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Quantum Chemical Studies on Photoinduced Cis−Trans Isomerization and Intramolecular Hydrogen Atom Transfer of 2′-Hydroxychalcone

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The reaction mechanism of the one-way isomerization of 2′-hydroxychalcone (2HC) was studied by calculating the potential energy surfaces of the twist of the C═C double bond and the intramolecular hydrogen atom transfer in the excited triplet state by the UB3LYP/6-31G** level. The calculations reveal the following. The potential energy curve of the triplet state between the keto forms (*trans*-2HC and *cis*-2HC) is similar to that of stilbene, which exhibits mutual isomerization. On the other hand, the potential energy curve between the enol forms (*trans*-2HC′ and *cis*-2HC′) is similar to that of styrylanthracene, which exhibits one-way isomerization from the cis to trans isomer. Although the hydrogen atom transfer has an energy barrier (<2 kcal mol^{-1}), the relative energy of the transition state with zero-point correction is lower than that of *trans*-2HC. Electronic spins localize around the C═C double bond in the intermediate states (*p*-2HC and *p*-2HC′) of isomerization. During the hydrogen atom transfer, electronic spins shift from the phenyl group to the 2-hydroxyphenyl moiety. The electronic charge on hydrogen-bonded proton does not change significantly during the hydrogen atom transfer process.

1. Introduction

A number of compounds having a C═C double bond exhibit mutual photoisomerization between cis and trans isomers upon photoexcitation. In these molecules, stable geometry in the excited state is the perpendicular form in which a C═C double bond is twisted by about 90°. Deactivation occurs from this state and yields a mixture of cis and trans isomers. On the other hand, some molecules undergo ‘one-way’ isomerization in which the trans or the cis isomer is more stable in the excited state and the deactivation occurs at either the trans or cis side. For example, 2-anthrylethylenes (**1a**,**b**) undergo one-way isomerization from cis to trans, because the trans isomer is more stable than the perpendicular form in the excited triplet state.[1] Another example is the series of compounds in which the cis isomer is stabilized by an intramolecular hydrogen bonding. The direction of isomerization of 2-(2-(2-pyridyl)ethenyl)indole (**2**) is from trans to cis due to either the occurrence of fast nonradiative decay or the high barrier of twisting by the hydrogen bond in the cis isomer.[2] Detailed information about the reaction dynamics and the potential surfaces of such molecules gives useful guidance for constructing optical storage materials or light-driven molecular devices utilizing high selective photoreactions.

Molecules that possess intramolecular hydrogen bonds undergo intramolecular hydrogen atom transfer (formally called proton transfer) in the excited state. A number of such molecules emit fluorescence with large Stokes' shift and the emitting species have been assigned as the enol tautomer in which the hydrogen atom has been transferred.[3−7] However, studies on this reaction have been limited to the excited singlet state because the reaction can be easily monitored by the fluorescence. Methods for the detection of the excited triplet state, however, require phosphorescence or transient absorption techniques. Several experimental studies on hydrogen atom transfer in the excited triplet state have been done,[3,8−16] although few theoretical studies have been done.[3,8,17−21]

Recently, another type of reaction mechanism of one-way photoisomerization has been proposed for 2′-hydroxychalcone (2HC), in which the cis-to-trans isomerization proceeds via intramolecular hydrogen atom transfer in the excited triplet state.[9,11,22] 2HC possesses a C═C double bond and an O−H:O intramolecular hydrogen bond between the hydroxyl group and the carbonyl oxygen. Upon photoirradiation, 2HC undergoes one-way photoisomerization from the cis to trans isomer, whereas chalcones that do not possess the intramolecular hydrogen bond exhibit mutual photoisomerization. The most notable feature of this one-way photoisomerization is the remarkable effect of the intramolecular hydrogen bond on the behavior of the excited state of 2HC, although the intramolecular hydrogen bond does not seem to play a role in the cis−trans isomerization.

