J. Org. Chem. **2001,** *66,* 681−688

Photochemical *E* (*trans*) → *Z* (*cis*) Isomerization in Substituted 1-Naphthylacrylates

K. Mani Bushan,[†] G. Venugopal Rao,[†] T. Soujanya,[†] V. Jayathirtha Rao,*[,†] S. Saha,[‡] and A. Samanta*[,‡]

Organic Chemistry Division II, Indian Institute of Chemical Technology, Hyderabad-500 007, India, and School of Chemistry, University of Hyderabad, Hyderabad-500 046, India

jrao@iict.ap.nic.in

Received May 30, 2000

Substituted naphthylacrylates, **1**−**3**, not showing rotamerism have been synthesized with a view to study photochemical *E* (*trans*) → *Z* (*cis*) isomerization. Photostationary state composition of the isomers upon direct excitation, triplet sensitized isomerization, quantum yield of isomerization, and steady state and time-resolved fluorescence behavior have been studied for these naphthylacrylates. The direct excitations of the compounds yield high *Z* ($\sim$80%) isomer composition, whereas the triplet sensitization results in less *Z* ($\sim$20%) isomer composition. This indicates that the singlet pathway is very efficient in converting the *E* isomer to the *Z* isomer. The naphthylacrylates **1** and **2** exhibit structured fluorescence at room temperature in hexane and upon changing the solvent to CH_3CN; the structure of the fluorescence is lost, indicating that the singlet excited-state develops a polar character in a polar environment. The polar nature of the singlet excited state becomes more clear in the case of **3** from its fluorescence solvatochromism. The naphthylacrylates did not exhibit excitation wavelength-dependent fluorescence at room temperature suggesting that the ground state conformers (rotamers) are not involved. Fluorescence lifetimes measured for these compounds displayed biexponential behavior, which is explained using a two-state model.

Photochemical *cis*−*trans* isomerization is a major area of interest in modern molecular photochemistry and photobiology.[1] The isomerization has practical application in vitamin A and vitamin D industrial processes,[2−4] and it is known to play an important role in many optomechanical and optoelectrical switching and storage devices.[5] The photochemical *cis*−*trans* isomerization is discussed by several researchers.[6−9] Triplet state mediated *Z* to *E* one way isomerization is also summarized.[10] The role of conformation on the photochemical *E* → *Z* isomerization is another aspect that has received less attention.[11] Our present efforts in understanding the photochemical *E* → *Z* isomerization[12] via the singlet excited state leads us now to report our results on substituted 1-naphthylacrylates. Substituted 1-naphthylacrylates that do not exhibit rotamerism[13,14] (conformational equilibrium) have been synthesized to study photochemical *E* → *Z* isomerization. The prepared 1-naphthylacrylates in these investigations undergo *E* → *Z* isomerization predominantly from the singlet excited state. The polar nature of the singlet excited state of these 1-naphthylacrylates is indicated based on the fluorescence studies. The biexponential fluorescence decay observed for these 1-naphthylacrylates is explained using the two-state model.

Results and Discussion

Photostationary State Composition. Substituted naphthalene derivatives, **1**−**5** (Chart 1) were synthesized to study the *E* → *Z* photoisomerization process. The 1-naphthylacrylates were synthesized from the corresponding 1-naphthaldehydes by adopting Horner−Wad-

---

* To whom correspondence should be addressed.

[†] Indian Institute of Chemical Technology.

[‡] University of Hyderabad.

(1) Liu, R. S. H.; Shichida, Y. *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH Publishers: New York, 1991; Chapter 18.

(2) (a) Liu, R. S. H.; Asato, A. E. *Tetrahedron*, **1984**, *40*, 1931. (b) Jayathirtha Rao, V.; Fenstemacher, R. J.; Liu, R. S. H. *Tetrahedron Lett.* **1984**, *25*, 1115.

(3) Braun, A. M.; Maurette, M. J.; Oliveros, E. *Photochemical Technology*; Wiley: New York, 1991.

(4) Kirk-Othmer, *Encyclopedia of Chemical Technology*, 4th ed.; Wiley: New York, 1996; Vol. 18, p 799.

(5) (a) *Photochromism, Molecules and Systems*; Durr, H., Bouas-Laurant, Eds.; Elsevier: Amsterdam, 1990. (b) Feringa, B. L. *Tetrahedron* **1993**, *49*, 8267.

(6) (a) Saltiel, J.; et al. In *Organic Photochemistry*; Chapman, O., Ed.; Marcel Dekker: New York, 1973; Vol. 3, p 1. (b) Saltiel, J.; Charlton, J. L. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Acadamic Press: New York, 1980; Vol. 3, p 25.

(7) Allen, M. T.; Whitten, D. G. *Chem. Rev.* **1989**, *89*, 1691.

(8) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415.

(9) Gorner, H.; Kuhn, H. J. *Adv. Photochem.* **1995**, *19*, 1.

(10) Arai, T.; Tokumaru, K. *Adv. Photochem.* **1995**, *20*, 1.

(11) (a) Saltiel, J.; Tarakalanav, N.; Sears, D. F. *J. Am. Chem. Soc.* **1995**, *117*, 5586. (b) Vroegop, P. J.; Lugtenberg, J.; Havinga, E. *Tetrahedron* **1973**, *29*, 1393. (c) Bartocci, G.; Masetti, F.; Mazzucato, U.; Spalletti, A.; Bruni, M. C. *J. Chem. Soc., Faraday Trans.* **1986**, *82*, 775. (d) Bartocci, G.; Masetti, F.; Mazzucato, U.; Marconi, G. *J. Chem. Soc., Faraday Trans.* **1984**, *80*, 1093. (e) Spalletti, A.; Bartocci, G.; Galiazzo, G.; Macchioni, A.; Mazzucato, U. *J. Phys. Chem. A* **1999**, *103*, 8994. (f) Muller, A. M.; Brunner, S. L.; Schmidt, W. E.; Werner, F. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 505.

(12) Jayathirtha Rao, V. *Organic Molecular Photochemistry: Molecular and Supramolecular Photochemistry*; Ramamurthy, V., Schanze, K., Eds.; Marcel Dekker: New York/Basel, 1999; Vol. 3, Chapter 4, p 169. (b) Jayathirtha Rao, V.; Bhalerao, U. T. *Tetrahedron Lett.* **1990**, *31*, 3441. (c) Mani Bushan, K.; Ayodele, E. T.; Raj Gopal, V.; Soujanya, T.; Jayathirtha Rao, V. *Chem. Lett.* **1999**, 171.

