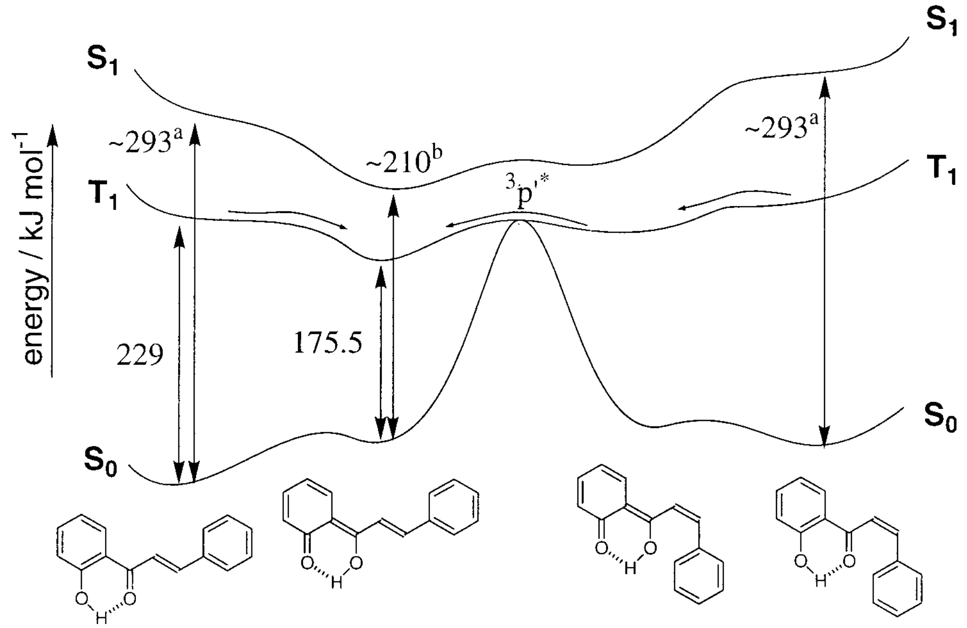
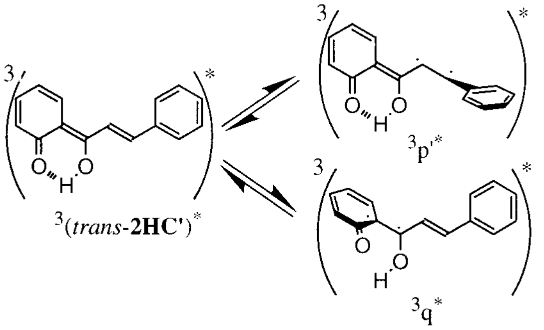


Figure 8. Potential energy surfaces of intramolecular hydrogen atom transfer and isomerization around double bond of **2HC**. (a) Calculated from absorption spectra. (b) Calculated from fluorescence spectra in ref 15.

SCHEME 1



Generally, since a spin−orbit coupling is hardly enhanced by solute−solvent interaction, these solvent effects on the triplet lifetime cannot be explained by the increase of the intersystem crossing rate constant. Thus, we can assume that there should be another triplet state (^{3}X*) which is in equilibrium with the observed triplet. As candidates for ^{3}X*, two types of twisted forms are considered: the perpendicular form around the double bond of the styryl group (^{3}p′*) and that of the quinoid ring (^{3}q*) (Scheme 1).

For the former candidate, one can discuss the triplet lifetime and the mode of isomerization from the triplet state. Generally, when an olefin exhibits two-way isomerization in the triplet state, the deactivation usually takes place from the perpendicular triplet state (^{3}p*), where ^{3}p* are often equilibrated with the planar trans triplet state (^{3}t*) with the equilibrium constant K_{tp} ($=[^3p^*]/[^3t^*]$). Then the triplet lifetime can be described by using the K_{tp} value and the decay rate constant from ^{3}t* (k_{dt} as assumed to be ca. 2×10^4 M^{-1} s^{-1}) and ^{3}p* (k_{dp} as assumed to be 2×10^7 M^{-1} s^{-1}) as shown in eq 18.