In those previous reports, the mechanism of the one-way isomerization of 2HC was studied by quantum yield measurements, nanosecond transient absorption spectroscopy, and semiempirical PM3 calculation.[9,11,22] The potential surface of the reaction revealed by those studies indicated that isomeriza-

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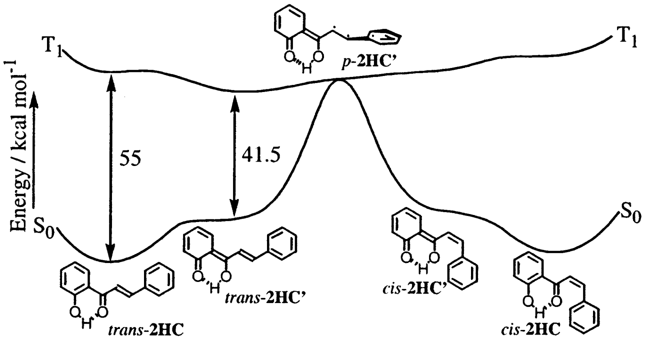

Figure 1. Energy diagram of the photochemical reaction of 2HC proposed by experimental observations (from refs 11 and 22).

tion occurs in the excited triplet state via intramolecular hydrogen atom transfer reaction, as shown in Figure 1. On direct photoexcitation, the trans isomer of 2HC (*trans*-2HC) gives the enol tautomer in the excited triplet state (^{3}(*trans*-2HC′)*) via the hydrogen atom transfer reaction in either the excited singlet or triplet state. Isomerization of a C=C double bond to the cis form does not occur because ^{3}(*trans*-2HC′)* is more stable than the perpendicular triplet (^{3}(*p*-2HC′)*), in which the C=C double bond is twisted by 90°. The lifetime of ^{3}(*trans*-2HC′)* in benzene is 1.2 μs, which was determined by transient absorption technique.[9,11,22] The deactivation from ^{3}(*trans*-2HC′)* to the ground state of the enol form (*trans*-2HC′), followed by back hydrogen atom transfer, gave the starting molecule (*trans*-2HC). On the other hand, upon photoirradiation, the cis isomer of 2HC (*cis*-2HC) gives *trans*-2HC. The isomerization occurs in the excited triplet state via the triplet enol of the cis form (^{3}(*cis*-2HC′)*), as suggested by the following three observations. (1) The transient absorption spectra of ^{3}(*trans*-2HC′)* is observed upon excitation of *cis*-2HC.[11,22] (2) The quantum yield of isomerization from *cis*-2HC to *trans*-2HC (0.05) is close to the quantum yield of the formation of ^{3}(*trans*-2HC′)* on excitation of *cis*-2HC (0.06).[11,22] (3) ^{3}(*trans*-2HC′)* is more stable than ^{3}(*cis*-2HC′)*, as revealed by PM3 calculation.[11] Thus, one-way isomerization of 2HC proceeds adiabatically along the potential surface of the excited triplet state. However, the potential surface of the reaction has not been determined theoretically. The only transient, which has been observed by using the transient absorption method, is the enol tautomer of the trans isomer (^{3}(*trans*-2HC′)*).[11,22] The reaction intermediate between the reactant (^{3}(*cis*-2HC)*) and the product (^{3}(*trans*-2HC′)*) has not been detected experimentally. Questions remain, such as whether the hydrogen atom transfer is really faster than the twist of the C=C double bond or whether these processes can compete and an equilibrium among transient species is established in the excited triplet state. Other questions include, does the electronic charge of O−H:O atoms change or not during the hydrogen atom transfer process, and how does the spin density affect the reactivity of 2HC?

In the present study, to answer these questions as well as to refine the reaction mechanism of the one-way isomerization of 2HC, we used density functional theory (DFT) to calculate the potential energy curve for the cis−trans isomerization and the intramolecular hydrogen atom transfer in the excited triplet state of 2HC.

