

ISOMERIZATION OF DODCI IN THE S_0 GROUND STATE

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The long-wavelength absorption spectrum of DODCI indicates the presence of a thermally populated isomer in the electronic ground state. The energy level of this isomer above the normal form is determined by temperature-dependent absorption measurements. The S_0 - S_1 absorption cross section spectrum of the isomer is determined.

1. Introduction

The dye DODCI (3,3'-diethyloxydicarbocyanine iodide) is widely used as a saturable absorber in passively mode-locked dye lasers [1-3]. It may also be applied as a laser dye [4-6]. Conventional flash tube photolysis [7], pulsed laser flash photolysis [7-22], and cw laser excitation spectroscopy [23,24] generate a photoisomer which absorbs and emits at longer wavelength than the normal form. In ref. [14] some evidence is given from rotational diffusion measurements that the normal (N) isomer has a 1,5 cis-cis form or similar coiled up conformation and that the photo (P) isomer has an all-trans or some other elongated form.

In this paper we show that both isomers are present in the electronic ground state (S_0) at room temperature. The P isomer is observed in the long-wavelength region of the S_0 - S_1 absorption spectrum. The level energy E_P of the P isomer above the N isomer ground state is determined from temperature-dependent absorption measurements. The S_0 - S_1 absorption cross section spectrum of the P isomer is determined from an analysis of the absorption spectra.

2. Theory

The photoisomerization dynamics of DODCI is explained by a three-well S_1 potential curve and a two-well S_0 potential curve versus a twisting coordinate

[13,18,21]. The S_0 potential curve is depicted in fig. 1. Relaxation of the photoexcited S_1 state populates both the N and the P state [7-24]. The P state relaxes to the N state across the potential barrier E_A with a rate constant [13,18,19]

$$k_{P \rightarrow N}(T) = A_{iso} \exp(-E_A/k_B T). \quad (1)$$

A_{iso} is the pre-exponential factor of the Arrhenius equation (1), k_B is Boltzmann's constant and T is the temperature. The potential barrier is $E_A \approx$

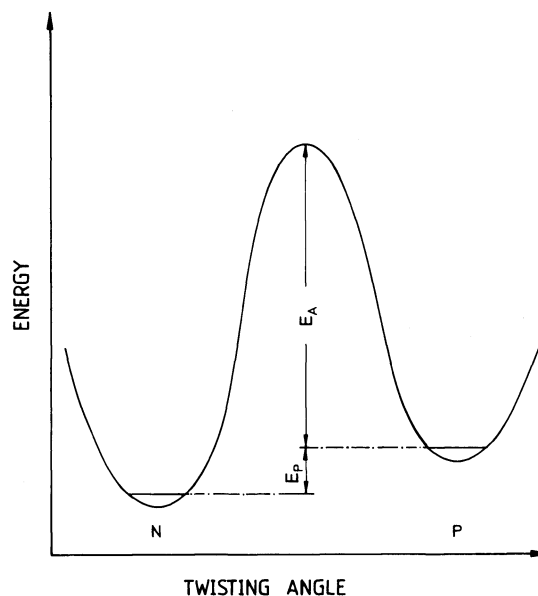


Fig. 1. S_0 ground-state configuration diagram of DODCI.

9.95×10^{-20} J [13]. The $P \rightarrow N$ relaxation time constant at room temperature is $\tau_{P \rightarrow N} = k_{P \rightarrow N}^{-1} \approx 2.53$ ms for DODCI in methanol and $\tau_{P \rightarrow N} \approx 2.60$ ms for DODCI in ethylene glycol [16].

The rate of the $N \rightarrow P$ transition in the electronic ground state is given by

$$k_{N \rightarrow P}(T) = A_{iso} \exp[-(E_P + E_A)/k_B T]. \quad (2)$$

The fraction of thermally populated P isomers is

$$\frac{N_{P0}}{N_0} = \frac{N_{P0}}{N_{N0} + N_{P0}} = \frac{\exp(-E_P/k_B T)}{1 + \exp(-E_P/k_B T)}. \quad (3)$$

N_{P0} and N_{N0} are the number densities of the P and N isomers, respectively. N_0 is the total number density. The absorption coefficient α is composed of N and P isomer contributions, i.e. $\alpha = N_{N0}\sigma_N + N_{P0}\sigma_P$. The total apparent absorption cross section $\sigma' = \alpha/N_0$ is given by

$$\sigma' = \sigma'_N + \sigma'_P, \quad (4)$$

where

$$\sigma'_N = \frac{\sigma_N}{1 + \exp(-E_P/k_B T)} \quad (5)$$

and

$$\sigma'_P = \frac{\exp(-E_P/k_B T)}{1 + \exp(-E_P/k_B T)} \sigma_P. \quad (6)$$

