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Enthalpy changes and reaction volumes of photoisomerization reactions in solution: azobenzene and *p*-coumaric acid

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Abstract

The photoisomerizations of azobenzene in ethanol and *p*-coumaric acid in water were studied by the transient grating and photoacoustic methods. The absorption spectrum of *cis*-*p*-coumaric acid and the quantum yield of the isomerization reaction in water were measured by a photostationary absorption method at two wavelengths (Φ_{iso}=0.46±0.05). The diffusion coefficient of *p*-coumaric acid in water at room temperature is 4.4×10^{-10} m^2 s^{-1}. This relatively small value suggests a hydrogen bonding between *p*-coumaric acid and water. Concomitant with the photoisomerization, the enthalpy changes (ΔH) and reaction volumes (ΔV) of azobenzene and *p*-coumaric acid were measured. The obtained values (ΔH=43±8 kJ/mol and ΔV=−3±5 cm^3/mol for azobenzene, ΔH=49±7 kJ/mol and ΔV=−0.7±0.5 cm^3/mol for *p*-coumaric acid) are discussed in terms of structural change in *trans* → *cis* isomerization. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Photoisomerization; Azobenzene; *p*-Coumaric acid; Volume change; Enthalpy change

1. Introduction

The *trans*–*cis* photoisomerization is one of the fundamental chemical reactions, and the reaction has been a target of extensive studies [1]. This photoisomerization reaction has been attracting many researchers not only as a typical chemical reaction but also as a triggering reaction of some photosensitive biological molecules. For instance, the photoreactions of rhodopsins are initiated by the photo-induced isomerization of retinals. In the photoactive yellow protein (PYP), which is known to be a photoreceptor protein of *Ectothiorhodospira halophila*, the reaction cycle starts with the photo-induced *trans* → *cis* isomerization of its chromophore: *p*-coumaric acid (3-(4-hydroxyphenyl)-2-propenoic acid) [2,3]. For studying these biological reactions, the time-resolved measurements of the volume change (ΔV) and the enthalpy change (ΔH) of the reaction are useful and powerful and, indeed, such studies have been conducted already [4–6]. However, to separate the origins of ΔV and ΔH into the chromophore part and the other protein part, ΔV and ΔH of the isomerization of the chromophore in solution are required.

Experimentally, however, these quantities are very difficult to be measured. It is impossible to measure these quantities for irreversible reactions by the pressure or temperature dependencies of the equilibrium constants. The photoacoustic (PA) spectroscopy could enable us to measure them, but it is not trivial to separate the thermal contribution from the volume contribution in the signal. Each contribution may be separated by measuring the PA intensity by varying the thermal expansion coefficient of the matrix. For aqueous solution, this can be achieved by varying the temperature. For organic solvents, the binary-solvents method was sometimes used. However, changing the solvent or temperature will change the reaction mechanism or reaction rate considerably in some cases.

For independent measurements of ΔV and ΔH, we have proposed a hybrid method of the transient grating (TG) and PA signal detections [7–10]. By this method, contributions of ΔV and ΔH can be separated in a time-resolved manner without any temperature and solvent variations. We have already applied this technique to the photodissociation of diphenylcyclopropenone (DPCP) [7,8] and diazo compounds [9]. In the present work, we apply this powerful technique to the *trans*–*cis* photoisomerization of two representative molecules: azobenzene and *p*-coumaric acid (Scheme 1). Azobenzene is a prototype of compounds that exhibit *trans*–*cis* photoisomerization. For instance, quantum

