

## Regioselective *E(trans)*–*Z(cis)* photoisomerization in naphthyldiene derivatives

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**Abstract.** Naphthyldiene derivatives, **1–4**, carrying electron-donating groups at one end and electron-withdrawing groups at the other, were synthesized to study the photoisomerization process. All the compounds showed efficient photoisomerization upon direct excitation leading to the formation of 4-*Z* isomer with high selectivity. Triplet sensitization studies indicated inefficient *E–Z* isomerization process. Room temperature fluorescence of **1** and **2** displayed fine structure in hexane solvent and the same was replaced by broad or structureless fluorescence in acetonitrile and methanol solvents. A mechanism involving a polarized or charge transfer singlet excited state is proposed for the observed photoisomerization in these naphthyldiene derivatives.

**Keywords.** Naphthyldiene derivatives; regioselective photoisomerization; direct excitation; triplet sensitization; fluorescence; singlet excited state.

### 1. Introduction

*E(trans)*–*Z(cis)* isomerism is one of the basic principles in chemistry in the broad area of isomerism. *E–Z* isomerism is induced photochemically and this is a major area of interest in modern molecular photochemical research.<sup>1</sup> Photochemical *E–Z* isomerization has a major role in many photobiological phenomena,<sup>2–4</sup> and has practical applications in vitamin A and vitamin D industrial processes.<sup>5–7</sup> More interestingly, compounds exhibiting photochemical *E–Z* isomerization are potential candidates for many opto-electrical and opto-mechanical switching and storage devices.<sup>8,9</sup> Olson<sup>10,12</sup> was the first to postulate that optical excitation of the ethylenic double bond involves rotation around the double bond in its excited state and this rotation leads to the observable *E–Z* isomerization. Lewis and coworkers<sup>13</sup> studied the photoisomerization of stilbene originating from the singlet excited state. Recently, Saltiel and coworkers<sup>14–16</sup> reported that the singlet excited state of stilbene undergoes *E–Z* isomerization which is an adiabatic process. Liu and Hammond<sup>17–19</sup> described a new mechanism for an excited olefin, involving simultaneous twisting of single and double bonds (Hula Twist) leading to *E–Z* isomerization. Our continuing interest<sup>20</sup> in photochemical *E–Z* isomerization in singlet excited state was extended to naphthyldiene derivatives. Various naphthyldiene derivatives, **1** to **4**, synthesized underwent efficient *E* to *Z* isomerization leading to predominantly 4-*Z* isomer formation. The structured fluorescence of **1** and **2** in hexane solvent was found changed to broad and structureless emission by changing the solvent to acetonitrile or methanol

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and together with the decrease in the quantum yield of fluorescence by changing the solvent polarity indicate that singlet excited state acquires highly polarized or charge-transfer character. Singlet excited state of these naphthyldienes is efficient in effecting *E* to *Z* isomerization, where as triplet sensitization studies indicate that the *E* to *Z* is not a preferred process.

## 2. Experimental

A Perkin–Elmer lambda-2 UV-Vis spectrophotometer was used for light absorption measurements. SPEX Fluorolog 0.22 m spectrometer was used for obtaining the fluorescence data. Identical conditions were maintained for all the fluorescence measurements. Quantum yield of fluorescence determined was relative to 9,10-diphenylanthracene.<sup>21</sup> <sup>1</sup>H-NMR spectra were recorded on 200 MHz Gemini and 400 MHz Unity instruments. A VG-Micromass 7070H instrument was used for mass spectra. Solvents were distilled prior to use. Details of the synthesis will be published elsewhere.

A 450 W medium pressure Hg arc lamp along with suitable solution filters<sup>21</sup> (>400 nm) and a Rayonet reactor equipped with RUL-3500 lamps (~350 nm) were used for irradiation. All reactions were monitored by HPLC. A Shimadzu LC-10A with UV-Vis detector coupled with CR-8 integrator HPLC system was used. An amino silica 5  $\mu$ , 4.6  $\times$  250 mm column was used for HPLC analysis. In a typical experiment, 10 ml of 0.001 M nitrogen-bubbled solution was used for irradiation. After the irradiation, products were isolated and purified by column chromatography and were characterized by comparison with the authentic materials prepared. Solvents used were of analytical grade.