(13) (a) Fischer, E. *J. Photochem.* **1981**, *17*, 331. (b) Hass, E.; Fischer, G.; Fischer, E. *J. Phys. Chem.* **1978**, *82*, 1638. (c) Fischer, E. *J. Phys. Chem.* **1981**, *85*, 1770.

(14) (a) Mazzucato, U.; Momicchioli, F. *Chem. Rev.* **1991**, *91*, 1679. (b) ref 11d.

10.1021/jo000819v CCC: $20.00

Chart 1

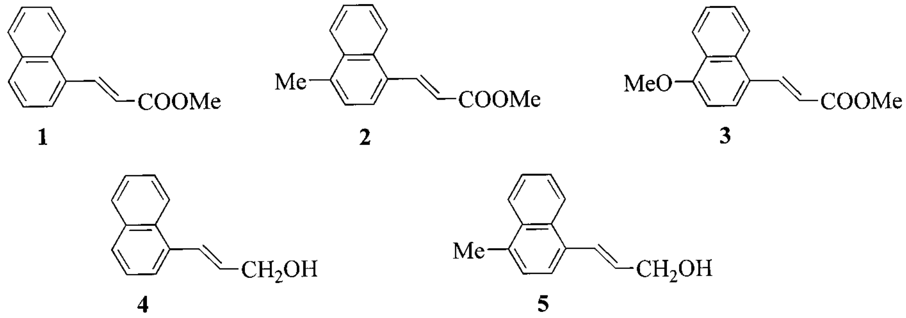


Table 1. Photostationary State *E* and *Z* Isomer Composition of 1, 2, and 3 in Various Solvents[a]

compound	solvent	% *Z* (cis)	% *E* (trans)
1	hexane	80	20
	benzene	80	20
	dichloromethane	79	21
	dioxane	78	22
	THF	80	22
	acetonitrile	80	20
	methanol	80	20
2	hexane	70	30
	benzene	67	33
	dichloromethane	70	30
	dioxane	68	32
	THF	70	30
	acetonitrile	72	28
	methanol	73	27
3	hexane	68	32
	benzene	73	27
	dichloromethane	77	23
	dioxane	77	23
	THF	79	21
	acetonitrile	85	15
	methanol	77	23
4	hexane	43	57
5	hexane	33	64

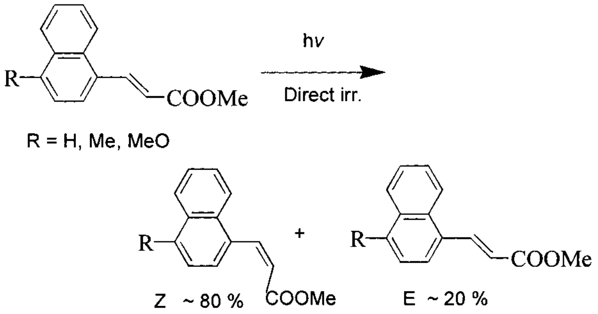
[a] The nitrogen-bubbled 0.001 M solutions were irradiated for 15 min. A 450 W Hg arc lamp with Pyrex filter was used. *E* and *Z* isomers were analyzed by HPLC: amino silica 5 μ, 0.5/25 cm, hexane/dichloromethane mixture as eluent; λ_{det} for **1** is 300 nm; λ_{det} for **2** is 328 nm; λ_{det} for **3** is 330 nm. For **5** and **6** the isomer composition was determined based on ^{1}H NMR integration after 45 min of irradiation; experimental error limit is ±0.5%.

sworth–Emmons (HWE) reaction.[15] The *Z* isomers were prepared from the corresponding 1-naphthaldehyde and a modified phosphonate (HWE reagent).[16] 1-Naphthaldehyde,[17] 4-methylnaphthaldehyde,[18] and 4-methoxynaphthaldehyde[19] were prepared by known procedures. The two alcohols **4** and **5** were prepared by reducing the corresponding naphthylacrylates (**1** and **2**). All products were characterized by spectral means (Experimental Section). Thus prepared naphthylacrylates **1**–**3** were irradiated (Pyrex filter, direct excitation, 0.001 M) in various solvents (Table 1), and the isomer composition was determined using HPLC. The photostationary state composition of the isomers is given in Table 1. Perusal of Table 1 indicates that *E* → *Z* isomerization is facile in these naphthylacrylates of **1**–**3** favoring the *Z* isomer formation in all solvents (eq 1). Photostationary state composition was also determined by changing the wavelength of excitation in methanol for **1**–**3**, where the formation of *Z* isomer is favored under these conditions, and the results are listed in Table 2. Prolonged irradiation (~14 h) of **1**–**3** did not yield any new products as judged by ^{1}H NMR. The two alcohols **4** and **5** were also irradiated and the isomer composition is listed in Table 1. The two alcohols yield less *Z* isomer upon direct excitation compared to **1**–**3** under the same conditions.

Table 2. Wavelength Dependent Photostationary State *E* and *Z* Isomer Composition for 1, 2, and 3 in Methanol Solvent[a]

compound	excitation wavelength	%*Z*	%*E*
1	>300 nm (450 W Hg lamp; Pyrex)	80	20
	~300 nm (Rayonet Reactor)	78	22
	~350 nm (Rayonet Reactor)	80	20
2	>300 nm (450 W Hg lamp; Pyrex)	73	27
	~300 nm (Rayonet Reactor)	75	25
	~350 nm (Rayonet Reactor)	80	20
	~420 nm (TL/03–20 W tubes)	80	20
3	>300 nm (450 W Hg lamp; Pyrex)	77	23
	~420 nm (TL/03–20 W tubes)	75	25

[a] Nitrogen-bubbled 0.001 M solutions were irradiated for 15 min; *E* and *Z* isomers were analyzed by HPLC; experimental error limit is ±0.5%.



(1)

The quantum yields of isomerization determined for compounds **1**, **2**, **3** (*E* to *Z*), and **1Z** and **2Z** (*Z* to *E*) upon direct excitation are listed in Table 3. The data on the quantum yields of isomerization determined reveal that the *E* → *Z* isomerization process is quite efficient. Interestingly, the quantum yield of *Z* to *E* isomerization is found to be less than that of *E* to *Z*.

Triplet sensitized *E* → *Z* isomerizations were conducted for **3E** and **3Z** to differentiate the involvement of the singlet/triplet excited pathway. Triplet sensitizers utilized in this study vary in their triplet energy over a range indicated in Table 4. The photostationary state compositions determined under triplet sensitization con-

---

[15] (a) Wadsworth, W. S. *Org. React.* **1977**, *25*, 73. (b) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863.

