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AM1 semiempirical calculated potential energy surfaces for the isomerization of symmetrical carbocyanines

Jeunghee Park *

Department of Chemistry, Korea University, 208 Seochangdong, Jochiwon, Chungnam 339-700, South Korea

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Abstract

Semiemipirical ground state (S_0) and first excited singlet state (S_1) potential surfaces were calculated for the isomerization of symmetrical carbocyanines such as 3,3′-diethylthiadicarbocyanine iodide (DTDCI), 1,1′-diethyl-2,2′-dicarbocyanine iodide (DDI), 1,1′-diethyl-2,2′-carbocyanine iodide (DCI), and cryptocyanine (1,1′-diethyl-4,4′-carbocyanine) iodide (CCI), as a function of the twist angle around a carbon–carbon bond of the polymethine chain. It was found that the isomerization potential surface depends on the polymethine chain length and its position on the quinoline moiety. The results of this study also indicate that steric hindrance associated with the rotation around a carbon–carbon bond plays an important role in the isomerization dynamics of cyanines, which correlates with the photoisomer lifetime that was measured from picosecond time-resolved fluorescence spectra. © 2000 Published by Elsevier Science Ltd.

Keywords: Photoisomerization; AM1; Potential energy surface; Cyanine dye

1. Introduction

Cyanine dyes have been used in a wide range of applications, including photo-sensitizers of silver halide particles [1], mode-locking dyes in passively mode-locked lasers, optical probes in membranes or model membrane systems [2], and initiators in photo-polymerization reactions [3]. From studies involving the photophysics of cyanine dyes, it has been shown that following light absorption cyanine molecules isomerize from the first excited all-*trans* singlet state (S_1) to the ground state (S_0) photoisomers a having *mono–cis* conformation [4–7].

The photoisomerization potential energy surface of 3,3′-diethyloxadicarbocyanine iodide (DODCI) was first reported by Rullière [8]. The isomerization coordinate is the twist angle (θ). Rullière's model assumes that at $\theta = 90°$ (the perpendicular conformation) a maximum exists in the S_0 potential surface, which corresponds to a minimum in the S_1 potential surface. This intermediate twisted species in S_1 state decays to the S_0 state with a branching ratio for the possible isomeric S_0 states. This model has been widely adopted to account for the photophysical behavior of cyanine dyes. Recently, semiempirical calculations for the potential surface of oxacarbocyanines and thia-

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Tel.: +82-415-860-1336; fax: +82-415-865-7542.
E-mail address: parkjh@tiger.korea.ac.kr

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carbocyanines were reported, showing that the shape of potential surface is consistent with Rullière's model for at least one rotational coordinate [9,10]. However, the potential energy surfaces for other cyanine molecules have not been reported.

We previously reported studies involving the photoisimerization dynamics of symmetrical cyanine dyes such as 3,3′-diethylthiadicarbocyanine iodide (DTDCI), 1,1′-diethyl-2,2′-dicarbocyanine iodide (DDI), 1,1′-diethyl-2,2′-carbocyanine iodide (DCI), and cryptocyanine (1,1′-diethyl-4,4′-carbocyanine) iodide (CCI), with the aid of steady-state and time-resolved fluorescence spectra and the ground state recovery profiles [11]. In order to enhance our understanding of the experimental results, we examined the S_0 and S_1 state potential energy surfaces of these cyanines as a function of varying θ around the carbon–carbon bond of polymethine chain, using semiempirical AM1 quantum mechanical calculations.

2. Experimental

The isomerization potential energy surfaces in the S_0 and S_1 states were calculated using Hyperchem and MOPAC packages on a Pentium PC. AM1 parameterization, which is known to be accurate for polar organic molecules [12], was used. The cyanine cations for 1,1′-diethyl-2,2′-dicarbocyanine iodide (DDI), 3,3′-diethylthiadicarbocyanine iodide (DTDCI), 1,1′-diethyl-2,2′-carbocyanine iodide (DCI), cryptocyanine iodide (CCI, 1,1′-diethyl-4,4′-carbocyanine iodide), considered as isolated molecules, were studied. A full geometry optimization for the S_0 state was performed by using a restricted Hartree–Hock (RHF) closed shell algorithm. No counter ion was considered in these calculations. The S_0 state isomerization potential energy surface was constructed by performing a stepwise rotation around a chosen carbon–carbon bond of the polymethine chain, starting with the normal form (all-*trans*) geometry and fully optimizing all other geometrical parameters. The isomerization potential surfaces for the S_1 state were constructed by performing a configuration interaction (CI) calculation with 100 microstates at the ground state optimized geometry. PPP (Pariser–Parr–Pople) MO calculations were conducted using a PISYSTEM package.