2. Computational Method

Geometry optimizations and vibrational frequency calculations were carried out using the Gaussian98 program package[23] on an SGI OCTANE (300 MHz CPU, 2.5GB RAM). The (U)B3LYP[24,25] method was employed with a 6-31G** basis set. Zero-point energy corrections were also calculated using computed harmonic frequencies. Because the expectation values of $\langle \hat{S}^2 \rangle$ in these UB3LYP calculations were between 2.02 and 2.07 ($2.02 \leq \langle \hat{S}^2 \rangle \leq 2.07$) for the triplet state at all geometries, the effect of the spin contaminations were reasonably small and the potential energy surface obtained has an error small enough to discuss the reaction mechanism of the one-way isomerization of 2HC.

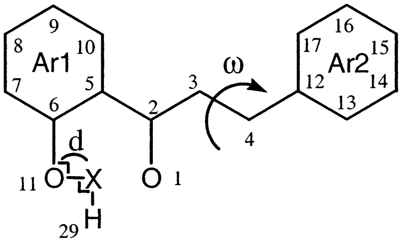

Figure 2. Numbering of atoms and molecular structure used in the calculation of the potential curves of the twist of a C=C bond and the intramolecular hydrogen atom transfer in 2HC.

TABLE 1: Relative Energies and C−C=C−C Torsion Angles (ω) of Energy-Minimum and Transition State (TS) Structures of 2HC[a]

	relative energy ((U)B3LYP/6-31G**) (kcal mol^{-1})	torsion angle, ω (deg)	relative energy (PM3/CI4) (kcal mol^{-1})[d]
	S$_0$		
trans-2HC[b]	0.0	180.0	0.0
cis-2HC	5.7	3.2	6.6
	T$_1$		
trans-2HC[c]	0.0 (0.0)	180.0	0.0
p-2HC	−0.7 (−0.7)	94.1	
TS (*trans*-2HC ↔ 2HC)	0.1 (0.1)	149.7	
TS (*trans*-2HC ↔ *trans*-2HC′)	1.4 (−0.9)	180.0	
trans-2HC′	−7.4 (−6.9)	180.0	−4.2
cis-2HC′	−1.4 (−0.5)	14.7	3.5

[a] The values in parentheses are the energies with zero-point energy correction. [b] Total energy is −729.292300 au. [c] Total energy is −729.209152 au. [d] From ref 11.

The potential energy surface of the isomerizations was calculated for various values of the C−C=C−C torsion angle (ω, Figure 2) in the range 0−180° in steps of 15°. All other geometry parameters were optimized at each point.

To investigate the potential energy surface of the hydrogen atom transfer, we defined a dummy atom (X) on the line connecting the phenolic oxygen and the carbonyl oxygen atoms (Figure 2). The O(phenolic)−X distance was varied in the range 1.0−1.6 Å in steps of 0.1 Å, whereas the O(phenolic)−X−H angle was fixed at 90°.

3. Results

3.1. Optimized Geometries and Relative Energies. The calculated relative energies and C−C=C−C torsion angles (ω) of energy-minimum and transition state (TS) structures are listed in Table 1, together with the relative energies obtained by PM3/CI4 reported in the previous work.[11] The most stable structure in the triplet state is the trans enol form (*trans*-2HC′). The energy difference between the keto and the enol forms is 7.4 kcal mol^{-1}. The energy difference of the trans keto form (*trans*-2HC) between the ground state (S$_0$) and the lowest excited triplet state (T$_1$) is 52.2 kcal mol^{-1}, which agrees well with the experimental value of 55.0 kcal mol^{-1}.[9,11,22] Compared to the previous calculation, the energy difference between *trans*-2HC and *trans*-2HC′ in the excited triplet state is slightly larger.

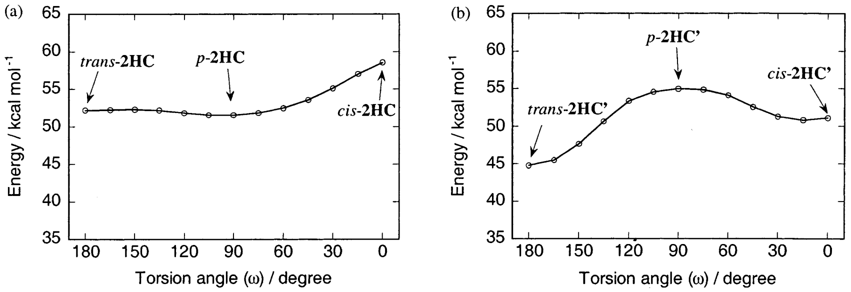

Figure 3. Potential energy curves of cis–trans isomerization of the keto (a) and the enol (b) forms of 2HC in T$_1$ calculated by using the UB3LYP/6-31G** method. In the plots, the energy of the S$_0$ state of *trans*-2HC is taken as 0 kcal mol^{-1}.