[16] Mahipal Reddy, A.; Raj Gopal, V.; Jayathirtha Rao, V. *Ind. J. Chem.* **1996**, *35B*, 312.

[17] (a) Vogel, A. I. *A Text Book of Practical Organic Chemistry*, 4th ed.; ELBS.: London, 1978; p 768. (b) Angyal, S. J.; Tetaz, J. R.; Wilson, J. G. *Org. Synth.* **1950**, *30*, 67. (c) Oliver, G.; Allen, B. *Org. Synth.* **1944**, *24*, 30.

[18] Lock, G.; Schnider, R. *Chem. Ber.* **1958**, *91*, 1770.

[19] Israelashvili, S.; Gottlieb, Y.; Imbeir, M.; Habas, A. *J. Org. Chem.* **1951**, *16*, 1519.

Table 3. Quantum Yield of *E* to *Z* and *Z* to *E* Isomerization in Various Solvents[a]

compound no.	hexane	benzene	THF	dichloromethane	CH_3CN	MeOH
1 $E \rightarrow Z$	0.268	0.283	0.293	0.304	0.288	0.252
2 $E \rightarrow Z$	0.405	0.325	0.388	0.363	0.353	
3 $E \rightarrow Z$	0.382	0.385	0.333	0.330	0.400	0.352
1 $Z \rightarrow E$	0.115				0.125	
2 $Z \rightarrow E$	0.135				0.156	

[a] Nitrogen-bubbled 0.0005 M solutions were irradiated; solution filters were used for isolating a suitable wavelength line of the Hg arc lamp; potassium ferrioxalate was used for photon counting; analysis by HPLC as given in Table 1 footnote; experimental error limit is ± 0.01.

Table 4. Triplet Sensitized Photoisomerization of 3E and 3Z[a]

compound	solvent	sensitizer	E_T (kcal/mol)	%*Z*	%*E*
3E	hexane	benzil	53	20	80
	MeOH	benzil	53	25	75
	hexane	fluorenone	50	22	78
	MeOH	fluorenone	50	25	75
	hexane	benzanthrone	47	18	82
	MeOH	benzanthrone	47	22	78
	hexane	acetophenone	74	20	80
3Z	MeOH	benzil	53	22	78
	MeOH	fluorenone	50	20	80

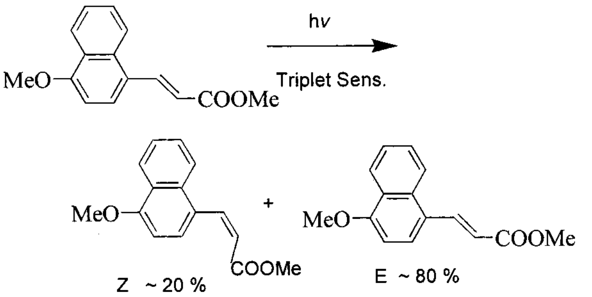
[a] Nitrogen-bubbled 0.001 M solutions with sensitizer (0.01 M) were irradiated for 60 min using a 450 W Hg arc lamp with filters; triplet energies are from ref 35; analysis by HPLC.

Table 5. Absorption and Fluorescence Data for Various Compounds[a]

compound	solvent	λ_{abs}(nm)	λ_{fluo}(nm)	ϕ_{fluo}
1	hexane	311	355, 374, 394, 410	0.021
	THF	314	395, 407(s)	0.067
	CH_2Cl_2	315	398	0.060
	CH_3CN	315	420	0.068
2	hexane	320	365, 385, 406	0.021
	THF	325	412	0.048
	CH_2Cl_2	326	416	0.022
	CH_3CN	325	420	0.023
3	hexane	331	406	0.033
	THF	340	416	0.026
	CH_2Cl_2	344	420	0.035
	CH_3CN	346	425	0.047
1Z	hexane	305	355, 375, 395	0.012
	THF	305	412	0.023
	CH_2Cl_2	307	420	0.010
	CH_3CN	307	420	0.007
4	hexane	294	340, 356, 368	0.140
	THF	296	340(s), 356, 368(s)	0.200
	CH_2Cl_2	297	344(s), 356, 374(s)	0.160
	CH_3CN	295	344(s), 356, 374(s)	0.190
5	hexane	302	344(s), 364, 380(s)	0.118
	THF	302	344(s), 364, 380(s)	0.133
	CH_2Cl_2	302	344(s), 364, 380(s)	0.167
	CH_3CN	302	344(s), 364, 380(s)	0.204

[a] Nitrogen-bubbled ~0.00005 M solutions were used for measuring the fluorescence at room temperature; quantum yields of fluorescence were determined using 9,10-Diphenylanthracence (ϕ_{fluo} = 0.9) as standard;[36] experimental error is ±10.0%.

ditions are given in Table 4. The results highlight that the formation of *Z* isomer is less favored under these (eq 2; Table 4) sensitized irradiations compared to direct excitation conditions (eq 1; Table 1). Triplet sensitized isomerization (Table 4) suggests that *Z* → *E* isomerization is the dominant pathway and the triplet energy of **3** is in the range of ~47 kcal/mol.



(2)

Absorption and Fluorescence Studies. Absorption and fluorescence studies were carried out in various solvents to understand the nature of the excited-state involved in the photoisomerization of these 1-naphthyl derivatives. Absorption and fluorescence properties of the various compounds in several solvents are listed in Table 5. There is a bathochromic shift observed for compound **3** in the UV−vis absorption maxima with an increase in the solvent polarity. Fluorescence emission and excitation spectra obtained for **1** and **2** in hexane are shown in Figures 1 and 2. Fluorescence emission for **1** and **2** in hexane is structured, and a broad fluorescence band replaces the structured band in polar solvents such as acetonitrile (Figures 3 and 4). This behavior suggests the proximity of two close-lying states of different symmetry. Fluorescence emission maxima shifted to longer wavelengths (fluorescence solvatochromism) in polar solvents for compound **3**. The alcohols **4** and **5**, which lack the electron-withdrawing group (acceptor), display structured fluorescence. Moreover, the two alcohols do not exhibit fluorescence solvatochromism (Table 5). The quantum yield of fluorescence for **1**−**3** is in the range of 2−7%, and the quantum yield of fluorescence for **4** and **5** is in the range of 16−24%. No significant influence of solvent on the fluorescence quantum yield could be observed. The room-temperature fluorescence spectra for all the compounds prepared do not show any dependence on the wavelength of excitation.