3. Results and discussion

The isomerization potential energy surfaces were constructed as a function of the twist angle (θ), by rotating one carbon–carbon bond of the polymethine chain at a time. In the case of DTDCI, the potential surfaces are shown in Fig. 1. For this discussion, the isomers formed from rotations involving (1), (2), and (3) are designated as P1, P2, and P3, respectively. Using the *E*/*Z* notation, the geometry of the normal form, P1, P2, and P3 isomers are (2*Z*,9*E*,11*E*), (2*E*,10*E*,11*E*), (2*Z*,9*Z*,11*E*), and (2*Z*,9*E*,11*Z*), respectively. Rotations around two of the C–C bonds along the polymethine chain have similar activation barriers, 11–12 kcal/mol and ~3 kcal/mol, respectively, in the S_0 and S_1 states (cf. Table 1). The shapes of the potential energy surfaces are very consistent with Rullière's model, showing a maximum in the S_0 state and a minimum in the S_1 state at $\theta = 90°$ (marked as T in Fig. 1). However, the rotations around the bond connecting the polymethine chain to the terminal thiaindoline moiety have a 6 kcal/mol activation barrier in the S_0 state, and a broad-shaped potential energy surface that does not have a sharp energy minimum at $\theta = 90°$ in S_1 state. Furthermore, the potential energy of the P3 isomer is higher than that of other isomers. This could result from steric hindrance between the sulfur atom and the C-12 hydrogen atom along the polymethine chain. Therefore, the formation of the ground-state P3 isomer is expected to be less favorable than forming P1 and P2 isomers.

Awad et al. reported the AM1 semiempirical potential energy surface for progressive isomerizations about successive polymethine bonds in DTDCI [9]. The rotation around the bond connecting the polymethine chain to the terminal thiaindoline moiety has a relatively low activation barrier in the S_0 state compared to rotations around C–C bonds along the polymethine chain, with no energy minimum in the S_1 state. These results are quite consistent with ours.

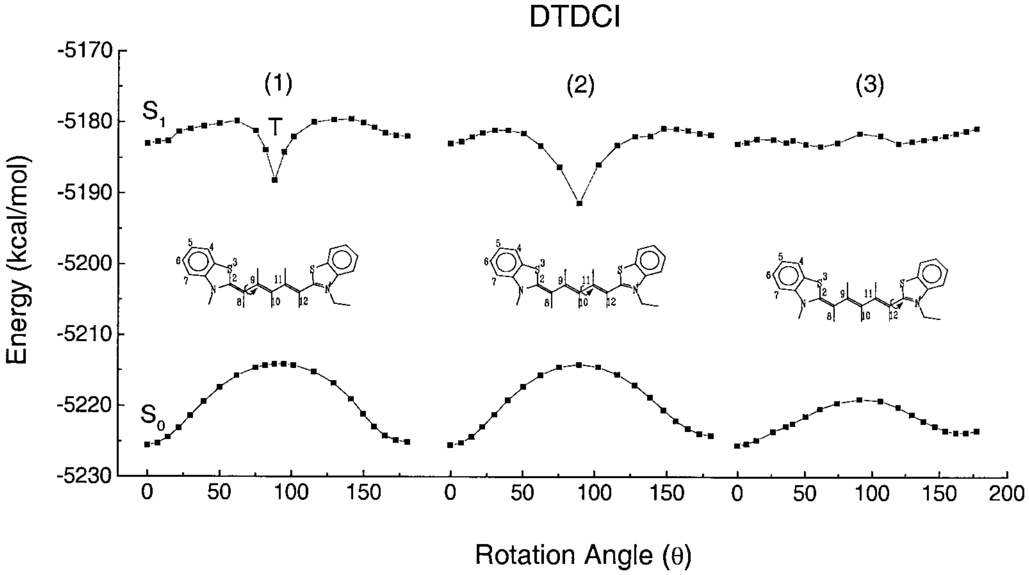

Fig. 1. Calculated isomerization potential energy surfaces for the S_0 and S_1 states of DTDCI. The locations of rotations around the polymethine bonds are shown, with the initial structure designated as the normal form. Filled circles and squares are values from actual calculations.