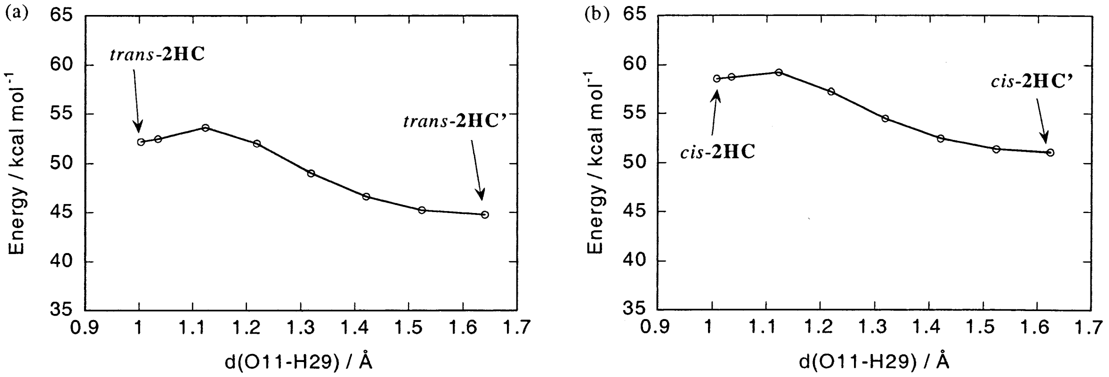

Figure 4. Potential energy curves of intramolecular hydrogen atom transfer of *trans*-2HC (a) and *cis*-2HC (b) in T$_1$ calculated by using the UB3LYP/6-31G** method. In the plots, the energy of the S$_0$ state of *trans*-2HC is taken as 0 kcal mol^{-1}.

The calculations also show that in the ground state, *trans*-2HC is more stable than *cis*-2HC by 5.7 kcal mol^{-1}. As expected, the perpendicular geometry (*p*-2HC) is the most unstable geometry in S$_0$ (data not listed).

The energy-minimum structure corresponding to ^{3}(*cis*-2HC)* was not obtained because the energy minimum could not be found. Thus, the potential energy surface between ^{3}(*cis*-2HC)* and ^{3}(*cis*-2HC′)* was calculated for a fixed ω of 0° for the olefin double bond.

3.2. Potential Energy Surface of Isomerization in T$_1$. Parts a and b of Figure 3 show the calculated potential energy curves of the isomerization of the keto and enol forms of 2HC in the T$_1$ state, respectively.

Figure 3a shows that the shape of the potential energy surface of the keto form in T$_1$ is similar to that of stilbene-like molecules, which exhibit mutual isomerization between cis and trans isomers.[1] There are two minima, around 180 (^{3}(*trans*-2HC)*) and 90° (^{3}(*p*-2HC)*). The ω of the calculated geometry in the transition state between these minima is 149.7°, and the energy of the transition state is 0.1 kcal mol^{-1} higher than that of ^{3}(*trans*-2HC)* (0.1 kcal mol^{-1} with zero-point correction).