The frequency dependence of the apparent absorption cross section σ_N is given by [25,26]

$$\begin{aligned} \sigma_N(\nu) &= \alpha_N(\nu)/N_{N0}, \quad \text{for } \nu > \nu_{01}^N, \\ &= \sigma_{em}^N(\nu) \exp[-h(\nu_{01}^N - \nu)/k_B T], \\ &\quad \text{for } \nu < \nu_{01}^N. \end{aligned} \quad (7)$$

σ_{em}^N is the stimulated emission cross section of the N isomer and ν_{01}^N is the frequency difference between the S_1 and S_0 electronic level of the N isomer. Its value is determined by the crossing point of the absorption and emission cross section spectra (see figs. 2 and 3).

The absorption cross section ratio, σ'_P/σ'_N , at $\nu_{P,max}$ ($\nu_{P,max} < \nu_{01}^N$) is

$$\begin{aligned} \frac{\sigma'_P}{\sigma'_N} &= \frac{\sigma_P \exp(-E_P/k_B T)}{\sigma_{em}^N \exp(-E_N/k_B T)} \\ &= \frac{\sigma_P}{\sigma_{em}^N} \exp[-(E_P - E_N)/k_B T], \end{aligned} \quad (8)$$

where $E_N = h(\nu_{01}^N - \nu_{P,max})$. E_P is determined by measuring the ratio σ'_P/σ'_N at two different temperatures T_1 and T_2 . Application of eq. (8) gives

$$\begin{aligned} E_P = E_N + \frac{k_B T_1 T_2}{T_1 - T_2} \left[\ln \left(\frac{\sigma'_P(\nu_{P,max}, T_1)}{\sigma'_N(\nu_{P,max}, T_1)} \right) \right. \\ \left. - \ln \left(\frac{\sigma'_P(\nu_{P,max}, T_2)}{\sigma'_N(\nu_{P,max}, T_2)} \right) \right]. \end{aligned} \quad (9)$$

After determining E_P and E_N the apparent S_0-S_1 P isomer absorption cross section spectrum may be determined from eq. (8):

$$\begin{aligned} \sigma_P(\nu, T) &= \frac{\sigma'_P(\nu, T)}{\sigma'_N(\nu_{P,max}, T)} \sigma_{em}^N(\nu_{P,max}, T) \\ &\times \exp[(E_P - E_N)/k_B T]. \end{aligned} \quad (10)$$

The stimulated emission cross section $\sigma_{em}^N(\nu)$ is determined from fluorescence quantum distribution measurements $\tilde{E}(\lambda)$ ($\int_{em} \tilde{E}(\lambda) d\lambda = 1$) [27]. It is

$$\sigma_{em}^N = [1 + \exp(-E_P/k_B T)] \sigma_{em}^{N'} \quad (11)$$

and [28-30]

$$\sigma_{em}^{N'} = \frac{\lambda^4 n_F \tilde{E}(\lambda)}{n_A} \frac{\int_{em} \tilde{E}(\lambda) \lambda d\lambda}{\int_{em} \tilde{E}(\lambda) \lambda^4 d\lambda} \int_{abs} \frac{\sigma_N(\lambda)}{\lambda} d\lambda. \quad (12)$$

n_F and n_A are the average refractive indices of the solution in the S_1-S_0 emission and the S_0-S_1 absorption band, respectively. The integrations extend over the S_1-S_0 emission band (em) and the S_0-S_1 absorption band (abs).

3. Experimental

10^{-4} molar solutions of DODCI in ethylene glycol and in methanol are investigated. The absorption cross section spectra were measured with a conventional spectrophotometer (Beckman model ACTA M4). The temperature was varied with a thermostat. The fluorescence quantum distribution measure-

ments were carried out with a home-made fluorimeter [27] applying the front-face collection technique. The excitation wavelength for the fluorescence detection was set to $\lambda_{\text{exc}} = 570$ nm. The excitation light was vertically polarized and the fluorescence signal was detected at the magic angle of 54.7° to the excitation polarization.