## 3. Results and discussion

Naphthyldiene derivatives **1–4** (chart 1) carrying electron-donating groups at one end and electron-withdrawing groups at the other end were synthesized to study the mechanism of

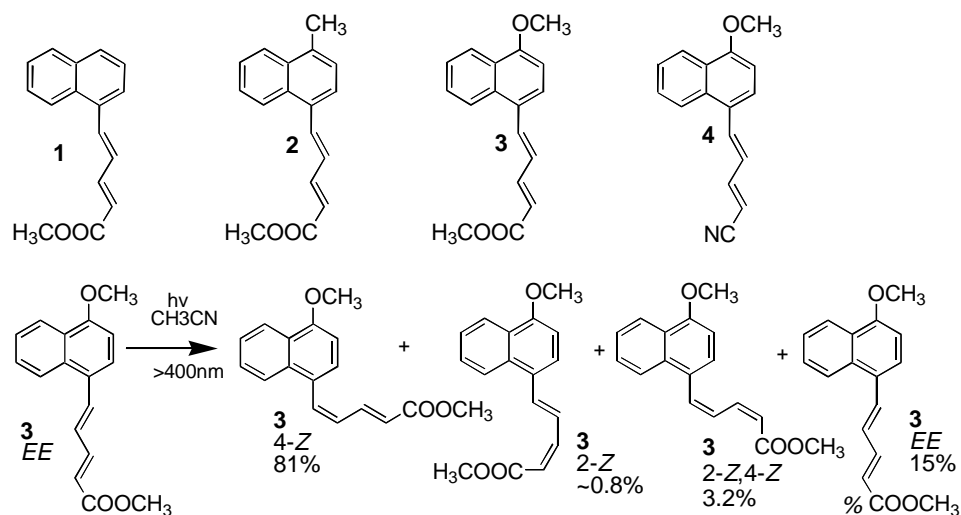


Chart 1.

the photoisomerization process. All the compounds underwent efficient photoisomerization upon direct excitation (table 1) leading to the formation of 4-*Z* with very high selectivity. The isomer distribution presented in table 1, analyzed by HPLC, is at the photostationary state (PSS) upon direct excitation. The percentage of 4-*Z* at PSS increases as the substituent changed to methoxy group (table 1). Interestingly, the formation of 2-*Z* isomer is very small (table 1) in the case of **3**. By changing the wavelength of irradiation to ~350 nm the selectivity for formation of 4-*Z* is maintained but the percentage of conversion, compared to the >400 nm irradiations (table 1), is decreased. The behaviour of **4**, carrying a nitrile end group, towards photoisomerization is also in parallel with **1-3** (table 1). Direct excitation of **1** to **4** involves mainly singlet excited state leading to the regioselective formation of 4-*Z* isomer. The formation of *Z* isomer is interesting because it is thermodynamically less stable than *E* isomer. The higher 2-*Z*, 4-*Z* formation observed (table 1) under ~350 nm irradiation conditions is due to the consecutive photoisomerization of 4-*Z* formed initially.

Triplet sensitization studies were conducted to clarify the participation of singlet excited state in these photoisomerization investigations. Triplet sensitizers employed differ in their triplet energy (table 2) and absorption properties. Sensitizer is the light absorbing species and is involved in the triplet energy transfer process to the substrate. The reaction was monitored by HPLC. The photostationary state compositions determined in sensitization experiments are given in table 2. The results indicate that the *E-Z* isomerization is not an efficient process compared to the direct excitation (table 1) and gives less yield of 4-*Z* isomer even after prolonged (3 h) irradiation.

**Table 1.** Photoisomerization of **1-4** upon direct excitation.

Compd.	Solvent	$\lambda$ Excitation	% 4- <i>Z</i>	% 2- <i>Z</i>	% 2- <i>Z</i> , 4- <i>Z</i>	% <i>E</i> , <i>E</i>
<b>1</b>	Acetonitrile	~350 nm	50	5	8	37
	Acetonitrile	>400 nm	48	4	4	44
	MeOH	~350 nm	60	9	12	19
	MeOH	>400 nm	57	4	6	33
<b>2</b>	Acetonitrile	~350 nm	56	7	17	20
	Acetonitrile	>400 nm	76	1	5	18
	MeOH	~350 nm	52	8	20	20
	MeOH	>400 nm	76	1	4	19
<b>3</b>	Acetonitrile	~350 nm	62	4	13	21
	Acetonitrile	>400 nm	81	0.8	3.2	15
	MeOH	~350 nm	61	3	13	23
	MeOH	>400 nm	77	1	5	17
<b>4</b>	Acetonitrile	~350 nm	51	11	15	23
	Acetonitrile	>400 nm	78	2	6	14
	MeOH	~350 nm	48	9	18	25
	MeOH	>400 nm	74	2	8	16