The shape of the potential energy curve of the enol form in T$_1$ (Figure 3b) is significantly different from that of the keto form (Figure 3a). There are two minima, one minimum at the trans side, another minimum at the cis side, and a maximum at the perpendicular triplet (^{3}(*p*-2HC′)*). In the cis side, the minimum is at $\omega = 14.7°$, and is higher in energy than ^{3}(*trans*-2HC′)* by 6.0 kcal mol^{-1}. The perpendicular triplet is no longer a minimum but a transition state. The energy of ^{3}(*p*-2HC′)* is higher than that of ^{3}(*trans*-2HC′)* by 10.2 kcal mol^{-1} or higher than that of ^{3}(*cis*-2HC′)* by 4.2 kcal mol^{-1}. This potential curve is similar to that of 1-alkyl-2-(2-anthyryl)ethylenes (**1a**), which exhibit one-way isomerization in T$_1$.[1] Thus, the twist of the C=C double bond from ^{3}(*trans*-2HC′)* is improbable, whereas the twist from ^{3}(*cis*-2HC′)* is possible.

3.3. Potential Energy Surface of Hydrogen Atom Transfer in T$_1$. The calculation of the potential energy curve for hydrogen atom transfer between *trans*-2HC and *trans*-2HC′ was carried out assuming C_s symmetry, because both energy-minimum structures had C_s symmetry. In addition, the calculation of the potential energy curve for the hydrogen atom transfer from *cis*-2HC′ was carried out for a fixed ω at 0°, because the energy-minimum structure corresponding to *cis*-2HC could not be obtained.

Parts a and b of Figure 4 show the calculated potential energy curves of the intramolecular hydrogen atom transfer of the trans and the cis isomers of 2HC in the T$_1$ state, respectively. The shapes of the two potential energy curves are similar to each other.

On the basis of these calculations, the distance of O11–H29 at the transition state is 1.13 Å, and the energy is higher than that of ^{3}(*trans*-2HC)* by 1.4 kcal mol^{-1}. However, the energy of the transition state (TS) between ^{3}(*trans*-2HC)* and ^{3}(*trans*-2HC′)* is smaller than the energy of ^{3}(*trans*-2HC)* by 0.9 kcal mol^{-1} with zero-point energy correction (Table 1). This result indicates that the intramolecular hydrogen atom transfer reaction can occur from ^{3}(*trans*-2HC)* without an activation barrier.

The potential energy curve of the intramolecular hydrogen atom transfer of *cis*-2HC was calculated for a fixed ω of 0°. The obtained potential curve (Figure 4b) is similar to that of *trans*-2HC and has a small activation barrier (0.6 kcal mol^{-1}), for which the transition state has an O11–H29 distance of 1.12 Å.

The potential energy curves of the twist of C=C bond and the intramolecular hydrogen atom transfer are summarized in Figure 5.

3.4. Spin Densities. Figures 6 and 7 show the calculated spin densities along the reaction coordinates. The sum of the spin densities of C5–C10 is plotted as Ar1 (see Figure 2) and that of C12–C17 as Ar2. Spins on hydrogen atoms are excluded in

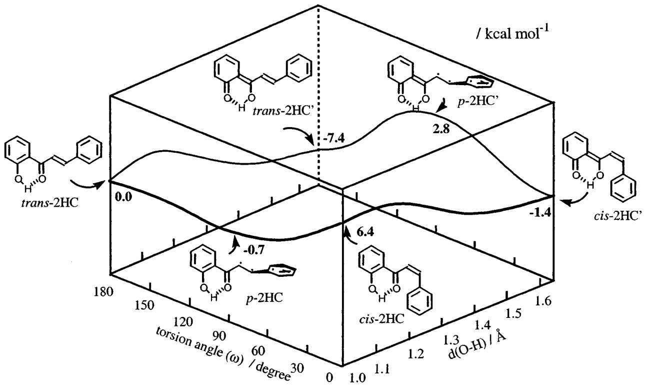

Figure 5. Potential energy curves of cis−trans isomerization and intramolecular hydrogen atom transfer of 2HC in T_1 calculated by using the UB3LYP/6-31G** method.

those plots. During the twisting of the C═C bond of the keto form (Figure 6a), the spin density gradually increases in the olefin carbons (C3 and C4), whereas the spin density of Ar2 decreases. The spin shifts from Ar2 to the isomerizing C═C bond. The spin densities of the other moieties do not change significantly. During the cis−trans isomerization in the enol form, on the other hand, the redistribution of the spin density of Ar1 is additionally involved (Figure 6b). It decreases during the twisting of the C═C bond. The spin densities of C3 and C4 increase near the perpendicular configuration (*p*-2HC′). The triplet state of *p*-2HC′ cannot be explained as a 3,4-biradical, because an unpaired electron is partly delocalized into Ar1, Ar2, and O11. In contrast, the triplet state of the keto form (*p*-2HC) is 3,4-biradical, where the two spins are localized on the C═C double bond.