4. Results

The absorption cross section spectra, $\sigma'(\lambda)$, and the stimulated emission cross section spectra $\sigma_{\text{em}}(\lambda)$ of DODCI in ethylene glycol and in methanol are plotted in figs. 2 and 3, respectively. These spectra were measured at room temperature ($T = 294.5$ K). $\sigma_{\text{em}}(\lambda)$ is approximately equal to $\sigma_{\text{em}}^N(\lambda)$. The shoulders in the long-wavelength region of the S_0 - S_1 absorption band indicates the P isomer contribution.

In figs. 4 and 5 the long-wavelength absorption

spectra are shown in more detail. In fig. 4a the absorption spectra $\sigma'(\lambda)$ (solid curves) at $T_1 = 294.5$ K (1) and $T_2 = 368$ K (2) are depicted for DODCI in ethylene glycol. At elevated temperatures DODCI gradually decomposes and the S_0 - S_1 absorption coefficient decreases. Therefore the spectra are adjusted such that $\sigma'(\lambda_{01}^N, T_2)$ is equal to $\sigma'(\lambda_{01}^N, T_1)$. The broken curves represent σ'_N (eqs. (5) and (7)). The differences $\sigma'_P = \sigma' - \sigma'_N$ (eq. (7)) are shown in fig. 4b by the broken curves. The absorption peak of the P isomer occurs at $\lambda_{P,\text{max}} \approx 620$ nm. At this wavelength the S_0 - S_1 absorption of the N isomer starts at $E_N = h(\nu_{01}^N - \nu_{P,\text{max}}) = hc_0[(\lambda_{01}^N)^{-1} - \lambda_{P,\text{max}}^{-1}] = 1.179 \times 10^{-20}$ J = 593 cm^{-1} above the S_0 ground level ($\lambda_{01}^N = 598$ nm). The level position of the ground state of the P isomer is calculated from eq. (9). Its value is $E_P = 1.45 \times 10^{-20}$ J = 727 cm^{-1} . This energy value gives a fraction of $N_{P0}/N_0 \approx 2.7\%$ of molecules in the P isomer state at 294.5 K (eq. (3)). The apparent S_0 - S_1 absorption

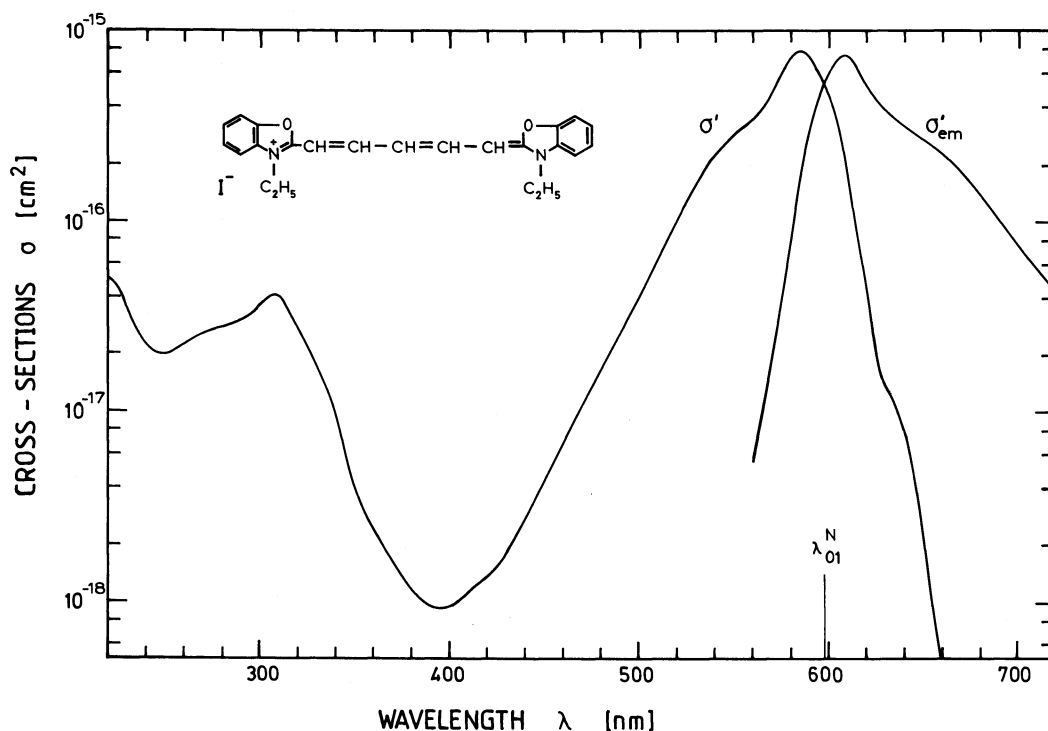


Fig. 2. Apparent absorption and emission spectra of 10^{-4} molar DODCI in ethylene glycol. $T = 21.5^\circ\text{C}$. Structural formula of DODCI is included.