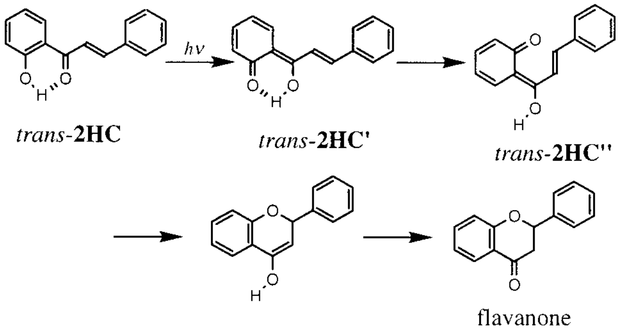
$$1/\tau_T = k_{dt}/(1 + K_{tp}) + k_{dp}K_{tp}/(1 + K_{tp}) \qquad (18)$$

Since the decay rate constant from ^{3}p* is about 10^3 times faster than that of ^{3}t*, one-way isomerization can be achieved in the case that $K_{tp} \ll 10^{-3}$. In that case, the triplet lifetime τ_T should be at least longer than 10 μs as previously observed. The τ_T becomes shorter when the equilibrium is shifted to the perpendicular triplet state compared to the planar triplet state and finally gives ca. 50 ns in the olefin where ^{3}p* is more stable than ^{3}t* as observed for stilbene and alkylstyrenes.[41]

Taking into account the above discussion, the solvent effect on the triplet lifetime of **2HC** seems to indicate the following. In benzene ^{3}(*trans*-**2HC′**)* is more stable than ^{3}p′* and the deactivation from the triplet state takes place from ^{3}(*trans*-**2HC′**)* to give one-way cis−trans isomerization, while in more polar protic solvent ^{3}p′* becomes to equilibrate with ^{3}(*trans*-**2HC′**)* (Scheme 1) and the deactivation may take place not only from ^{3}(*trans*-**2HC′**)*, but also from ^{3}p′*, to exhibit mutual cis−trans isomerization (two-way isomerization). However, we observed only one-way cis−trans isomerization in all solvents. Therefore, ^{3}p′* cannot be a candidate for the ^{3}X*.

For the latter case, a lengthening or a breaking of the intramolecular hydrogen bond is required to give the twisted conformer (^{3}q*) (Scheme 1). In nonpolar solvents such as benzene and cyclohexane, ^{3}q* cannot be stabilized and the equilibrium between the planar ^{3}(*trans*-**2HC′**)* and the twisted ^{3}q* shifts to ^{3}(*trans*-**2HC′**)*. In protic and aprotic polar solvents, on the other hand, ^{3}q* can be stabilized by interaction with solvent molecules and the equilibrium may be established. The equilibrium constant should depend on the solvent properties. ^{3}q* should have a shorter triplet lifetime because its ground state (^{1}q) is unstable and S_0−T_1 energy gap is very small. Thus, the intersystem crossing should be faster from ^{3}q* than from ^{3}(*trans*-**2HC′**)* and the observed triplet lifetime becomes shorter in polar solvents. Deactivation from ^{3}q* yield rotational isomers of the starting compound *trans*-**2HC**, but no stable photochemical product is formed by this mechanism. This equilibrium model can explain the solvent effect on the triplet lifetime and the absence of trans−cis isomerization. Therefore, the ^{3}X* can be assigned to the twisted conformer ^{3}q*. The twisting of the quinoid ring may be explained by the phase of the frontier molecular orbitals (Figure 7a and b). In the excited state (either singlet or triplet) of the normal form (^{1}(*trans*-**2HC**)* or ^{3}(*trans*-**2HC**)*), orbitals on both C_2 and C_5 atoms are in the same phase. Thus, the C_2−C_5 bond has bonding character indicative of no twisting of the quinoid ring, which takes place in the excited states. On the other hand, in the tautomer form, the C_2−C_5 bond

SCHEME 2



has antibonding character in the excited states, while it has bonding character in the ground state. This indicates that the twisting of the quinoid ring may take place in the excited state of the tautomer form. Therefore, the equilibration between the tautomer triplet and the conformer triplet (^{3}q*) can be supported by the PM3 calculation for the frontier molecular orbitals.

In any solvent, the above-mentioned novel solvent effect on the triplet lifetime was observed without affecting the mode of isomerization in the triplet state.