The spin density analysis reveals that the intramolecular hydrogen atom transfer process is accompanied by a shift in electronic spin between the aromatic rings (Figure 7). The spin distribution of Ar1 drastically increases, whereas that of C3 and Ar2 decrease. The pronounced shift occurs between 1.1 and 1.2 Å of the O−H distance, corresponding to the energy maximum in the reaction coordinate. This drastic rearrangement near the transition state indicates that a shift in molecular orbitals is involved in the excited state during intramolecular hydrogen atom transfer.

4. Discussion

4.1. Deactivation Process from *trans*-2HC in T_1.

Previous studies show that from the triplet state of *trans*-2HC (^{3}(*trans*-2HC)*), the cis isomer of 2HC is not produced because of the formation of the enol of the *trans*-2HC (^{3}(*trans*-2HC′)*) via the intramolecular hydrogen atom transfer in the excited triplet state.[9,11,22] To clarify the fate of ^{3}(*trans*-2HC)*, on the basis of theoretical and experimental results, we discuss here the two possible reaction pathways, namely, cis−trans isomerization and hydrogen atom transfer.

Both pathways have activation barriers (see Figures 3a and 4a), whose values are 0.1 and 1.4 kcal mol^{-1} for the twist of the C═C double bond and the hydrogen atom transfer, respectively (Table 1). However, the activation barrier of the hydrogen atom transfer is buried with zero-point energy correction. Thus, the intramolecular hydrogen atom transfer process seems to be faster than the twist of the C═C bond. On the other hand, the activation barrier of the twist of the C═C bond (0.1 kcal mol^{-1}) can be easily overcome at room temperature. For example, stilbene exhibits a rapid equilibrium between trans and twisted conformers in T_1, because there is only a small barrier of 0.2 kcal mol^{-1} from trans to perpendicular conformers of the stilbene triplet.[26] Thus, ^{3}(*trans*-2HC)* can possibly exhibit the twist of the C═C double bond as well as the hydrogen atom transfer. An establishment of the equilibrium between ^{3}(*trans*-2HC)* and ^{3}(*p*-2HC)* seems to contradict the experimental observation that no cis isomer is produced by the triplet sensitization or direct excitation.[9,11,22] However, the one-way isomerization mechanism can be elucidated by taking into account the rates of the intersystem crossing from T_1 to S_0. Reactions on the T_1 surface of 2HC are controlled thermodynamically rather than kinetically because the deactivation processes from T_1 are much slower than the adiabatic reactions along the T_1 surface. In general, the decay rate constants of a planar triplet and a perpendicular triplet are ~10^4 and ~10^7 s^{-1}, respectively.[1] According to the lifetime of ^{3}(*trans*-2HC′)*, the decay rate constant of ^{3}(*trans*-2HC)* is ~10^6 s^{-1}.[9,11,22] On the other hand, the twist of the C═C double bond is very fast (less than 1 ns). Although the kinetics of the hydrogen atom transfer in T_1 are still unknown, the absence of an activation barrier (Table 1) indicates that the transfer process is much faster or comparable to the cis−trans isomerization. In conclusion, even if the twist of the C═C double bond is possible, the deactivation from the twisted triplet (^{3}(*p*-2HC)*) is less likely to occur, because the equilibrium among the species, including the enol form (^{3}(*trans*-2HC′)*), is established rapidly. This equilibrium is far to the enol side because ^{3}(*trans*-2HC′)* is more stable than ^{3}(*p*-2HC)* or ^{3}(*trans*-2HC)* by about 7 kcal mol^{-1}. The observation of ^{3}(*trans*-2HC′)* by the transient absorption also supports this argument.[9,11]