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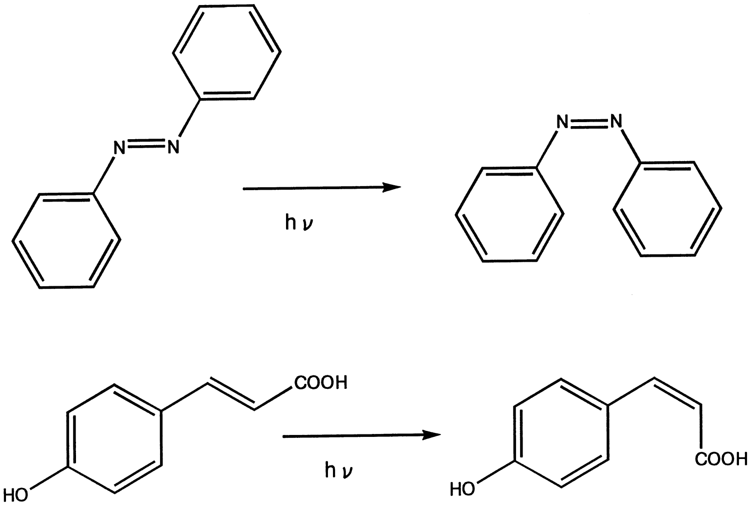

Scheme 1.

yields for the *trans* → *cis* and *cis* → *trans* processes were measured in various organic solvents, and the dependence of these values on excitation wavelength were reported in detail [11–14]. Reaction mechanism has been discussed on the basis of these data. *p*-Coumaric acid is a chromophore of PYP and the isomerization initiates the cyclic photo-induced transformation. Although this isomerization became one of the important photoreactions, the fundamental properties of the reaction have not been studied yet. We first determine the absorption spectrum of *cis*-*p*-coumaric acid and the quantum yield of the isomerization. With this value and the TG–PA measurements, ΔV and ΔH of azobenzene in ethanol and *p*-coumaric acid in water concomitant with the *trans–cis* photoisomerization are determined. The results are discussed in terms of the *trans–cis* molecular structural change.

2. Experiment

The TG setup has been described previously [15,16]. Briefly the second harmonic (532 nm) of a Nd:YAG laser (Spectra-Physics-CGR-170-10) for azobenzene and the third harmonic (355 nm) for *p*-coumaric acid were used for the photoexcitation. The laser light was split by a beam splitter and crossed inside a quartz sample cell (1 cm path length). The created interference pattern (transient grating) was probed by a He:Ne laser (633 nm) or a diode laser (840 nm) as a Bragg diffracted signal (TG signal). The TG signal was detected by a photomultiplier (Hamamatsu R928), averaged by a digital oscilloscope, and transferred to a computer.

A PA signal was detected by a piezoelectric transducer as described previously [17]. The signal was directly detected by the digital oscilloscope and averaged about 100–300 times.

The repetition rate of the laser was about 3 Hz and the sample was gently stirred during measurement to prevent accumulation of *cis* isomers by photoirradiation. Concentrations of the samples and references (bromocresol purple (BCP) or malachite green (MG)) were adjusted so that the absorbance in the cell was the same at the excitation wavelength (absorbance was about 0.5).

The quantum yield of the *trans* → *cis* isomerization of *p*-coumaric acid was measured from the absorption change after photoirradiation with a certain number of photons. As a reference, the photodissociation quantum yield of DPCP in hexane was used. The irradiation light was the third harmonic of the Nd:YAG laser and the absorption change was measured with a Shimadzu UV-3000 spectrophotometer. The spectrum of the *cis* isomer of *p*-coumaric acid was determined from the spectrum of photostationary states at two excitation wavelengths [18]. The photostationary absorption spectra were measured by irradiation of monochromatic light from a xenon lamp passed through a monochromator (fwhm of the light is about 10 nm). The spectrum was recorded by a spectro multi channel photo-detector (MCPD-1000 (Otsuka Electronics)). The temperature of all the measurements was 22°C.

Azobenzene and *p*-coumaric acid were purchased from Nakalai Tesque, Inc. Azobenzene was recrystallized from ethanol twice before use. The *p*-coumaric acid solution was prepared in the dark.