Table 1
Experimental fluorescence data and calculated absorption maxima and activation energies (E_{act}) in kcal/mol for S_0 and S_1 isomerizations

Name	Notation	Conformer	λ_{em} in EG[a] (nm)	τ in EG[b] (ns)	λ_{0-0} (nm) (Exp)	λ_{0-0} (nm) PPPMO[d]	E_{act} (AM1)	
							S_0	S_1
DTDCI	N	2*E*,10*E*,11*E*	685	1.5	660	660		
	P1	2*Z*,10*E*,11*E*	$\leqslant$ 660[c]	0.30		620	11	3.5
	P2	2*E*,10*Z*,11*E*				680	12	3
	P3	2*E*,10*E*,11*Z*	720	2.1		670	6	0
DDI	N	2*Z*,9*E*,12*E*	750	0.085	715	700		
	P1	2*E*,9*E*,12*E*				705	11	3
	P2	2*Z*,9*Z*,12*E*	775			720	12	3
	P3	2*Z*,9*E*,12*Z*	$\leqslant$720[c]	0.27		640	6	0
DCI	N	2*E*,10*E*	650	0.065	610	590		
	P1	2*Z*,10*E*				530	12	1.7
	P2	2*E*,10*Z*	675			610	6.5	0
CCI	N	4*E*,10*E*	730	0.33	710	700		
	P1	4*Z*,10*E*	$\leqslant$670[c]	0.075		620	12	0
	P2	4*E*,10*Z*	745			680	10	0

[a] The emission peak measured from the steady-state fluorescence spectrum [11].

[b] The emission lifetime measured from the picosecond time-resolved fluorescence spectrum [11].

[c] The emission band position estimated from the picosecond time-resolved fluorescence spectrum [11].

[d] The absorption peaks calculated by PPP MO semi-empirical method [11].

Rodriguez et al. calculated reverse isomerization activation energies of 9.6 and 1.2 kcal/mol for the S_0 and S_1 states, respectively [10], which are close to our values. The experimental activation barriers for isomerization in methanol for the S_0 and S_1 states were reported as 12.0 and 6.5 kcal/mol, respectively [7]. The experimental data for the ground state are in good agreement with the calculated values. However, the optimized geometry of the excited state is estimated from ground state data; therefore, a certain degree of uncertainty in the calculated potential energy of excited state can not be avoided.

Two fluorescence lifetimes were observed for the photoisomers in EtOH (ethanol) and EG (ethylene glycol) solutions; one at a shorter wavelength range ($\lambda \leqslant 660$ nm) than that of the normal form ($\lambda = 685$ nm), and the other one at a longer wavelength range ($\lambda \geqslant 720$ nm). In EG, the emission of the normal form decays with the lifetime $\tau = 1.5$ ns, while the two photoisomers detected at $\lambda \leqslant 660$ nm and $\lambda \geqslant 720$ nm show lifetimes of $\tau = 0.30$ ns and 2.1 ns, respectively. PPP MO semiempirical calculations predict the absorption maxima of the normal form, P1, P2, and P3 isomers to be 660, 620, 680, and 670 nm, respectively. Therefore, the structure with lifetime $\tau = 0.30$ ns and observed at $\lambda \leqslant 660$ nm was assigned as arising from the P1 isomer. Sundstöm et al. reported the recovery profile for the photoisomer at 550 nm with the lifetime 0.27 ps [13]. Bilmes et al. reported an absorption at 650 nm for the photoisomer [14]. These experimental results are consistent with our findings.

The decay time (τ) of 2.1 ns at $\lambda \geqslant 720$ can be attributed to either P2 or P3 isomers. Since the activation energy barriers for pathways (1) and (2) are very similar, the emission decay times for the P1 and P2 isomers are probably similar. Therefore, we can rule out the possibility of a P2 isomer and conclude that a P3 isomer is associated with the $\tau = 2.1$ ns peak. Since photoisomerization to the P3 isomer in the S_0 state is unfavorable, it is possible that the excited P3 isomer or the twisted conformer trapped in the S_1 surface gives a stimulated emission, following absorption of an emission from the excited normal form or the laser pulse at $\lambda = 590$ nm.