4.2. One-Way Isomerization from *cis*-2HC in T_1.

There are two possible reaction pathways from ^{3}(*cis*-2HC)*, namely, the twist of the C═C double bond and the hydrogen atom transfer. The former process has no potential barrier (Figure 3a) to yield ^{3}(*p*-2HC)*, whereas the latter has a small barrier (0.6 kcal mol^{-1}, Figure 4b). The products of each reaction are more stable than ^{3}(*cis*-2HC)* by 7.1 kcal mol^{-1} (^{3}(*p*-2HC)*) and 7.8 kcal mol^{-1} (^{3}(*cis*-2HC′)*), respectively. It is difficult to judge which pathway is dominant because the difference between the calculated potential curves (Figures 3a and 4b) is only the presence or absence of the small activation barrier. Furthermore, as described in the Introduction, experimental evidence showing the reaction pathways is lacking. The only observed transient is ^{3}(*trans*-2HC′)*, which was previously assigned to the final product of adiabatic reaction along the T_1 surface via ^{3}(*cis*-2HC′)*.[9,11,22] Along either pathway, however, ^{3}(*trans*-2HC′)* is produced as a consequence, which is consistent with the experimental results.[11,22] If the twist of the C═C double bond occurs first, then ^{3}(*p*-2HC)* is formed. As discussed in the preceding section, ^{3}(*p*-2HC)* forms ^{3}(*trans*-2HC)*, and finally forms ^{3}(*trans*-2HC′)*. On the other hand, ^{3}(*cis*-2HC′)* is formed if the hydrogen atom transfer dominates. The calculated potential curve of *cis*-to-trans isomerization from ^{3}(*cis*-2HC′)* (Figure 3b) is similar to that of 1-alkyl-2-(2-anthryl)ethylene (**1a**).[1] Thus, the isomerization can occur from ^{3}(*cis*-2HC′)* to ^{3}(*trans*-2HC′)* adiabatically along this surface. The cis triplet of **1a** has been detected by using the transient absorption method because the activation energy for the *cis*-to-trans isomerization is 6 kcal mol^{-1}.[1] However, ^{3}(*cis*-2HC′)* was not detected by the transient absorption,[9,11,22] probably due to its lower activation energy (4.2 kcal mol^{-1}) than that of **1a**.

4.3. Change in Charge Distribution near Hydrogen-bonded Proton. Is There Zwitterionic Character in the Intramolecular Hydrogen Atom Transfer?

As described in the Introduction, numerous compounds that have an intramo-

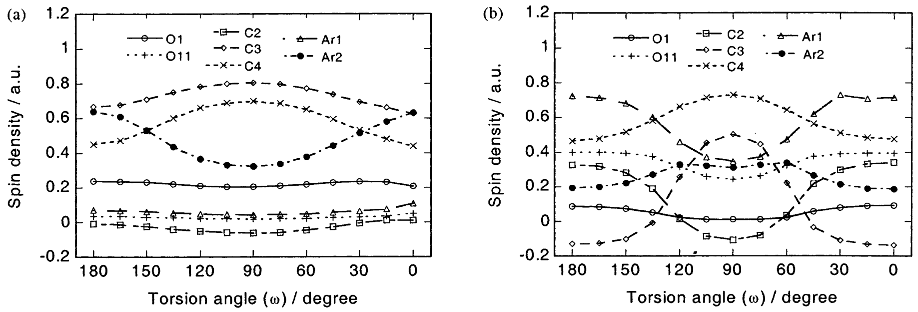

Figure 6. Spin densities during cis−trans isomerization of the keto (a) and the enol (b) forms of 2HC in T_1 calculated by using the UB3LYP/6-31G** method.