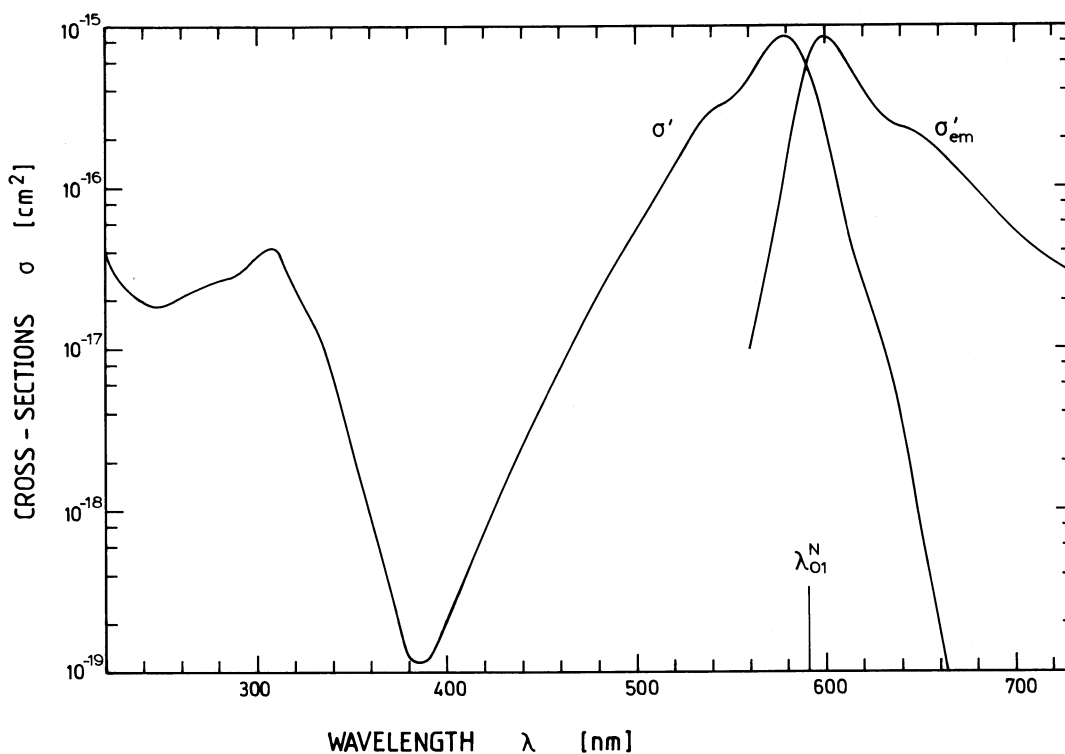


Fig. 3. Apparent absorption and emission spectra of 10^{-4} molar DODCI in methanol. $T=21.5^\circ\text{C}$.