3. Analysis

The procedure for determination of ΔV and ΔH from the TG and PA signals was reported previously [7–10]. If the absorptive contribution is negligible, the TG signal intensity is proportional to the square of the peak-null difference of the refractive index in the grating pattern. There are two main contributions to the refractive index change; the thermal effect and a change of chemical species by the reaction. We represent the former as $\delta n_{\mathrm{th}}(t)$ (thermal grating), the latter as $\delta n_{\mathrm{spe}}(t)$ (species grating). Therefore, the square root of the TG signal ($I_{\mathrm{TG}}^{1/2}$) may be given by

$$\begin{aligned} I_{\mathrm{TG}}^{1/2}(t) &= A|\delta n_{\mathrm{th}}(t) + \delta n_{\mathrm{spe}}(t)|, \\ \delta n_{\mathrm{th}}(t) &= \delta n_{\mathrm{th}} \exp(-q^2 D_{\mathrm{th}} t), \\ \delta n_{\mathrm{spe}}(t) &= \sum_i \delta n_{\mathrm{spe}}^i \exp(-q^2 D_i t) \end{aligned} \tag{1}$$

where A is a constant representing the sensitivity of the system, D_{th} the thermal diffusivity, D_i the diffusion coefficient of species i and q is the grating wavenumber. δn_{th} and $\delta n_{\mathrm{spe}}^i$ are magnitudes of the refractive index changes caused by the released heat from the excited state and creation (or extinction) of species i, respectively. There are two contributions in $\delta n_{\mathrm{spe}}^i$; the refractive index change due to the change of the absorption spectrum (population grating) and due to the molecular volume change (volume grating).

Since D_{th} is usually one or two orders of magnitude larger than D_i in solution, the thermal component can be easily separated from the species grating signal. The magnitude of the thermal grating is given by

$$\delta n_{\mathrm{th}} = \frac{\mathrm{d}n}{\mathrm{d}T} \frac{h\nu\phi W}{\rho C_{\mathrm{p}}} \Delta N, \quad \phi \equiv 1 - \frac{\Phi \Delta H}{h\nu} \tag{2}$$

where W is the molecular weight, C_{p} the heat capacity, ρ the density, $h\nu$ the photon energy of excitation light, ΔN the number of reacting molecules in the unit volume and Φ is the reaction quantum yield. We can determine $\Phi\Delta H$ by comparison with the signal intensity of a reference sample. The ratio of the refractive index change for the sample (δn_{th}(sample)) to that for the reference (δn_{th}(ref)) is given by

$$\frac{\delta n_{\mathrm{th}}(\mathrm{sample})}{\delta n_{\mathrm{th}}(\mathrm{ref})} = 1 - \frac{\Phi \Delta H}{h\nu} \tag{3}$$

On the other hand, the intensity of the PA signal (I_{PA}) is given by

$$I_{\mathrm{PA}} = A' \Delta N \left| \frac{h\nu\phi W}{\rho C_{\mathrm{p}}} \alpha_{\mathrm{th}} + \Phi \Delta V \right| \tag{4}$$

where A' is a proportional constant which includes the sensitivity of the apparatus and α_{th} is the thermal expansion coefficient. If we know the value of ϕ from TG signal analysis, we can determine $\Phi\Delta V$ from the PA intensity of the sample (I_{PA}(sample)) and of the reference (I_{PA}(ref)) by using the following relation.

$$\frac{I_{\mathrm{PA}}(\mathrm{sample})}{I_{\mathrm{PA}}(\mathrm{ref})} = \phi + \Phi \Delta V \left(\frac{\rho C_{\mathrm{p}}}{h\nu W \alpha_{\mathrm{th}}} \right) \tag{5}$$

4. Results and discussion

4.1. Azobenzene

Azobenzene undergoes the photochemical *trans–cis* isomerization upon the $n\pi^*$ or the $\pi\pi^*$ excitation [11–14]. For the $\pi\pi^*$ excitation, quantum yield of the *trans* → *cis* isomerization was reported to be 0.28 [13].