Cyclization Mechanism. Photoirradiation of *trans*-**2HC** yielded a cyclization product, flavanone. As can be seen in Table 1, the quantum yields were very low. The Φ_{dis} values are in fair agreement with the Φ_{fla} values indicating that consumption of *trans*-**2HC** leads to the formation of flavanone. The effect of molecular oxygen on the quantum yields seems to indicate that the cyclization takes place both in the excited singlet and triplet states. On this point, the contributions of the spin multiplicity on the cyclization (${}^1\Phi_0$ and ${}^3\Phi_0$) were roughly estimated by eqs 19 and 20:

$$\Phi_{\mathrm{fla}}{}^{\mathrm{Ar}} = {}^1\Phi_0 + {}^3\Phi_0 \qquad (19)$$

$${}^1\Phi_0 = (\tau_{\mathrm{T}}{}^{\mathrm{Ar}}\Phi_{\mathrm{fla}}{}^{\mathrm{O2}} - \tau_{\mathrm{T}}{}^{\mathrm{O2}}\Phi_{\mathrm{fla}}{}^{\mathrm{Ar}})/(\tau_{\mathrm{T}}{}^{\mathrm{Ar}} - \tau_{\mathrm{T}}{}^{\mathrm{O2}}) \qquad (20)$$

where τ_{T} is the triplet lifetime and the superscripts (Ar and O_2) indicate under argon and oxygen atmosphere, respectively. The calculated values of ${}^1\Phi_0$ and ${}^3\Phi_0$ are listed in Table 1. In nonpolar solvents, the cyclization mainly takes place in the excited singlet state. In aprotic polar solvents (ethyl acetate and acetonitrile), the reaction proceeds equally both in the excited singlet and triplet state, while the triplet state is the main pathway in methanol. The cyclization reaction was previously reported by Matsushima et al.[31,32] They pointed out that the intramolecular hydrogen atom transfer is required for the cyclization (Scheme 2). However, the proposed mechanism does not explain the larger quantum yield in acetonitrile and the spin multiplicity dependence. Another possibility is that the efficiency of the cyclization might depend on the distribution of rotamers in the ground state.

Conclusion

The photochemical properties of **2HC** were studied by quantum yield measurements, laser flash photolysis, and semiempirical (PM3/CI4) calculations. *trans*-**2HC** does not give any *cis*-**2HC**, but undergoes very inefficient cyclization to form flavanones. While *cis*-**2HC** undergoes one-way photoisomerization to give *trans*-**2HC**. On excitation of *trans*-**2HC** and *cis*-**2HC**, the tautomer form of *trans*-**2HC** in the excited triplet state was observed by laser-flash photolysis. The assignment of the transient absorption was made by the quenching experiments and semiempirical calculations. The one-way cis−trans isomerization was induced by the intramolecular hydrogen atom transfer in the excited triplet state. There was a large solvent dependence on the lifetimes of the triplet tautomer of *trans*-**2HC**. The solvent effect was discussed in terms of the fast equilibrium between the isomers. The present findings of the one-way isomerization of **2HC** indicate that the mode of carbon−carbon double bond can be controlled by the remote intramolecular hydrogen bonding.

Experimental Section

Materials. The solvents benzene, cyclohexane, hexane, acetonitrile, ethyl acetate, and methanol are spectroscopic grade (Dojin Chem. Co. or Kanto Chem. Co.) and were used as received. Benzil was purchased from Wako Chem. Co. and recrystallized four times from hexane. Anthracene was purchased from Wako Chem. Co. and recrystallized from ethanol and benzene.

trans-2′-Hydroxychalcone, *trans*-2′-methoxychalcone, *trans*-3′-hydroxychalcone, and *trans*-4′-hydroxychalcone were prepared by Aldol condensation between benzaldehyde and corresponding acetophenone. Chalcone was purchased from Tokyo Chem. Industry Co. and recrystallized from ethanol.

***trans*-2′-Acetoxychalcone.** Acetic anhydride (35 mL) was added to a solution of *trans*-2′-hydroxychalcone (3.1 g, 13.8 mmol) in 150 mL of pyridine. The mixture was stirred at room temperature for 12 h. The reaction mixture was poured into ice water, and extracted with ether. The organic layer was washed with saturated sodium carbonate and 1 N hydrochloric acid. The mixture was separated by column chromatography with silica gel to give 3.5 g of *trans*-2′-acetoxychalcone (96%). ^{1}H NMR (200 MHz, $CDCl_3$) δ(ppm): 2.24 (3H, s), 7.17 (1H, d, $J = 16.0$ Hz), 7.18 (1H, d, d, $J = 1.0$ Hz, 8,0 Hz), 7.31−7.45 (4H, m), 7.51−7.60 (3H, m), 7.59 (1H, d, $J = 16.0$ Hz), 7.71 (1H, d, d, $J = 1.8$ Hz, 7.6 Hz).