The calculated isomerization potential energy surfaces for DDI are shown in Fig. 2. These surfaces are quite similar to those calculated for DTDCI. Again, we have defined the three different isomers formed via pathways (1), (2), and (3) as P1, P2, and P3, respectively. Using the (*E*,*Z*) notation, the geometries of the normal form, P1, P2, and P3 isomers can be described as (2*E*,10*E*,12*E*), (2*Z*,10*E*,12*E*), (2*E*,10*Z*,12*E*), and (2*E*,10*E*,12*Z*), respectively. Rotations around bonds (1) and (2) of the polymethine chain required activation energies of 11–12 and 3 kcal/mol in the S_0 and S_1 states, respectively. However, rotation around the bond connecting the polymethine chain to the terminal quinoline moiety [pathway (3) of Fig. 2] requires activation energies of 6 and ~0 kcal/mol in the S_0 and S_1 states, respectively. In the vicinity of $\theta = 90°$, the potential energy surface of S_1 state has a broad shape without a sharp minimum, which results from steric hindrance between the hydrogen atoms of quinoline ring and polymethine chain. Therefore, we would expect that photoisomerization to S_0 state isomers takes place mainly via pathways (1) and (2) channels. The formation of the S_0 state P3 isomer via pathway (3) would be less favorable.

The fluorescence decay profiles of EG solutions of DDI following picosecond laser pulse ($\lambda = 590$ nm) excitation were found to be dependent on the detection wavelength. The decay profile at $\lambda = 720$-760 nm has a lifetime $\tau = 85 \pm 5$ ps and exhibits mono-exponential decay. If the detection wavelength is below 720 nm, the decay profile becomes bi-exponential, due to another decay time component, $\tau = 270 \pm 20$ ps, which was assigned to the photoisomer. We performed PPP MO semiempirical calculations to estimate the absorption wavelengths of all possible isomers. Results showed that the P3 isomer has an absorption at 640 nm, which is shorter than that of the normal form (700 nm). Therefore, we believe that the P3 isomer is responsible for fluorescence having the longer decay time ($\tau = 270$ ps).

The potential energy surface calculated in this aspect of our study indicates that photoisomerization into the ground state P3 isomer is not favored. A plausible explanation is that the excited P3 isomer or the trapped twisted conformer gives

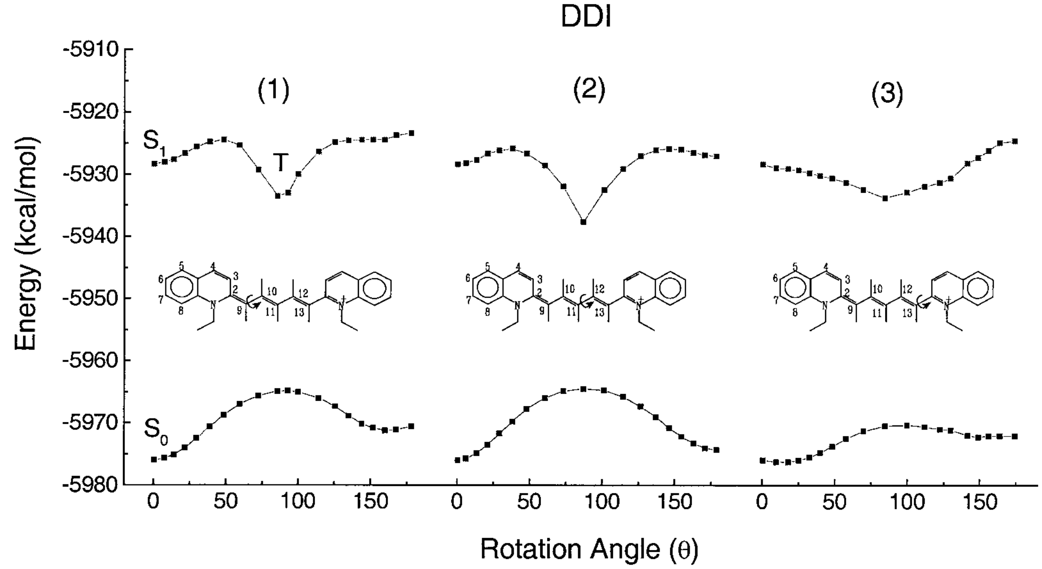

Fig. 2. Calculated isomerization potential energy surfaces for the S_0 and S_1 states of DDI. The locations of rotations around the polymethine bonds are shown, with the initial structure designated as the normal form. Filled circles and squares are values from actual calculations.

a stimulated emission with the decay time 270 ps following laser excitation. The fluorescence lifetime of the P1 and P2 isomers might be too short to be detected under our experimental conditions. The lifetime assignments for the isomers are listed in Table 1.