Fig. 1(a and b) depict the time profile of the TG signal of azobenzene in ethanol. After the excitation, the signal rises immediately and decays biexponentially. The fast decaying component is the thermal grating signal caused by the released heat from the excited state. The decay rate constant is given by $2D_{\mathrm{th}}q^2$. The slower component is due to the species grating caused by the creation of the *cis* isomer and the extinction of the *trans* isomer. If the diffusion coefficient of the *cis* isomer (D_{cis}) and the *trans* isomer (D_{trans}) are different significantly, the decay of the species grating signal should be given by a biexponential function. However, the difference between D_{cis} and D_{trans} is so small that the two components cannot be separated under this condition. As the decay rate of the species grating signal is almost two orders of magnitude slower than that of the thermal grating signal, the intensity can be regarded as a constant in the early time range of Fig. 1(a), and the square root of the TG signal can be fitted by the sum of one exponential function and a constant. The pre-exponential factor gives the magnitude of the thermal grating δn_{th}, from which we can calculate $\Phi\Delta H$ using Eq. (3) by comparing with δn_{th} of the reference sample. Fig. 2 shows the plots of δn_{th} of azobenzene and reference versus excitation laser energy. From the ratio of two slopes, we obtained $\Phi\Delta H$=12±2 kJ/mol which leads to ΔH=43±8 kJ/mol with Φ=0.28 (Table 1).

The energy difference between the *trans* and *cis* isomers was calculated to be 61 kJ/mol by an ab initio calculation [19]. The energy difference was also experimentally determined from the heat of combustion in the crystal state to be ΔH=41 kJ/mol [20]. As far as we know, this is the first measurement of ΔH of azobenzene in the solution phase. It is rather surprising to find that our determined ΔH in ethanol solution is very close to that reported in the crystal phase, because it is expected that the *cis* isomer is solvated more than the *trans* isomer and ΔH is expected to be smaller than that in the crystal phase. The small difference in ΔH between the solution and crystal phases suggests that the solvation is not so much altered by the photoisomerization.

The PA signal of azobenzene is recorded as shown in Fig. 3. From a comparison of the intensity I_{A} with that of the reference sample, $\Phi\Delta V$ is determined as −0.8±1.3 cm^3/mol. Again, using Φ=0.28, we obtain ΔV=−3±5 cm^3/mol. This result shows that a slight volume contraction occurs concomitant with the *trans* → *cis* isomerization.

Table 1
Enthalpy change (ΔH) and volume change (ΔV) by the photoisomerization of azobenzene and *p*-coumaric acid

Solute	ΔH (kJ/mol)	ΔV (cm^3/mol)
Azobenzene	43±8	−3±5
p-Coumaric acid	49±7	−0.7±0.5