***cis*-2′-Acetoxychalcone.** *trans*-2′-Acetoxychalcone (3.5 g) was dissolved in 1000 mL of benzene and irradiated for 15 h by 400 W high pressure mercury lamp. The deep UV light was eliminated by passing the light beam through 10 mm path length of acetone solution. Nitrogen gas was passed during the photoirradiation. The photoirradiation gave approximately 1:1 mixture of *trans*- and *cis*-2′-acetoxychalcone. The mixture was separated by HPLC and 620 mg of *cis*-2′-acetoxychalcone was obtained. ^{1}H NMR (200 MHz, $CDCl_3$) δ(ppm): 2.32 (3H, s), 6,46 (1H, d, $J = 12.6$ Hz), 6.97 (1H, d, $J = 12.6$ Hz), 7.09 (1H, d, d, $J = 1.2$ Hz, 8.1 Hz), 7.19−7.26 (4H, m), 7.40−7.53 (3H, m), 7.78 (1H, d, d, $J = 1.6$ Hz, 7.8 Hz).

***cis*-2′-Hydroxychalcone.** *cis*-2′-Acetoxychalcone (620 mg) was dissolved in 150 mL of methanol and refluxed for 26 h. The solvent was removed and mixture was separated by column chromatography with silica gel to give 100 mg of *cis*-2′-hydroxychalcone (19%). ^{1}H− NMR (200 MHz, $CDCl_3$) δ-(ppm): 6.63 (1H, d, $J = 12.8$ Hz), 6.82 (1H, d, d, d, $J = 1.2$ Hz, 7.2 Hz, 9.2 Hz), 6.99 (1H, d, d, $J = 1.0$ Hz, 8.4 Hz), 7.02 (1H, d, $J = 12.8$ Hz), 7.27−7.29 (3H, m), 7.36−7.49 (3H, m), 7.76 (1H, d, d, $J = 1.6$ Hz, 8.0 Hz), 12.25 (1H, s).

Quantum Yields of Isomerization and Quantum Yields of Formation of Flavanone. The solutions were purged with argon or oxygen gas and irradiated with 400 W high-pressure mercury lamp. Glass filters (Toshiba U360 and L35) were used to obtain a monochromatic 366 nm light. The isomer yields were determined by HPLC using internal standard. Irradiation time was controlled so that the product yields were within 5%. For the estimation of the light quanta absorbed by the sample solutions, potassium ferroxalate was used.

Quantum Yields of Disappearance of *trans*-2HC. The sample solutions were irradiated by the same optical system as described above. The consumption of *trans*-**2HC** was estimated by measuring of the absorbance at 350 and 366 nm. Irradiation time was controlled so that the isomer yields were within 5%. Potassium ferroxalate was used as actinometer.

Transient Absorption Spectroscopy. Laser flash photolyses were performed with 308-nm pulses (XeCl, 10 ns fwhm) from an excimer laser (Lambda Physik LPX-100) or with 425 nm pulses (Stilbene 3, 10 ns fwhm) from an excimer laser-pumped dye laser (Lambda Physik FL-3002). A pulsed xenon arc (Wacom, KXL-151, 150 W) was used as a monitoring light source. The detailed setup was described previously.[35] Some of the sample solutions were deaerated by bubbling argon.

Quantum Yields of Intersystem Crossing. The quantum yields of intersystem crossing (Φ_{ISC}) were determined by laser flash photolysis comparing the absorbance (ΔO.D.) of the triplet state of sample and standard compound generated by direct excitation and sensitized excitation. The value of quantum yield of intersystem crossing was estimated by eq 21.

$$\Phi_{\mathrm{ISC}} = \Phi_{\mathrm{std}} \frac{\Delta \mathrm{O.D.}^{\mathrm{dir}}}{\Delta \mathrm{O.D.}_{\mathrm{std}}^{\mathrm{dir}}} \frac{\Delta \mathrm{O.D.}_{\mathrm{std}}^{\mathrm{sens}}}{{}^{\Delta}\mathrm{O.D.}^{\mathrm{sens}}} \qquad (21)$$

where Φ_{std} is the quantum yield of intersystem crossing of the standard. The superscripts "dir" and "sens" indicate direct and sensitized excitation, respectively. The subscript "std." means standard.

Calculations. The semiempirical calculations were performed using CAChe MOPAC ver. 94.10 on a Macintosh G3 with parameters in ref 42. The energy parameters, the weight of each electronic configuration, and the MO coefficients were calculated through the semiempirical PM3 method. In the calculation, totally optimized molecular geometries in each electronic state or those in the ground state were used.

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

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