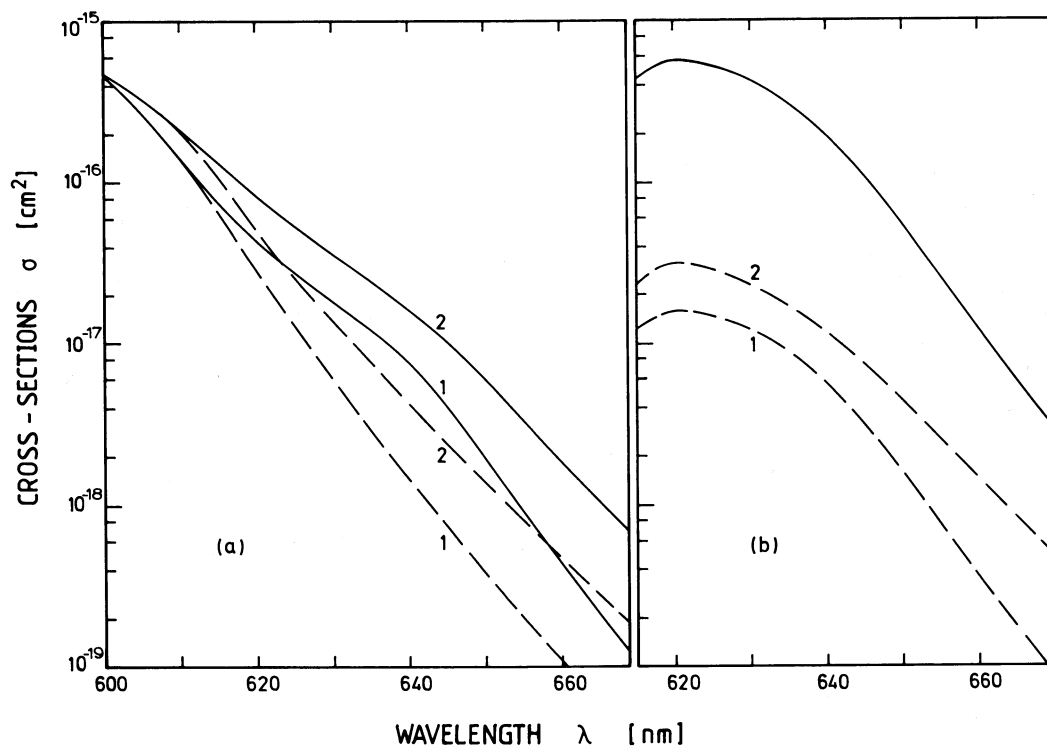


Fig. 4. Long-wavelength S_0-S_1 absorption spectra of DODCI in ethylene glycol. (1) $T=294.5\text{ K}$; (2) $T=368\text{ K}$. (a) Solid curves, apparent absorption cross sections $\sigma' = \sigma_N + \sigma_P$. Broken curves, apparent absorption cross sections σ_N . (b) Broken curves, apparent absorption cross sections σ_P . Solid curve, $\sigma_P(\lambda)$ at $T=294.5\text{ K}$.

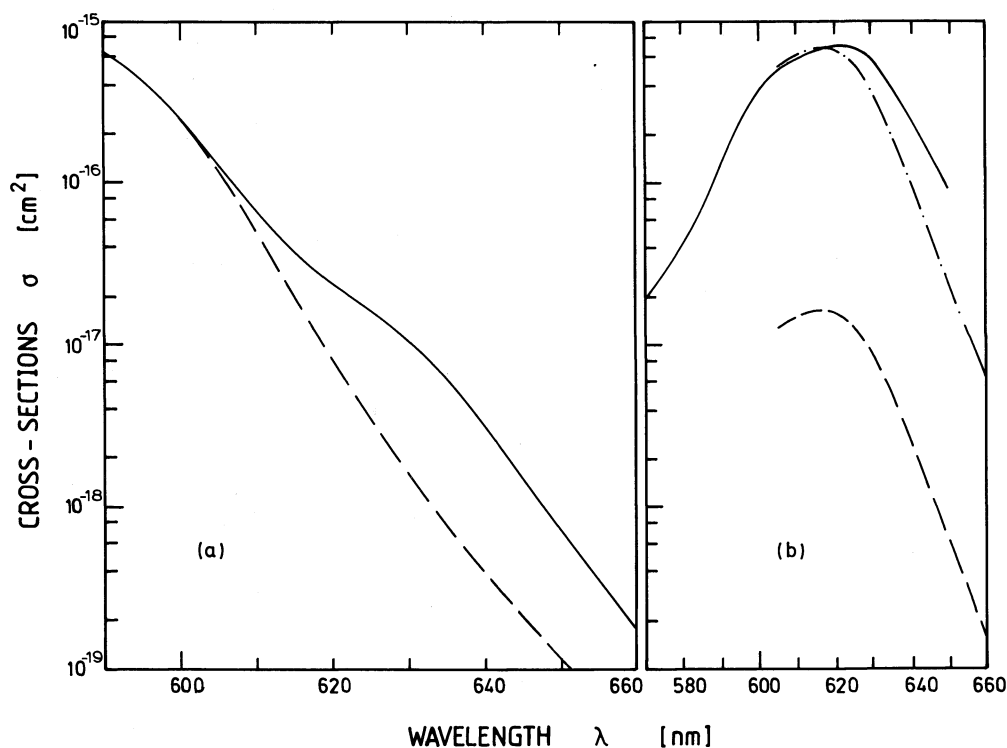


Fig. 5. Long-wavelength S_0 - S_1 absorption spectra of DODCI in methanol. Temperature $T=21.5^\circ\text{C}$. (a) Solid curve, apparent absorption cross section spectrum σ' . Broken curve, apparent absorption cross section spectrum σ'_N . (b) Broken curve, apparent absorption cross section spectrum; $\sigma'_P(\lambda)$. Solid curve, apparent absorption cross section spectrum $\sigma_P(\lambda)$, taken from ref. [7]. Dash-dotted curve, $\sigma_P(\lambda)$ curve calculated from eq. (10).