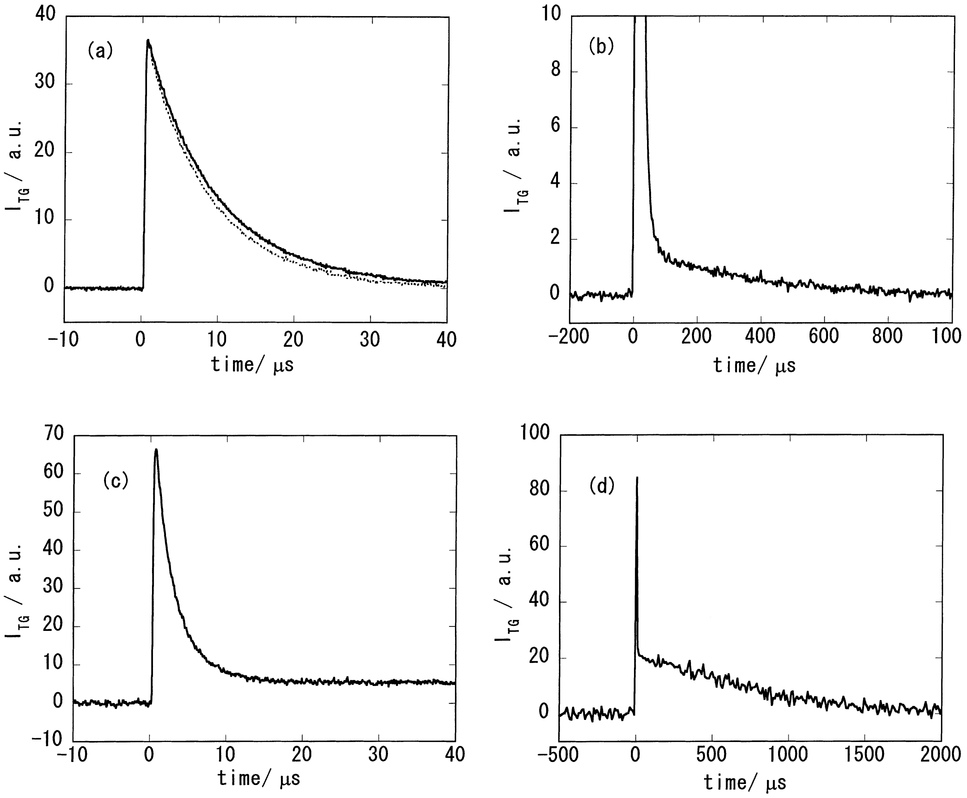

Fig. 1. Time profiles of the TG signals after photoexcitation of azobenzene in ethanol (a and b) and *p*-coumaric acid in water (c and d) in different time scales. The solid and dotted lines in (a) represent azobenzene and the reference sample (malachite green), respectively.

4.2. p-Coumaric acid

p-Coumaric acid is excited in the $\pi\pi^*$ band following the *trans* → *cis* isomerization by irradiation of ultraviolet light. We first determine the absorption spectrum and the molar extinction coefficient of the *cis* isomer, then, measure ΔH and ΔV of this reaction.

When the *p*-coumaric acid solution is photoilluminated, the absorption spectrum changes, which is caused by the *trans* → *cis* phototransformation. When the photoillumination is ceased, the absorption spectrum does not change within 30 min. Therefore, we conclude that the created *cis* form is sufficiently stable at room temperature in an order of hours. The steady state absorption spectra at two different excitation wavelengths (300 and 330 nm) are shown in Fig. 4. From these absorption spectra, we can calculate the extent of this *trans* → *cis* conversion in the steady state by a method described in [18]. From this extent of conversion, the absorption spectrum of the *cis* form can be calculated

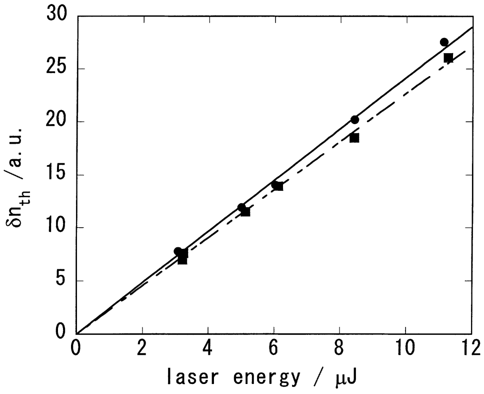

Fig. 2. The plots of δn_{th} (the magnitude of the thermal grating) of azobenzene (■) and reference (●) vs. excitation laser energy. The least square fitting of the data with a linear function of the power are shown by the lines. ((– – –) azobenzene; (—) reference).

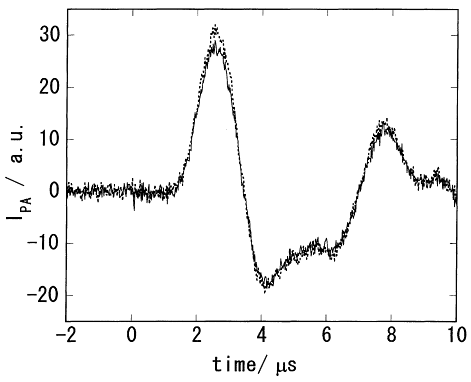

Fig. 3. The PA signal after the photoexcitation of azobenzene (solid line) and MG (dotted line).

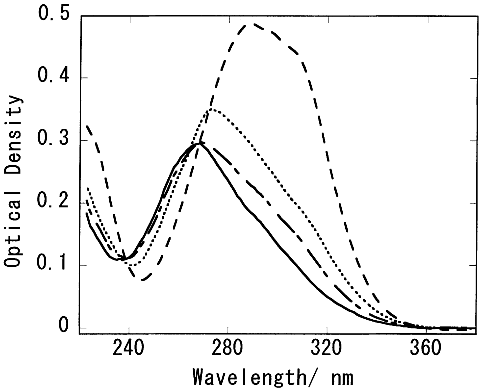

Fig. 4. Absorption spectrum of the *trans* form of *p*-coumaric acid (- - -), the steady state absorption spectra at two different excitation wavelengths ((· · ·) 300 nm and (– – –) 330 nm) and calculated absorption spectrum of the *cis* form (—).

and depicted in Fig. 4. The peak value of ε for the *cis* form (at 265 nm) is about 1.1×10^4 dm^3 mol^{-1} cm^{-1}.