Fluorescence lifetimes were measured for various compounds in selected solvents, and the results are arranged in Table 6. Decay profiles were obtained using a single photon counting apparatus[20] with a time resolution of approximately 1.0 ns. Satisfactory fits to a double exponential were obtained for **1**−**3** and **1Z**, and satisfactory fits to a single exponential were obtained for **4** and **5**. The decay times obtained by nonlinear least-squares fit to the decay curves were found to be independent of the exciting wavelength. The χ^2 values and the pre-exponentials are listed. The short-lived singlet is found to contribute more to the fluorescence compared to the long-lived singlet. No appreciable change in lifetime with the change of the solvent could be observed.

Photoisomerization. Perusal of data collected in Table 1 reveals that direct excitation of **1** to **3** in various solvents produces predominantly *Z* isomer as a major one. Direct excitation populates a singlet excited state and hence the singlet may be the excited-state respon-

---

(20) O'Gorner, D. V.; Philips, D. *Time-Resolved Single Photon Counting*; Academic Press: New York, 1984.

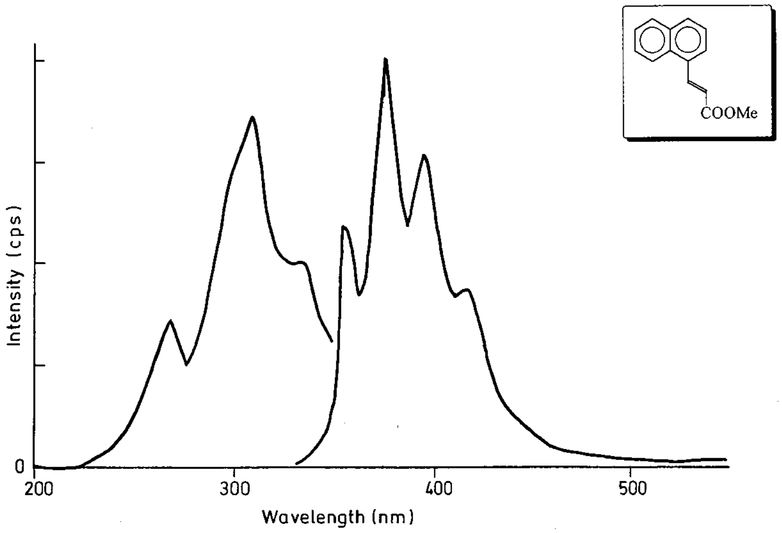


Figure 1. Fluorescence excitation and emission spectra of compound **1** in hexane.

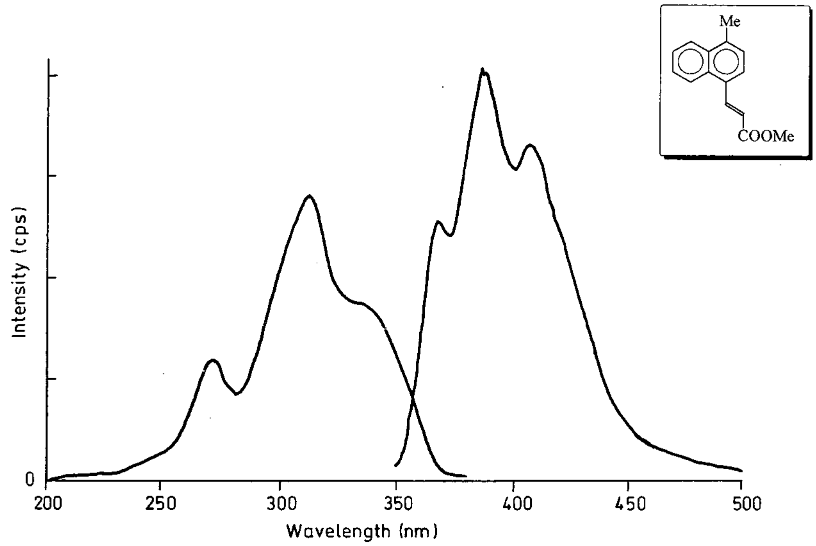


Figure 2. Fluorescence excitation and emission spectra of compound **2** in hexane.

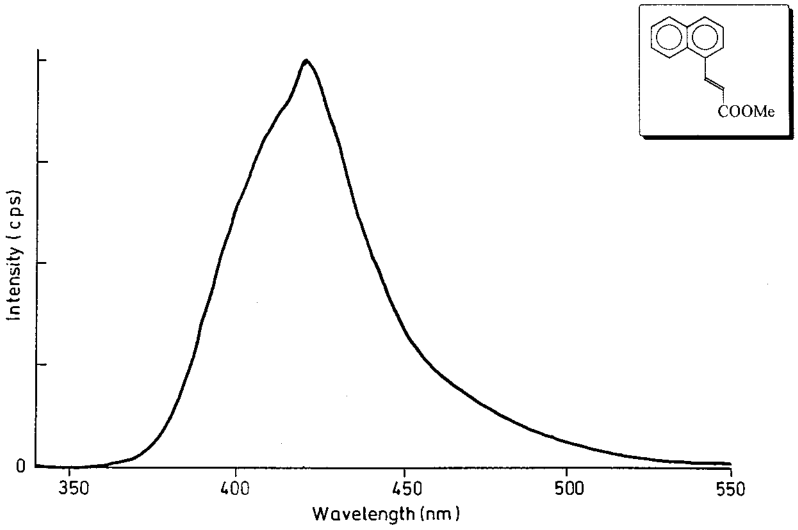


Figure 3. Fluorescence emission spectra of compound **1** in acetonitrile.

sible for *E* → *Z* isomerization. Triplet sensitized isomerization studies with various sensitizers show that (Table 4) the *E* isomer is the major component in the photostationary state, and hence, *Z* → *E* is the preferred pathway. These results indicate that *E* → *Z* isomerization is the dominant pathway from the singlet excited manifold.

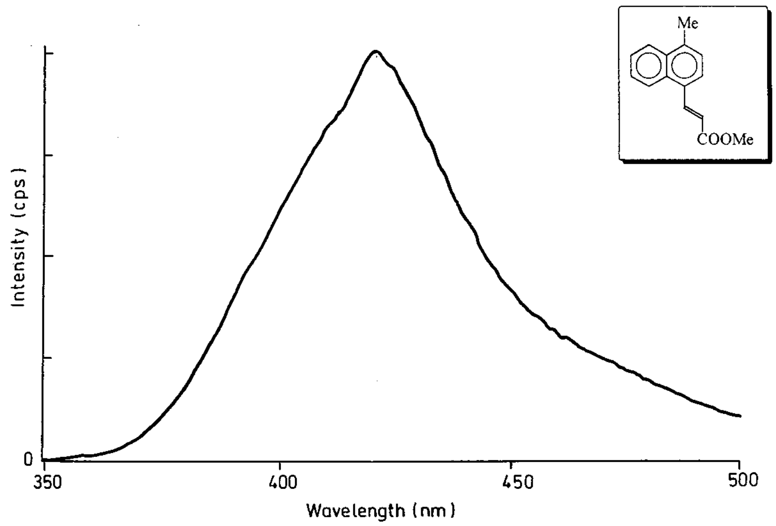


Figure 4. Fluorescence emission spectra of compound **2** in acetonitrile.