cross section spectrum $\sigma_P(\lambda, T_1=294.5\text{ K})$ is depicted by the solid curve in fig. 4b. It is calculated from eq. (10). The peak absorption cross section is found to be $\sigma_P(620\text{ nm})=5.7\times 10^{-16}\text{ cm}^2$. This value is not considered to be very accurate because of its exponential dependence on E_P-E_N . (The standard deviation of $\sigma_P(620\text{ nm})$ is $\approx 2\times 10^{-16}\text{ cm}^2$.)

The long-wavelength S_0 - S_1 absorption spectrum of DODCI in methanol is shown in fig. 5a. The temperature is $T=294.5\text{ K}$. The solid curve presents $\sigma'(\lambda)$, the broken curve gives $\sigma'_N(\lambda)$ (eqs. (5) and (7)). $\sigma'_P(\lambda)=\sigma'(\lambda)-\sigma'_N(\lambda)$ (eq. (6)) is shown by the broken curve in fig. 5b. The P isomer S_0 - S_1 absorption peak is at $\lambda_{P,\text{max}}=615\text{ nm}$. The value of E_N is $hc_0[(\lambda_{01}^N)^{-1}-\lambda_{P,\text{max}}^{-1}]=1.31\times 10^{-20}\text{ J}=660\text{ cm}^{-1}$ ($\lambda_{01}^N=591\text{ nm}$). The P isomer absorption cross section spectrum $\sigma_P(\lambda)$ (solid curve in fig. 5b) is taken from ref. [7] where it was determined from absorp-

tion changes in flash photolysis experiments for DODCI in ethanol. E_P is determined from the broken and solid curve in fig. 5b by application of eq. (6). The value $E_P=1.51\times 10^{-20}\text{ J}=760\text{ cm}^{-1}$ is ob-

Table 1
Spectroscopic parameters of DODCI. $T=21.5^\circ\text{C}$. Concentration 10^{-4} mol/dm^3

Parameter	Solvent	
	ethylene glycol	methanol
$\lambda_{P,\text{max}}\text{ (nm)}$	620	615
$\sigma_{P,\text{max}}\text{ (cm}^2\text{)}$	$(5.7\pm 2)\times 10^{-16}$	$(7\pm 0.7)\times 10^{-16}$ [7]
N_{P0}/N_0	0.027	0.024
N_N/N_0^a	0.054	0.039
$E_P\text{ (cm}^{-1}\text{)}$	727	760
$E_N\text{ (cm}^{-1}\text{)}$	593	660

^{a)} Fraction of N isomers absorbing effectively at $\lambda_{P,\text{max}}$.

tained. Eq. (10) gives the dash-dotted curve in fig. 5b for $\sigma_P(\lambda)$. The fraction of molecules in the P isomer state at $T=294.5$ K is $N_{P0}/N_0 \approx 2.4\%$ (eq. (3)).

The spectroscopic data obtained for DODCI in ethylene glycol and methanol are collected in table 1.

5. Discussion

Analysis of the S_0 - S_1 absorption spectra of DODCI in the long-wavelength absorption region enables us to determine the P isomer absorption cross section spectrum, the energy level position of the ground state of the P isomer, and the fraction of P isomers in thermal equilibrium with the N isomers. The potential energy curve of the S_0 state of DODCI versus the twisting coordinate between the isomer configurations [14] is shown in fig. 1. The activation energy $E_A \approx 9.95 \times 10^{-20}$ J = 5005 cm^{-1} is taken from ref. [13]. The time constant for P isomer formation is estimated to be $\tau_{N \rightarrow P} = k_{N \rightarrow P}^{-1} = k_{P \rightarrow N}^{-1} \exp(E_P/k_B T) = 0.092$ s for DODCI in ethylene glycol and 0.10 is for DODCI in methanol at $T=294.5$ K.

6. Conclusions

The technique of long-wavelength absorption analysis described here may be applied to study the thermal formation of ground-state isomers in molecules which form isomers by photo-excitation.

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