The quantum yield of this *trans* → *cis* photoisomerization (Φ_{cou}) is measured from the absorbance change at 340 nm ($\Delta(\mathrm{OD})_{\mathrm{cou},340}$) by the laser irradiation. The absorbed photon is calibrated by using the absorbance change of DPCP at 320 nm ($\Delta(\mathrm{OD})_{\mathrm{dpcp},320}$) under the same excitation condition. The photodissociation quantum yield of DPCP in hexane (Φ_{dpcp}) was reported to be 1.0 [21]. Fig. 5 depicts the absorption change of *p*-coumaric acid and the reference (DPCP in hexane) monitored at 320 or 340 nm after photoirradiation with a certain number of photons. (As the absorbance of the solution decreases as the number of laser shots increases, the absorption change is not a linear function with the laser shots. However, in the region where the decrease of the absorbance is much smaller than the absorbance of the original solution, it is approximately linear with the laser shots.) The difference of ε between the *trans* and *cis* forms at 340 nm ($\Delta\varepsilon_{\mathrm{cou},340}$) is 2.8×10^3 dm^3 mol^{-1} cm^{-1} and ε of DPCP in hexane is 7.9×10^3 dm^3 mol^{-1}cm^{-1} at 320 nm ($\varepsilon_{\mathrm{dpcp},320}$). Using these values, we obtain $\Phi_{\mathrm{cou}}=0.46$ from the ratio of two slopes by the next equation.

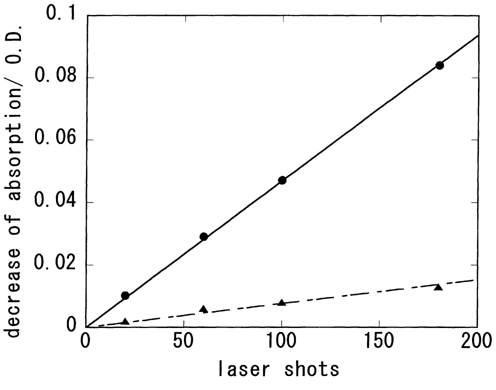

Fig. 5. The absorption change of *p*-coumaric acid in water (▲) and DPCP in hexane (●) monitored at 320 or 340 nm after a certain number of laser shots. The least square fittings with linear functions of the laser shot are shown by the lines. ((—) DPCP at 320 nm; (– – –) *p*-coumaric acid at 340 nm).

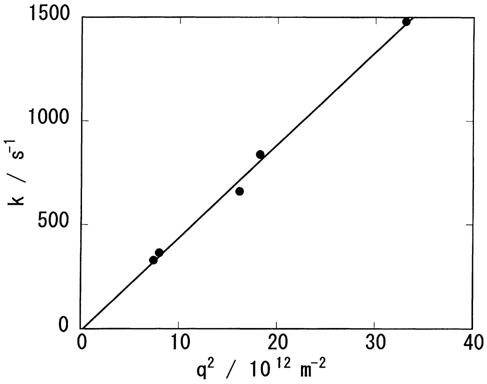

Fig. 6. The q^2 plot of the decay rate constant (k) of the species grating signal of *p*-coumaric acid in water and the least-square fit.

$$\frac{\Delta(\mathrm{OD})_{\mathrm{cou},340}}{\Delta(\mathrm{OD})_{\mathrm{dpcp},320}}=\frac{\Phi_{\mathrm{cou}}\Delta\varepsilon_{\mathrm{cou},340}}{\Phi_{\mathrm{dpcp}}\varepsilon_{\mathrm{dpcp},320}} \tag{6}$$

