One-way *cis* to *trans* Photoisomerization in Styrylnaphthalene Derivative: Role of Substituents and Solvent

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One-way *cis* to *trans* photoisomerization is achieved in styrylnaphthalene derivative (3) by suppressing the *trans* to *cis* isomerization with the use of suitable substituents and solvents.

Photochemical *cis* - *trans* isomerization has academic[1, 2] and industrial[3] significance. Photochemical *cis* - *trans* isomerization in stilbene and stilbene derivatives[4] have been discussed. The extensive investigations carried out by Arai and Tokumaru[5] revealed that aryl olefins with a large aromatic group having low triplet energy such as anthracene and others, undergo "one-way" *cis* to *trans* isomerization in the triplet excited surface via a quantum chain process. We have prepared several diaryl ethylenes and studied the photoisomerization process. The results obtained indicate that 4-methoxynaphthyl-4-nitrostyrene **3** undergoes one-way *cis* to *trans* isomerization in polar solvent and the same **3** displays two-way isomerization in nonpolar solvents. A rationale put forwarded is that a highly polar singlet excited state of **3E** is formed upon direct excitation and it quickly undergoes internal conversion to ground state in polar solvents rather than undergoing *trans* to *cis* isomerization. Earlier theoretical studies carried out [6] also supports the above rationale.

Photoisomerization process was studied for various compounds (Chart) in various solvents and the results are arranged in Table 1 for compounds **1**, **2** & **3** and for compounds **4**, **5** & **6** in Table 2. The compounds **1**, **2**, **4**, **5** & **6** underwent mutual two-way E $\rightleftarrows$ Z (*trans* $\rightleftarrows$ *cis*) isomerization in all solvents (Eq. 1) with different polarity. The Z (*cis*) isomer content was found to be high in non polar solvents compared to polar solvents (Table 1 & 2). The 'Z'(*cis*) isomer content at photostationary state composition is found to be low in polar solvents like acetonitrile and methanol (Table 1 & 2) with the compounds **2**, **5** & **6** having electron donating group associated with the naphthalene part of the molecule. The compound **3** exhibited two-way isomerization in nonpolar solvents (Table 1). Strikingly the 'Z' (*cis*) isomer content reaches 1% or even less than 1% in dichloromethane (DCM) and acetonitrile solvents respectively, and in methanol solvent it is hardly detectable (Table 1). In compound **3** the donor/acceptor strength, within the molecule is very high compared to the other molecules prepared (**1**, **2**, **4**, **5** & **6**). These results reveal that variation in donor/acceptor strength within the molecule and coupled wih the polarity of the medium has a role to play in changing the 'Z' (*cis*) isomer content at photostationary state composition.

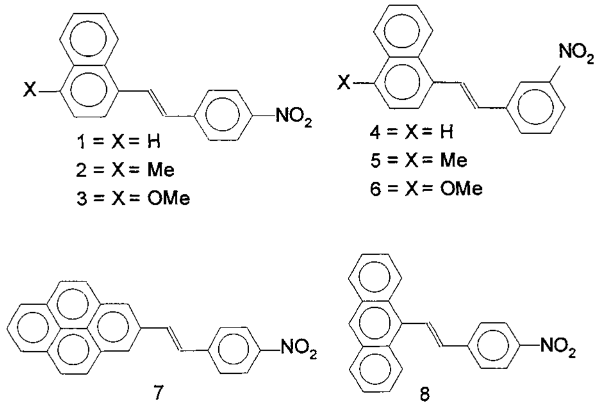


Table1. Photostationary State Composition in Various Solvents for Compounds 1, 2 and 3

	Compound 1[a]		Compound 2[a]		Compound 3[b]	
Solvent	%Z	%E	%Z	%E	%Z	%E
Hexane	83	17	53	47	45	55
Benzee	76	24	45	55	22	78
Dioxan	79	21	47	53	10	90
THF	76	24	47	53	3	97
CH_2Cl_2	62	38	8	92	<1	99
CH_3CN	36	64	8	92	<<1	99
MeOH	33	67	5	95	0	100

[a] irradiated at >350 nm. [b] irradiated at >400 nm.; nitrogen bubbled 0.001 M solutions; 450 W Hg lamp or Philips TL 05, 20 W lamp (>400 nm) used; 15 minutes of irradiation; analysis by HPLC-amino silica column, 5μ, 0.5/25 cm, hexane/ethylacetate mixture as eluent, 1 ml/min flow rate, UV-Visible detector.