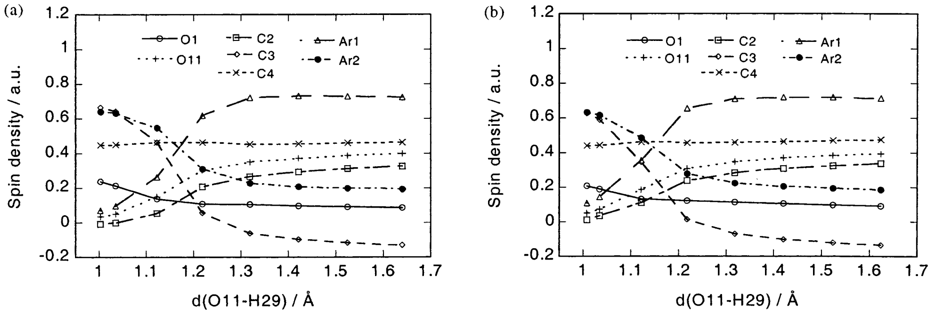

Figure 7. Spin densities during intramolecular hydrogen atom transfer of *trans*-2HC (a) and *cis*-2HC (b) in T_1 calculated by using the UB3LYP/6-31G** method.

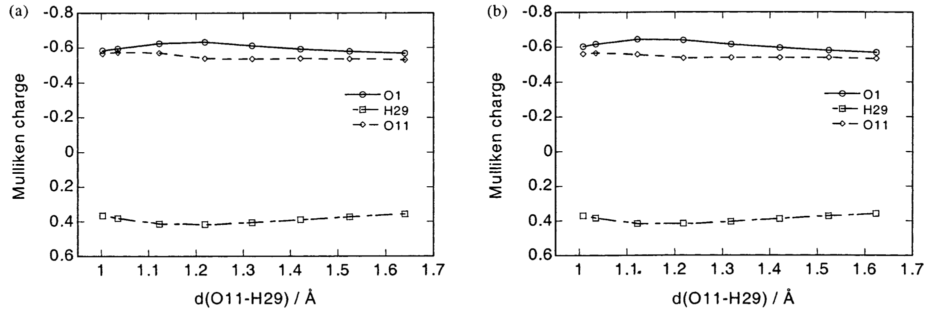

Figure 8. Mulliken charges during intramolecular hydrogen atom transfer of *trans*-2HC (a) and *cis*-2HC (b) in T_1 calculated by using the UB3LYP/6-31G** method.

lecular hydrogen bond exhibit emissions with large Stokes' shifts. At first, this phenomenon was called "intramolecular proton transfer" and the emitting species were drawn as zwitterionic structures.[27−29] However, recent extensive experimental and theoretical studies of methyl salicylate and related 2-hydroxybenzoyl compounds indicated that the final emitting species did not have zwitterionic character.[3,30−33] These studies were limited to the excited singlet state, and the charge distribution around the hydrogen bond in the excited triplet state has not been reported. To clarify if the charge density changes as the hydrogen atom moves from the phenolic oxygen to the carbonyl oxygen, we analyzed the Mulliken charge density for the hydrogen atom transfer reactions of both *trans*- and *cis*-2HC.

Parts a and b of Figure 8 show the Mulliken charge of the O−H:O moiety during the intramolecular hydrogen atom transfer reaction of *trans*- and *cis*-2HC, respectively. The plots are similar to each other. For example, the charge density of the carbonyl oxygen atom (O1) slightly increases to negative at the transition state (O−H distance of 1.1−1.2 Å), whereas that of the phenolic hydrogen atom (H29) decreases in the same region of the O−H distance. The difference in charge density between the keto form and the transition state is 0.05 for both O1 and H29 in *trans*-2HC. The smallest difference in charge density ($<$0.01) is seen in the phenolic oxygen atom (O11). No significant difference is seen in the charge distribution between the keto and the enol form in either *trans*-2HC or *cis*-2HC. These results suggest that the enol form has no zwitterionic character.

5. Conclusions

Potential energy curves of the cis−trans isomerization and the intramolecular hydrogen atom transfer of 2′-hydroxychalcone in the T_1 state were calculated by the UB3LYP/6-31G** method. These calculated curves suggest that an equilibrium among the triplet species exists due to no or small potential barriers among them and to their relatively small deactivation rates to the ground state. Spin density analysis suggests that spins localize around the olefin carbons during the twisting of the C═C double bond, whereas they delocalize during the hydrogen atom transfer reactions.

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