Fig. 1(c and d) show the TG signal after excitation of *p*-coumaric acid in water. Similar to azobenzene, the decay of the thermal grating followed by the species grating was observed. The decay of the species grating can be fitted by a single exponential function. The decay rates k are plotted against q^2 in Fig. 6. The plots intercept with the ordinate at nearly $k=0$. This is consistent with the slow rate of the reverse reaction. The diffusion coefficient is determined from the slope as 4.4×10^{-10} m^2 s^{-1}. (D_{trans} and D_{cis} are indistinguishable under this condition.) This D is surprisingly small compared with those of organic molecules with similar sizes in water. For example, the diffusion coefficient of naphthalene (the van der Waals volume calculated by the method of the next section (V_{vdw}) is 77.5 cm^3/mol, and this volume is similar to V_{vdw} of *p*-coumaric acid (89.2 cm^3/mol)) in water is about 1×10^{-9} m^2 s^{-1} [22,23]. This small D is probably due to the hydrogen bonding between *p*-coumaric acid and water. Tominaga et al. [22,23] found that the intermolecular hydrogen bonding decreases the diffusion coefficient and also reported that multiple hydrogen bonding further decreases the diffusion. Considering the ratio of D of *p*-coumaric acid to D of naphthalene, we speculate that both of the carboxyl group and the hydroxyl group of *p*-coumaric acid make the hydrogen bonds to water. (The pK_a of –OH and –COOH groups of *p*-coumaric acid are 9.0 and 4.4, respectively [24,25]. Under these experimental conditions, the proton of –OH is not dissociated at all but that of –COOH is dissociated ~20%.) This hydrogen bonding of *p*-coumaric acid may play an important role in the photocyclic reaction of PYP [2,3].

Following the same steps as the azobenzene analysis, $\Phi\Delta H$ and $\Phi\Delta V$ are determined. Using $\Phi=0.46$, we obtain $\Delta H=49\pm7$ kJ/mol, $\Delta V=-0.7\pm0.5$ cm^3/mol. Due to small thermal expansion coefficient of water, ΔV can be measured more precisely than that of azobenzene in ethanol. Our result shows ΔH of *p*-coumaric acid is slightly larger than that of azobenzene.

4.3. Volume change by the photoisomerization

As it is often pointed out, a reaction volume in solution has two components, ΔV_i the intrinsic volume change related to the size of molecules or ions, and ΔV_s the solvational volume change associated with changes in polarity, electrostriction, and dipole interactions [10,26]. Furthermore, ΔV_i has following contributions:

1. The van der Waals volume change of the reactant molecule itself.
2. Formation or destruction of empty space that is too small to be occupied by a molecule of solvent.

To compare with our experimental data, we calculated the van der Waals volume (V_vdw) and solvent excluding volume (V_ex) of both isomers. We determined these volumes with the GEPOL93 program [27]. We used the standard van der Waals radii for C, H, O, and N atoms and probe radii of 1.4 Å (water) and 2.3 Å (ethanol), respectively, for calculation of the solvent excluding volume. The molecular structure was optimized using the semiempirical program package MOPAC 6.0 and the MNDO Hamiltonian.

V_vdw of *cis*- and *trans*-azobenzene from the molecular structures determined by MOPAC are listed in Table 2 and it is found that the difference in V_vdw is very small. However, when we calculated V_vdw using the structure determined from the X-ray diffraction in crystals [28,29], V_vdw of the *cis* isomer is found to be smaller than V_vdw of the *trans* form. To consider ΔV_i including the contribution of 2, we also calculated solvent-excluding volume (V_ex). Using the geometry from the MOPAC calculation, ΔV_i is about 4 cm^3/mol (expansion). As the empty space which cannot be occupied by solvent molecules is expected to be larger for the *cis* isomer, the positive ΔV_i is reasonable. When we use the structure from the X-ray experiment, ΔV_i is calculated to be -2.5 cm^3/mol (contraction). Again the contraction volume becomes less than ΔV_vdw.