Table 2. Photostationary state Composition in various Solvents for compounds 4,5 and 6

Solvent	Compound 4[a]		Compound 5[a]		Compound 6[b]	
	%Z	%E	%Z	%E	%Z	%E
Hexane	58	42	48	52	69	31
Benzene	57	43	40	64	50	50
Dioxane	56	44	39	61	48	62
THF	50	50	32	68	28	72
CH_2Cl_2	42	58	28	72	18	82
CH_3CN	35	65	27	73	10	90
MeOH	43	57	17	83	4	96

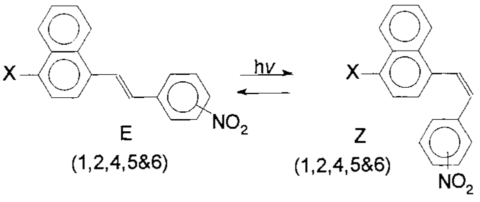
[a] irradiated at >350 nm. [b] irradiated at >400 nm.

Table 3. Triplet Sensitized Isomerization Studies

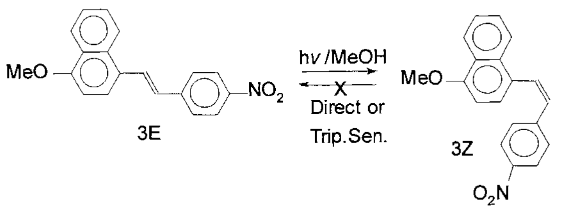
Compound	Sensitizer	Triplet Energy (Kcal/mol)	%Z	%E
3E	Fluorenone	50	----	100
3E	Benzil	53	----	100
3Z	Fluorenone	50	<0.5	99.5
3Z	Benzil	53	<0.5	99.5
3Z	Benzanthrone	47	<0.5	99.5

nitrogen bubbled 0.001 M methanol solutions; sensitizer concentration is 0.01 M; Philips TL 05, 20 W lamps used for irradiation's (> 400 nm);

Triplet sensitization studies on compound **3** (Table 3) reveal that 'Z' (*cis*) to 'E' (*trans*) isomerization exists in methanol solvent (Eq. 2; Table 3) but not E to Z (*trans* to *cis*) isomerization. All the three, **1**, **2**, & **3** compounds exhibited fluorescence solvatochromism (~100 nm red shift from benzene to acetonitrile) indicating the involvement of intramolecular charge transfer (ICT) singlet excited state.[7] The quantum yield of fluorescence for 3E (ϕ_f =0.006) reaches very low in acetonitrile solvent and in methanol it is very much negligible. The two compounds pyrene[8] analog **7** and anthracene[9] analog **8** displayed fluorescence and photoisomerization similar to the behaviour of **3**. The two compounds **7** & **8** were found to have low quantum yield of intersystem crossing (ISC) in polar solvent.[8,9]



Eq.1



Eq.2

The rationale put forward is that excited ICT state of 3E follows quick internal conversion (IC) as the dominating deactivation pathway in polar methanol solvent. This is supported by the following data that (i) the quantum yield of fluorescence is very negligible, (ii) the 'E' to 'Z' isomerization is totally suppressed from both singlet and triplet states and (iii) the very low ISC possible[8,9] in the nitro derivatives. Further the red shifted emission maxima in polar solvent narrows the energy gap between excited state and ground state and this facilitates the internal conversion[6] (IC) process to be more effective.

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