Nitrogen-bubbled 0.001 M, 10 ml solutions were irradiated in a Rayonet reactor (~350 ± 15 nm) and also using 450 W Hg lamp with solution filters (>400 nm); analysis by HPLC, amino silica 5  $\mu$ , 4.6/250 mm, hexane/chloroform as eluent,  $\lambda$ -det for **1** is 330 nm, for **2** is 345 nm, for **3** is 350 nm and for **4** is 360 nm; 30 min of irradiation (PSS was reached within 12 min)

Fluorescence, fluorescence quantum yield and absorption data is generated for **1–3** (table 3) with the purpose of understanding the nature of the singlet excited state. There is a red shift in the absorption maxima (table 3) for all the compounds upon changing the non-polar solvent hexane to polar solvent acetonitrile or methanol. This red shift observed in the absorption spectra of **1–3** suggests that a  $\pi-\pi^*$  is involved in these light absorption studies. Fluorescence spectra of **1** and **2** are structured in non-polar solvent hexane and become broad or structureless upon changing the solvent to acetonitrile or methanol (figure 1, table 3). Further the fluorescence emission maxima is red shifted in a polar solvent like acetonitrile or methanol (table 3). The red shift observed in the emission maxima and the loss of fine structure in the fluorescence spectrum upon changing the solvent to acetonitrile or methanol informs that there are some structural changes occurring to the molecule in their singlet excited state. The quantum yield of fluorescence is relatively less for all the compounds (table 3) and interestingly the quantum yield of fluorescence decreases with increase in solvent polarity (table 3) from hexane to acetonitrile or methanol. Change in the fluorescence emission spectra (collapse of fine structure and the red shift) and decrease in the fluorescence quantum yield upon changing the solvent hexane to acetonitrile or methanol indicate that the singlet excited state acquires polar character.

**Table 2.** Triplet sensitized isomerization studies.

Compd.	Sensitizer	$E_T$ kcal/mol	% 4-Z	% 2-Z	% 2-Z, 4-Z	% E, E
<b>3</b>	Fluorenone	50	10	2	–	88
	Benanthrone	47	8	2	–	90
	Eosin	43	5	2	–	93
	Erythrocin	42	5	2	–	93
<b>1</b>	Fluorenone	50	18	2	–	80
	Benanthrone	47	15	2	–	83

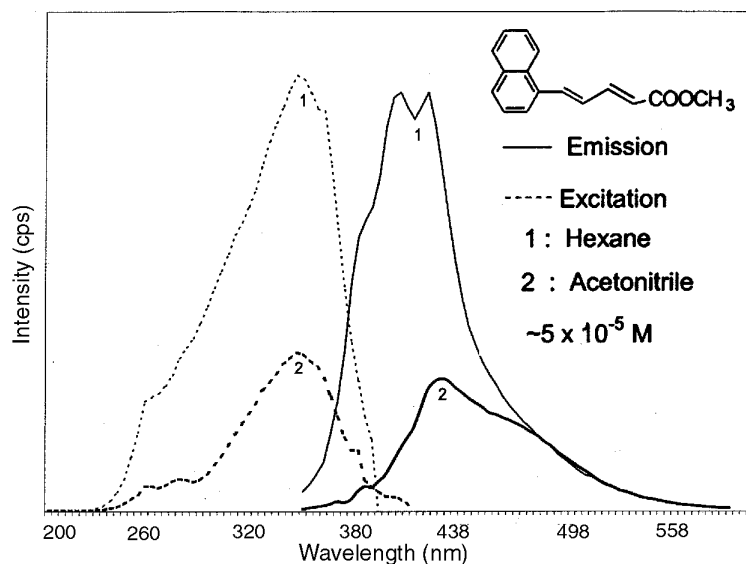
Nitrogen-bubbled 0.0005 M, 10 ml solution containing 0.01 M sensitizer were irradiated using 450 W Hg lamp with solution filters (>400 nm); analysis by HPLC; 30 min of irradiation