Table 6. Fluorescence Lifetimes for Various Compounds in Different Solvents[a]

compound	solvent	τ_1 (ns)	τ_2 (ns)	χ^2
1	hexane	8.14 (0.02)	0.188 (0.98)	1.14
	THF	8.09 (0.02)	0.138 (0.98)	1.07
2	hexane	6.80 (0.02)	0.270 (0.98)	1.18
	THF	6.15 (0.03)	0.267 (0.97)	1.22
	CH_3CN	5.25 (0.05)	0.254 (0.95)	1.30
3	hexane	4.93 (0.002)	0.157 (0.998)	1.12
	THF	6.50 (0.002)	0.141 (0.998)	1.13
	CH_3CN	5.41 (0.022)	0.748 (0.978)	1.09
1Z	hexane	4.68 (0.035)	0.399 (0.965)	1.08
	THF	5.26 (0.018)	0.327 (0.982)	1.07
4	hexane	5.21		1.35
	CH_3CN	5.62		1.01
5	hexane	3.66		0.99
	THF	3.83		0.96
	CH_3CN	4.01		1.12

[a] The quantities in brackets indicate the relative weightage of individual components present in the decay curves.

Triplet sensitization studies indicate that triplet formation (ISC) is an inefficient pathway under direct excitation conditions, since the *Z* isomer predominates (Table 1) upon direct excitation. Our results are consistent with the singlet excited-state involving *E* → *Z* isomerization as proposed by Saltiel[21] et al., although a triplet pathway[22] was also proposed. In these *E* → *Z* photoisomerizations we believe that the ground-state s-trans, s-trans conformer is participating. The involvement of the s-trans naphthyl−acrylic conformer is in accordance with the naphthyl−vinyl s-trans conformer studied by Fischer and co-workers[23] and Mazzucato and co-workers.[24] The s-trans enone of acrylate conformation is in agreement with the s-trans enone conformational investigations carried out by the Havinga[25] et al. and Lewis[26] et al. The mono exponential decay observed for **4** and **5** in the fluorescence lifetime studies also indicates that the naphthyl−acrylic link has s-trans conformation.

Nature of the Singlet Excited State. UV−vis absorption and fluorescence studies were carried out to understand the nature of the singlet excited state. Absorption and fluorescence data are arranged in Table 5. UV−vis absorption is broad and structureless for all these compounds. The absorption maximum is almost unaffected by the change in polarity of solvent in the case of **1** and **2**, whereas in the case of **3** a red shift is observed. This solvent polarity induced red shift is due to the electron donating effect of the substituent present on the naphthalene ring.[27] Fluorescence studies conducted on these compounds are more interesting. For **1** and **2**, the fluorescence (Figures 1 and 2) is structured in hexane, whereas in polar solvents such as CH_3CN the fluorescence is broad and relatively red-shifted (Figures 3 and 4). The solvent induced red shift in the fluorescence emission maxima gradually increases as one passes from **1** to **3** (Table 5). The broad absorption spectrum gives rise to structured emission in nonpolar solvent and broad emission in polar solvent for **1** and **2**. This is indicative of the fact that the molecule is undergoing structural changes in the excited singlet surface, and further, the structural change is sensitive to the polarity of the surrounding environment.[28] The solvent polarity induced (solvatochromism) red shift of the fluorescence maximum of **3** is a definite indication of the involvement of an intramolecular charge transfer[29,30] excited state. A similar behavior was observed in the fluorescence studies on benzyl-1-naphthoate.[31] On the basis of the solvent polarity effect on the fluorescence emission maxima, one can conclude that the magnitude of the charge transfer character associated with the singlet excited state is

---

(21) (a) Saltiel, J. *J. Am. Chem. Soc.* **1967**, *89*, 1036. (b) Saltiel, J.; Megarity, E. D. *J. Am. Chem. Soc.* **1972**, *94*, 2742. (c) ref 6.

(22) (a) Tanaka, H.; Honda, K.; Suzuki, N. *J. Chem. Soc., Chem. Commun.* **1977**, 506. (b) Tanaka, H.; Takamuku, S.; Sakurai, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 801.

(23) (a) Fischer, G.; Fischer, E. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1264. (b) ref 12.

(24) Castel, N.; Fischer, E.; Bartocii, G.; Masetti, F.; Mazzucato, U. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1969. (b) ref 13.

(25) Kronenberg, M. E.; Havinga, E. *Recueil* **1965**, *84*, 17.

(26) Lewis, F. D.; Elbert, E. J.; Upthagrove, A. L.; Hale, P. D. *J. Org. Chem.* **1991**, *56*, 553.

(27) Reichhardt, C. In *Solvents and Solvent Effects in Organic Chemistry*; VCH: Weinheim, 1988.

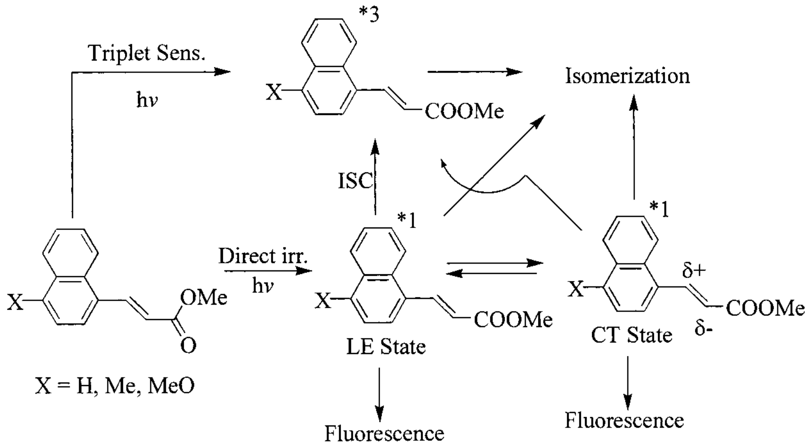
(28) Raj Gopal, V.; Jayathirtha Rao, V.; Saroja, G.; Samanta, A. *Chem. Phys. Lett.* **1997**, *270*, 593.