ΔV_s is caused by the change of the intermolecular interactions between the solvent and solute such as the electrostatic interaction or hydrogen bonding. Generally, the reaction volume decreases when these interactions become larger by the reaction. In case of azobenzene, the *cis* isomer has a dipole moment of ~3 D from the MOPAC calculation, while the *trans* isomer has no dipole moment. Therefore, the electrostatic interactions with polar solvents are larger in the *cis* isomer than in the *trans* isomer, and we expect the volume contraction of the molecule.In terms of a simple electrostatic theory, the volume change by the electrostriction effect due to a dipolar molecule (ΔV_el) is given by the following expression [30–32]:

$$\Delta V_\mathrm{el} = -\left(\frac{\mu^2}{r^3}\right)\frac{(\varepsilon+2)(\varepsilon-1)}{(2\varepsilon+1)^2}\kappa_\mathrm{T} \tag{7}$$

where μ is the dipole moment of the solute, r is its effective cavity radius, ε is the solvent dielectric constant, and κ_T is the isothermal compressibility of the solvent. For example, using an estimate of r=3.5 Å for the cavity radius (obtained from V_vdw) and μ=3 D for the dipole moment in Eq. (7), we obtain ΔV_el=-3.5 cm^3/mol for azobenzene at room temperature. We have to note that ΔV_el from Eq. (7) is very sensitive to r. Not only the electrostriction, making hydrogen bonding also causes the volume contraction. Terazima found a large volume contraction by the keto → enol transformation of 2-methylbenzophenone in ethanol and ascribed it to the hydrogen bonding [10]. Rodríguez et al. [33] measured ΔV of azobenzene derivatives (azobenzenecarboxylic acid) concomitant with *trans*–*cis* photoisomerization in aqueous and organic solvents by PA methods. They attributed the observed contractions (about 3 cm^3/mol) of azobenzenecarboxylates in potassium phosphate buffer to the difference in the chromophore–water hydrogen bonding strength between the photoisomer and the parent compound. The small volume change of azobenzene indicates that the strengths of the hydrogen bonding to *trans*- and *cis*-azobenzene are not so much different. Our experimental data ΔV=0 suggests that the negative contribution of ΔV_s is compensated by the positive contribution of ΔV_i.

The measured ΔV for *p*-coumaric acid in water is negative and small. The van der Waals volume and solvent-excluding volume are calculated from MOPAC and GEPOL93 [27] (Table 2). ΔV_i is positive, but the contribution to total ΔV is smaller than that of azobenzene. Furthermore, the change of the dipole moment is small (Table 3), so that ΔV_s has a little contribution to total ΔV. The experimental results (ΔV is nearly equal to 0) can be explained by the small ΔV_i and ΔV_s.

In summary, the quantum yield of the *trans* → *cis* isomerization of *p*-coumaric acid and the absorption spectrum of the *cis* isomer were measured. Using this quantum yield, we applied the method for molecular volume change (ΔV)

Table 2
Calculated van der Waals volumes (V_vdw, cm^3/mol) and solvent excluding volumes (V_ex, cm^3/mol) of the *trans* and *cis* isomers

Solute	Volume	*Trans*	*Cis*	ΔV
Azobenzene (MOPAC)	V_vdw	106.2	106.3	+0.1
	V_ex	110.7	115.1	+4.4
Azobenzene (crystal)	V_vdw	104.1	99.8	−4.3
	V_ex	108.6	106.2	−2.5
p-Coumaric acid(MOPAC)	V_vdw	89.2	89.5	+0.3
	V_ex	91.6	94.1	+2.5

Table 3
Calculated dipole moment (D) of each of the *trans* and *cis* isomers

Solute	*Trans*	*Cis*
Azobenzene	0.01	2.99
p-Coumaric acid	2.61	1.30

and enthalpy change (ΔH) measurement by the TG and PA hybrid technique to the *trans* → *cis* photoisomerization of azobenzene in ethanol and *p*-coumaric acid in water. For both molecules ΔV is small and negative. This small volume change can be explained by the small change of the van der Waals volume, solvent-excluding volume and the dipole moment by the reaction. Also it indicates that the hydrogen bonding with solvent molecule is not so much different between the *trans* and *cis* isomers. Therefore, any volume change detected for a biological system using the photoisomerization of *p*-coumaric acid (such as PYP) will be attributed to the molecular rearrangement of the protein part. ΔH of the *trans* → *cis* photoisomerization of azobenzene and *p*-coumaric acid are found to be similar. Again these values are important for the interpretation of ΔH in a biological system and such a study will be published elsewhere.

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