**Table 3.** Fluorescence and absorption properties of **1–3**.

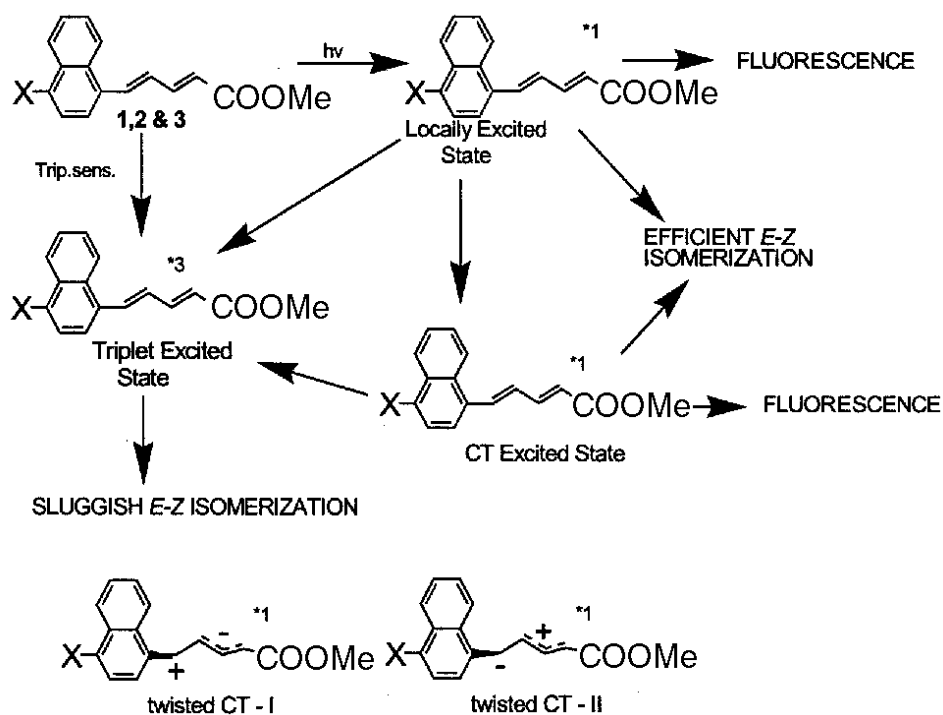
Compd.	Solvent	$\lambda$ Absorption	$\lambda$ Fluorescence	$\Phi_{\text{fluo}}$
<b>1</b>	Hexane	330 nm	382, 400, 420 nm	0.046
	Acetonitrile	335 nm	430 nm	0.0015
	MeOH	335 nm	430 nm	0.004
<b>2</b>	Hexane	345 nm	392, 408, 424 nm	0.036
	Acetonitrile	349 nm	444 nm	0.022
	MeOH	349 nm	446 nm	0.029
<b>3</b>	Hexane	355 nm	425 nm	0.032
	Acetonitrile	362 nm	495 nm	0.007
	MeOH	362 nm	495 nm	0.009

Nitrogen-bubbled 0.00005 M solutions were used for fluorescence studies; quantum yield of fluorescence is relative to 9,10-diphenylanthracene (as standard); error value  $\pm 10\%$

The mechanism proposed is illustrated in scheme 1. The primary event is light absorption by the naphthylidene derivative to form a locally excited state. This excited



**Figure 1.** Fluorescence emission and excitation spectra of **1** in hexane and acetonitrile solvents.



**Scheme 1.**

state can involve itself in various processes (as shown in scheme 1) such as fluorescence emission, *E*–*Z* isomerization, intersystem crossing to a triplet manifold and also can be transformed into a charge transfer excited state. The charge transfer excited state thus formed can display *E*–*Z* isomerization, fluorescence and form a triplet excited state. The change in fluorescence spectra (figure 1) upon changing solvent polarity<sup>22,23</sup> is cited as the cause of the charge transfer excited state. The proposed involvement of two singlet excited states stems from the analogy with the earlier work carried out by us.<sup>24</sup> The formation of a triplet from the two possible singlet excited states is less probable because the *E* to *Z* isomerization process is very efficient upon direct excitation and it is found to be sluggish as determined from the triplet sensitization studies. The regioselectivity observed can arise from the preferential twisting of double bond at position 4–5 from the charge transfer excited (CT) state as proposed in scheme 1 as twisted CT-I and twisted CT-II. Between the two twisted CT states proposed, twisted CT-I is more stable and probable because the charges are well stabilized with naphthalene ring conjugation. The proposed twisted CT states in the mechanism are also supported by the theoretical studies carried out earlier.<sup>25–28</sup>

#### 4. Conclusions

Synthesized naphthylidene derivatives **1** to **4** displayed efficient *E* to *Z* photoisomerization with regioselectivity. The *E* to *Z* isomerization primarily originates from a singlet excited state. Triplet sensitization studies indicate that *E* to *Z* isomerization is not an efficient process from the triplet excited manifold. Fluorescence studies indicated that the singlet excited state having CT or polar character is responsible for *E* to *Z* isomerization. A mechanism involving two excited singlet states is proposed.

#### Acknowledgements

We thank the Department of Science & Technology, New Delhi for the financial Support. US thanks University Grants Commission for a fellowship. IICT Publication No. 020221.

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