(29) (a) Jayathirtha Rao, V. *J. Photochem. Photobiol. Chem. A* **1994**, *83*, 211. (b) Raj Gopal, V.; Mahipal Reddy, A.; Jayathirtha Rao, V. *J. Org. Chem.* **1995**, *60*, 7966. (c) ref 28.

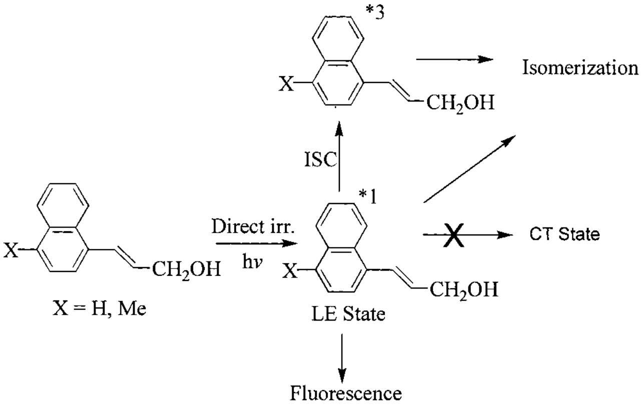
(30) (a) Barbara, P. F.; Jarzeba, W. *Adv. Photochem.* **1990**, *15*, 1. (b) Lippert, E. *Z. Naturforsch.* **1955**, *109*, 541. (c) Lippert, E. Z.; Rettig, W.; Bonacic-Koutecky, V.; Heisel, F.; Meihe, J. A. *Adv. Chem. Phys.* **1987**, *68*, 1. (d) Kosower, E. M.; Huppert, D. *Annu. Rev. Phys. Chem.* **1986**, *37*, 127.

(31) Costa, S. M.; Macanita, A. L.; Prieto, M. J. *J. Photochem.* **1979**, *11*, 109.

Scheme 1



Scheme 2



relatively less in the case of **1** and **2** compared to **3**. The fluorescence data obtained for the **1Z** isomer also fall in line with the singlet excited-state behavior of **1**–**3**. For systems **4** and **5** the fluorescence maxima did not respond to the solvent polarity (Table 5), indicating the requirement of the electron-withdrawing ester group for the formation of intramolecular charge-transfer excited state.[28,29b] The fact that two alcohols, **4** and **5**, show less *Z* isomer formation (Table 1) clearly substantiates the role of the charge-transfer excited singlet state in leading higher *Z* isomer content.

Mechanism. The proposed mechanism of photochemical *E* → *Z* isomerization for these naphthyl derivatives is depicted in Schemes 1 and 2. Initial light absorption results in the molecule being in the locally excited (LE) singlet state, which transforms into a charge transfer (CT) singlet state. The two LE and CT states proposed are supported by the fluorescence lifetimes measured. The same two-state model proposed here is also consistent with the earlier reports,[32] where multiple adiabaticity was formulated. The charge transfer nature of one of the singlet excited states stems from the fluorescence studies carried out. The solvent induced broadening of emission and solvent induced red shift in the emission maxima observed strongly indicate the involvement of a CT excited singlet state. The two singlets formed, the LE state and CT state, can be responsible for *E* → *Z* isomerization. It is possible that both the LE and CT states (Scheme 1) undergo intersystem crossing to form a triplet excited state. Thus, the formed triplet excited state can undergo *E* → *Z* isomerization. The sensitization experiments suggest that (Table 4) the triplet excited state is very much effective in converting the *Z* isomer to the *E* isomer but not as effective in *E* → *Z* isomerization. The mechanism proposed (Scheme 2) in the case of the alcohols (**4** and **5**) is slightly different. The two compounds, **4** and **5**, did not show any solvent induced changes in the fluorescence and exhibit monoexponential fluorescence decay behavior. On the basis of this, it is proposed (Scheme 2) that only the singlet LE state is involved in case of **4** and **5**. Further, it is proposed that *E* → *Z* isomerization may be quite effective from the singlet as well as from the triplet excited state in the case of **4** and **5**.

Conclusions

Substituted naphthylethylene derivatives, which do not show rotamerism, have been synthesized to study the *E* → *Z* isomerization process. *E* → *Z* isomerization is found to be very efficient, and it occurs predominantly from the singlet excited state. Triplet sensitization experiments show that *Z* → *E* conversion is an efficient process on the triplet excited surface. Fluorescence studies clearly indicate the involvement of a polar singlet excited state of charge transfer in nature in these isomerizations. Fluorescence lifetime measurements suggest the presence of two singlets viz the LE state and the CT state. The alcohols do not show solvent induced changes in the fluorescence and exhibit a monoexponential fluorescence decay behavior. This observation suggests the requirement of an electron-withdrawing end group to form the charge-transfer excited state. The monoexponential decay of fluorescence also indicates that the LE state is long-lived compared to the the CT state.

Experimental Section

^1H and ^{13}C NMR spectra were recorded in chloroform-*d* on a 200 MHz spectrometer, and chemical shifts are reported in ppm downfield from TMS. UV–vis absorption and fluorescence spectra were measured using commercial spectrometers. TLC was performed on a precoated plate of silica gel 60F, and flash column chromatography was carried out using silica gel 60–120 mesh or 100–200 mesh. Solvents were distilled prior to use. Other chemicals are commercially available, and some others were prepared as per the published procedures. Methyl dimethyl phoshphanoacetate and methyl bis-1,1,1-trichloro-

---

(32) (a) Rettig, W. *Topics in Current Chemistry*; Springer-Verlag: New York, 1994; Vol. 169, p 253. (b) Letard, J. F.; Lapouyade, R.; Rettig, W. *J. Am. Chem. Soc.* **1993**, *115*, 2441.

ethyl phoshphanoacetate were prepared according to published procedure.[16] The starting compounds, aldehydes, 1-naphthaldehyde,[17] 4-methyl-1-naphthaldehyde,[18] and 4-methoxy-1-naphthaldehyde, were prepared according to published procedures.