For DDI and DTDCI, rotations around C–C bonds along the polymethine chain yield photoisomers that fluoresce with shorter decay times than the normal form. The longer decay time component of fluorescence might be attributed to a trapped conformer on the S_1 potential energy surface, which results from a rotation around the bond connecting the polymethine chain to the terminal quinoline (or thiaindoline) moiety.

In the case of DCI, rotations around two of the C–C bonds yields activation energy barriers of 12 and 6.5 kcal/mol for the S_0 state and 1.5 and ~ 0 kcal/mol for the S_1 state potential energy surfaces, as shown in Fig. 3(A). Isomerization via rotation around the bond connecting the polymethine chain to the terminal quinoline moiety, pathway (2) of Fig. 3(A), is less favored than pathway (1), due to the less stable $\theta = 90°$ conformer. Here also we define the two isomers formed from pathways (1) and (2) as P1 and P2, respectively. Using (*E*,*Z*) notations, the geometry of normal form, P1, and P2 can be described as (2*E*,10*E*), (2*Z*,10*E*), and (2*E*,10*Z*), respectively. PPP MO calculations predict that the normal form, P1, and P2 isomers have absorption maxima at 591, 527, and 607 nm, respectively. Experimental results showed only a lifetime of 65 ps in EG, which can be attributed to the normal form. The steady state emission spectrum showed that the quantum yield depends on the excitation wavelength; as the excitation wavelength becomes shorter, the quantum yield for the isomerization increases. Since DCI was excited by 590 nm light via 0–0 band of the S_0–S_1 transition, the quantum yield for isomerization was almost negligible and thus no emission from the photoisomers was found.

For CCI, rotations around two different C–C bonds yield the type of potential energy surface shown in Fig. 3(B). The energy barriers on the S_0 surface were calculated as 12 and 10 kcal/mol for the formation of P1 and P2 isomers, respectively. P1 and P2 notations were used for the isomers formed from pathways (1) and (2), respectively. On the S_1 potential energy surface, there is almost no energy barrier and there is an energy minimum at $\theta = 90°$ for both pathways. These results reflect