Preparation of Methyl-3-(1-naphthyl)-*E*-propeonate 1.[15] Methyldimethylphosphanoacetate (2 g, 11 mmol) in DMF (10 mL) was added slowly at room temperature to a suspension of NaH (264 mg, 11 mmol, 60% in mineral oil) in DMF (15 mL). After complete addition, reaction mixture was stirred for 10 min. Then, 1-naphthaldehyde (1.56 g 10 mmol) in DMF (10 mL) was added slowly to the reaction mixture and stirred for 2 h. The reaction mixture was poured into ice cold water and extracted with ether and washed with water, and the organic layer was dried over anhydrous sodium sulfate and the ether was evaporated and the product was vacuum distilled. Yield (1.69 g) 80%, bp 147 °C/1 mm Hg. ^{1}H NMR ($CDCl_3$): 3.85 (s, 3H), 6.44−6.6 (d, $J = 15.8$ Hz, 1H), 7.41−7.65 (m, 3H), 7.70−7.8 (d, $J = 7.7$ Hz, 1H), 7.82−7.94 (m, 2H), 8.13−8.3 (d, $J = 7.3$ Hz, 1H), 8.42−8.6 (d, $J = 15.8$ Hz, 1H). ^{13}C NMR ($CDCl_3$): 166.5, 141.4, 133.4, 130.2, 128.4, 126.5,125.8, 125.1, 124.9, 123.1, 120, 51.3. UV−vis absorption: hexane, 315 nm ($\epsilon = 14\,610$). IR (neat): 3400−3000, 1700 cm^{-1}. MS (EI): *m/z* 212 (M+, 75). HRMS: calcd 212.083730 for $C_{14}H_{12}O_2$ (M+), found 212.083561.

The Synthesis of Methyl-3-(1-naphthyl)-*Z*-propeonate 1Z.[16] Methyl bis-1,1,1-trichloroethyl phasphanoacetate (2.07 g, 5 mmol) in DMF (10 mL) was added slowly at room temperature to a suspension of NaH (240 mg., 5 mmol, 60% in mineral oil) in DMF (20 mL). After complete addition, the reaction mixture was stirred for 15 min. Then reaction mixture was cooled to −78 °C and 1-naphthaldehyde (800 mg., 4.8 mmol) in DMF (10 mL) was added slowly. After complete addition, the reaction mixture was brought to room temperature and stirred for 4 h. The reaction mixture was poured into crushed ice, extracted with ether, and washed with water and the organic layer was dried over anhydrous sodium sulfate, the ether was evaporated, and the compound was purified by column chromatography using silica gel (100−200 mesh) and pet. ether as the eluent, giving a viscous oil. Yield (0.86 g) 85%. ^{1}H NMR ($CDCl_3$): 3.58 (s, 3H), 6.03−6.2 (d, $J = 13$ Hz, 1H), 7.45−7.54 (m, 4H), 7.55−7.64 (d, $J = 13$ Hz, 1H), 7.8−7.95 (m, 3H). UV−vis absorption: hexane, 305 nm ($\epsilon = 12\,060$).

The above procedures were adopted to make **2**, **3**, and **4** using the corresponding aldehydes.

Methyl-3-(4-methyl-1-naphthyl)-*E*-propeonate 2. Yield 86%, white solid, mp 75 °C. ^{1}H NMR ($CDCl_3$): 2.65 (s, 3H), 3.75 (s, 3H), 6.35−6.47 (d, $J = 15.5$ Hz, 1H), 7.18−7.3 (d, $J = 8$ Hz, 1H), 7.42−7.53 (m, 2H), 7.54−7.62 (d, $J = 8$ Hz, 1H), 7.9−8.0 (m, 1H), 8.10−8.20 (m, 1H), 8.38−8.5 (d, $J = 15.8$ Hz, 1H). ^{13}C NMR ($CDCl_3$): 167.1, 141.7, 137, 132.4, 131.1, 129.7, 126.1, 125.7, 124.4, 123.5, 119.2, 51.3, 19.4. UV−vis absorption: hexane, 320 nm ($\epsilon = 12\,290$). IR (KBr): 3000, 1700 cm^{-1}. MS (EI): *m/z* 226 (M+, 36). HRMS: calcd 226.099380 for $C_{15}H_{14}O_2$ (M+), found 226.099267.

Methyl-3-(4-methyl-1-naphthyl)-*Z*-propeonate 2Z. Yield 85%, white solid, mp 72 °C. ^{1}H NMR ($CDCl_3$): 2.72 (s, 3H), 3.6 (s, 3H), 6.18−6.28 (d, $J = 11.5$ Hz, 1H), 7.28−7.38 (d, $J = 9$ Hz, 1 Hz), 7.41−7.47 (d, $J = 9$ Hz, 1H), 7.48−7.6 (m, 2H), 7.61−7.68 (d, $J = 11.5$ Hz, 1H), 7.88−7.99 (m, 1H), 8.01−8.12 (m, 1H). UV−vis absorption: hexane, 310 nm ($\epsilon = 11\,300$).

Methyl-3-(4-methoxy-1-naphthyl)-*E*-propeonate 3. Yield 89%, solid, mp 80 °C. ^{1}H NMR ($CDCl_3$): 3.85 (s, 3H), 4.03 (s, 3H), 6.35−6.50 (d, $J = 15.5$ Hz, 1 H), 6.77−6.88 (d, $J = 9$ Hz, 1H), 7.45−7.65 (m, 2H), 7.68−7.78 (d, $J = 9$ Hz,1H), 8.10−8.2 (d, $J = 7$ Hz, 1H), 8.23−8.33 (d, $J = 7.3$ Hz, 1H), 8.39−8.52 (d, $J = 15.5$ Hz, 1H). ^{13}C NMR ($CDCl_3$): 167.2, 157.2, 141.5, 132.4, 127.3, 125.6, 125.4, 125.3, 123.9, 122.9, 122.6, 117.5, 103.4, 55.3, 51.3. UV−vis absorption: hexane, 331 nm ($\epsilon = 15\,780$); IR (KBr): 3300−3000, 1720 cm^{-1}; Mass *m/z* (EI) 242 (M+, 70). HRMS: calcd 242.094294 for $C_{15}H_{14}O_3$ (M+), found 242.092910.

Methyl-3-(4-methoxy-1-naphthyl)-*Z*-propeonate 3Z. Yield 74%, solid, mp 76 °C. ^{1}H NMR ($CDCl_3$): 3.59 (s, 3H), 4.02 (s, 3H), 6.02−6.13 (d, $J = 11$ Hz, 1H), 6.72−6.81 (d, $J = 7$ Hz, 1H), 7.4−7.46 (m, 2 H), 7.47−7.54 (d, $J = 11$ Hz, 1H), 7.55−7.61 (d, $J = 9$ Hz, 1H), 7.76−7.85 (d, $J = 9$ Hz, 1H), 8.20−8.3 (d, $J = 8$ Hz, 1H). ^{13}C NMR ($CDCl_3$): 166.9, 156.4, 142.2, 128.1, 126.9, 124.3, 123.9, 122.8, 120.9, 96.2, 55.2, 50.9. UV−vis absorption: hexane, 320 nm ($\epsilon = 13\,390$). MS (EI): *m/z* 242 (M+, 70). HRMS: calcd 242.094294 for $C_{15}H_{14}O_3$ (M+), found 242.093820.