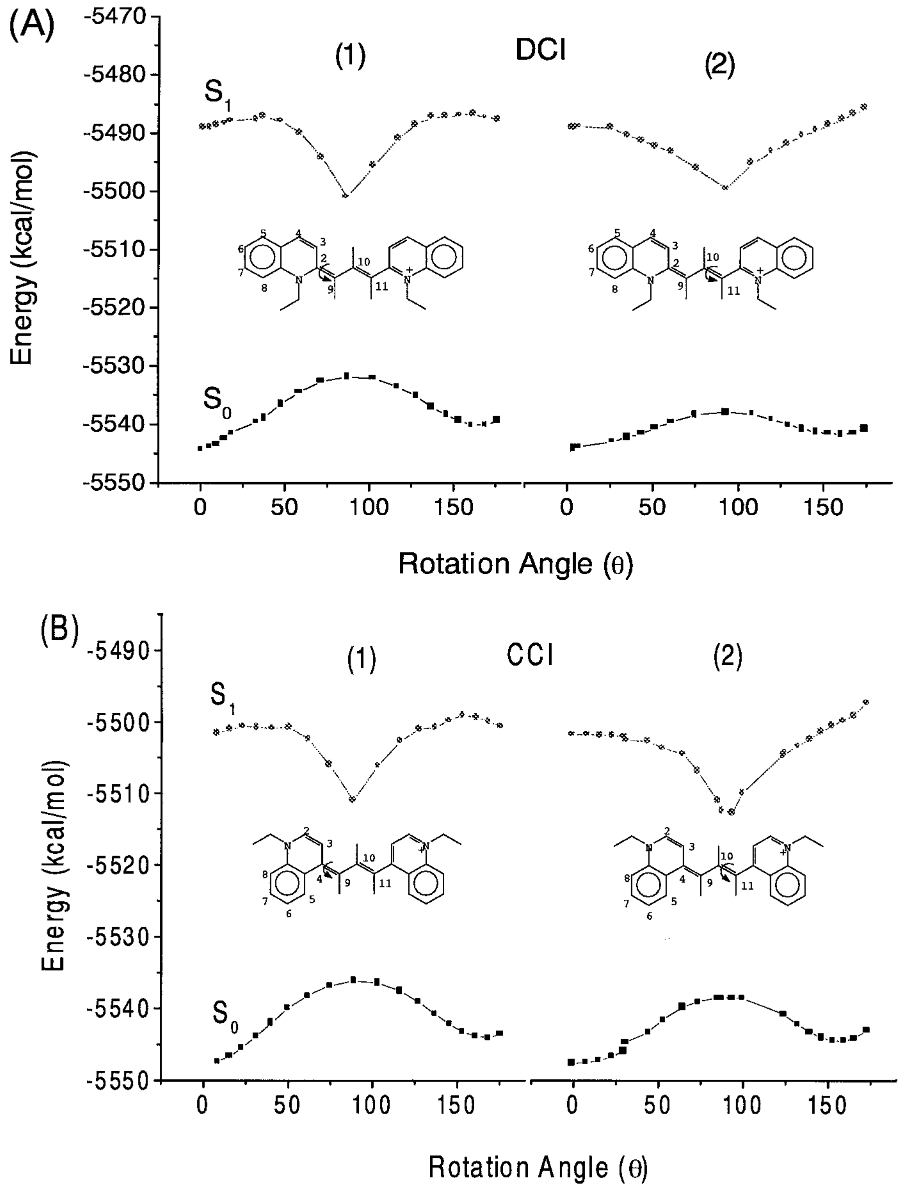

Fig. 3. Calculated isomerization potential energy surfaces for the S_0 and S_1 states of (A) DCI and (B) CCI. The locations of rotations around the polymethine bonds are shown, with the initial structure designated as the normal form. Filled circles and squares are values from actual calculations.

the fact that the quinoline ring is located far from the hydrogen atoms of polymethine chain, leading to little steric hindrance for all isomerization pathways. Using the (*E*,*Z*) notation, the geometries of the normal form, P1, and P2 isomers are (4*E*,10*E*), (4*Z*,10*E*), and (4*E*,10*Z*), respectively. PPP MO calculations predict that the normal form, P1, and P2 isomers have absorption maxima at 700, 620, and 680 nm, respectively. The fluorescence decay profile for CCI in EG solution shows decay times of 0.33±0.05 ns for the normal form and 75±5 ps for the isomer, following 590 nm excitation. Fluorescence from the photoisomer was detected at 670 nm, which is much shorter than the emission peak for the normal form (730 nm). Thus this fluorescence arising from CCI/EG solutions may be due to the P1 isomer. Taken together with the results of DTDCI and DDI, we can conclude that the ground-state photoisomer formed from the less hindered rotation always has a shorter lifetime than the normal form.

It has been suggested that there is no energy barrier in the excited state of 1,1′-diethyl-4,4′-cyanine dye [15]. We calculated the potential energy surfaces for the dye cation, finding a barrierless S_1 surface. The normal form is twisted by ~30° and the activation energy barrier in the S_0 state is 6 kcal/mol, which is fairly consistent with the experimental value of ~7 kcal/mol in MeOH solution. For pseudoisocyanine (PIC, 1,1′-diethyl-2,2′-cyanine) dye, the activation energy barrier in the S_0 state is ~3 kcal/mol. The calculated ground state of PIC is twisted by ~40°, which is less than the experimental value, 54° [16].

In summary, the potential energy surface surfaces for S_0 and S_1 for the carbocyanine dye cation of DTDCI, DDI, DCI, and CCI, as a function of the twisting angle (θ) around the carbon–carbon bonds of the polymethine chain, have been determined. Potential energy surfaces were calculated using AM1 semiempirical MO calculations. The calculated potential surfaces were used to explain experimental results from time-resolved fluorescence spectra of the aforementioned compounds in EG solutions. Rotations around bonds with less steric hindrance between the hydrogen atom in polymethine chain and the atoms in the quinoline or thiainoline moiety produce ground-state photoisomers that have a shorter fluorescence decay time than the normal form. For DDI and DTDCI, there is steric hindrance to rotations around the bond connecting the polymethine chain to the terminal quinoline (or thiaindoline) moiety. A trapped conformer on the S_1 surface may give a longer fluorescence decay time than the normal form. These results indicate that steric hindrance plays an important role in the photoisomerization dynamics of carbocyanines.

Acknowledgements

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