The synthesis of 3-(1-naphthyl)-E- propene-1-ol 4.[29b] DIBAL−H (9.4 mL of a 1 M hexane solution, 9.4 mmol) was added slowly to a suspension of methyl-3-(1-naphthyl)-*E*-propeonate (1.0 g, 4.7 mmol) in hexane (25 mL) at −78 °C under nitrogen atmosphere; after complete addition, the reaction mixture was brought to room temperature and was stirred for 2 h. Then, the reaction mixture was cooled to −78 °C and quenched with NaF/H_2O; the hexane layer was decanted and extracted with ether and the combined organic layers were washed with water and dried over anhydrous sodium sulfate. The solvent was evaporated, and the compound was purified by column chromatography using silica gel (60−120 mesh) and 4:1 hexane/DCM as the eluent. Yield (0.82 g) 75%. ^{1}H NMR ($CDCl_3$): 4.3−4.5 (d, $J = 5.7$ Hz, 2H), 6.28−6.48 (m, 1H), 7.2−7.35 (d $J = 14.2$ Hz, 1H), 7.36−7.6 (m, 4H), 7.7−7.9 (m, 2H), 8.05−8.19 (m, 1H). ^{13}C NMR ($CDCl_3$): 134.4, 133.6, 131, 128.5, 128, 127.9, 125.9, 125.8, 125.7, 125.5, 123.8, 123.7, 123.5, 63.7. MS (EI): *m/z* 184 (M+, 62). HRMS: calcd 184.089314 for $C_{13}H_{12}O$ (M+), found 184.088815.

The Synthesis of 3-(1-Naphthyl)-*Z*-propene-1-ol 4Z.[29b] The above procedure was adopted by using **1Z**. Yield 75% as a viscous oil. ^{1}H NMR ($CDCl_3$): 4.25 (d, $J = 7$ Hz, 2H), 6.01−6.2 (m, 1H), 7.0−7.11 (d, $J = 10$ Hz, 1H), 7.18−7.26 (d, $J = 7$ Hz, 1H), 7.31−7.58 (m, 3H), 7.71−7.88 (m, 2H), 7.89−8.0 (m, 1H).

The Synthesis of 3-(4-Methyl-1-naphthyl)-*E*-propene-1-ol 5.[29b] The above procedure was adopted by using **2**. Yield 85%, solid, mp 54−55 °C. ^{1}H NMR ($CDCl_3$): 2.65 (s, 3H), 4.33 (d, $J = 7$ Hz, 2H), 6.19−6.4 (m, 1H), 7.17−7.31 (m, 2H), 7.37−7.55 (m, 3H), 7.89−8.02 (m, 1H), 8.05−8.14 (m, 1H). MS (EI): *m/z* 198 (M^+, 80).

General Procedure for Photolysis. A Rayonet reactor equipped with RUL-3000 (∼300 nm) and RUL-3500 (∼350 nm) lamps, Philips TL/03−20 W 2 ft lamps (>400 nm), and 450 W medium-pressure Hg arc lamps along with suitable filters[35] were used for irradiation. All reactions were monitored by HPLC. An amino silica 5 μ, 0.5 cm × 25 cm column was used for HPLC analysis. In a typical experiment, 10 mL of a 0.001 M solution of **1**−**3**, N_2 bubbled, was used for irradiation. After irradiation, products were characterized by comparison with authentic materials. Triplet sensitized reactions were carried out by using a mixture of sensitizer (0.01 M) and substrate (**3E** and **3Z**, 0.001 M) in MeOH (10 mL), N_2 bubbled, which was irradiated for 1 h using a 450 W Hg lamp with filters.

Preparative photoisomerization was carried out using 200 mg of **1**−**3** in 250 mL of benzene or dichloromethane, N_2 bubbled, which was irradiated using a Rayonet chamber (Excitation 350 nm) for 1 h; the reaction was monitored by HPLC and the *Z* isomer was isolated by column chromatography using silica gel (100−200 mesh). Prolonged irradiation, ∼14 h, did not show any new products as analyzed by ^{1}H NMR.

Fluorescence. A fluorimeter equipped with a 450 W Xe lamp was used for fluorescence studies. Dry solvents were used, and identical conditions were maintained for all the fluorescence measurements. The slit widths were 2 mm × 2 mm × 2 mm × 2 mm. The emission spectral range was 350−650 nm. All operations were at room temperature. The quantum yield of fluorescence was determined relative to that of 9,10-diphenylanthracene (0.9).[36]

---

(33) Vogel, A. I. *A textbook of Practical Organic Chemistry*; ELBS: London; p 755.

(34) Lock, G.; Walter, E. *Berestche* **1942**, *75*, 1158.

(35) (a) Scaiano, J. C. *Handbook of Organic Photochemistry*; CRC press: Boca Raton, FL, 1989; Vol. 1. (b) *Photochemistry*; Calvert, J. G., Pitts, J. N., Jr., Eds.; Wiley: New York, 1966; Chapter VII.

Quantum Yield of Isomerization. The quantum Yield of isomerization was determined in an applied photophysics model QYR-20 quantum yield reactor equipped with a 200 W Hg arc lamp. Solution filters were employed to isolate 300−350 nm light. Potassium ferrioxalate was used as an actinometer.[35] Conversions were kept below 7% in all measurements, and all experiments were conducted at room temperature.

Acknowledgment. We thank the Department of Science and Technology, New Delhi, for the financial support. K.M.B. thanks UGC for Senior Research Fellowship GVGR, and T.S. thanks CSIR for fellowship. A.S. thanks CSIR for financial support IICT Communication No. 4555

Supporting Information Available: ^{1}H NMR spectra for compounds **1**−**5**E and **1**−**4**Z; ^{13}C NMR, MS (EI), and HRMS spectra for **1**−**5**E and HPLC charts for compounds **1**−**3**. The material is available free of charge via Internet at http://pubs.acs.org.

JO000819V

---

(36) (a) Mciejewski, A.; Steer, R. P. *J. Photochem.* **1986**, *35*, 59. (b) Meech, S. R.; Phillips, D. *J. Photochem.* **1983**, *23*, 193.