

Photochemical *E*(*trans*)–*Z*(*cis*) Isomerization in 9-Anthraceneacrylic Esters

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Several (**1**–**6**) 9-anthraceneacrylic esters were synthesized in order to study photochemical *E*(*trans*)–*Z*(*cis*) isomerization. All of the compounds **1**–**6** underwent selective *E*-to-*Z* isomerization upon direct excitation (> 400 nm) in organic solvents, leading to the formation of a thermodynamically less stable *Z* isomer over 96%. Triplet sensitized isomerization selectively produces the *Z*-to-*E* isomer in over 98%. The higher quantum yield of isomerization observed in the triplet-sensitized *Z*-to-*E* isomerization process informs us that a "quantum chain" process is in operation. Fluorescence data generated on all compounds indicate that the *E*-to-*Z* isomerization process involves a charge-transfer or polar singlet excited state.

Photochemical *cis–trans* isomerization of stilbenes,[1–4] diphenyl polyenes,[5–7] vitamin-A, and vitamin-A related compounds[8,9] have been studied for the past several years. Mainly because of its role as (i) models for photoisomerization around a double bond related to biological systems,[10] (ii) a practical application of the reaction in vitamin A and vitamin D industrial processes,[11,12] and (iii) as possible candidates for electronic applications.[13,14] The photochemical *cis–trans* isomerization reaction in stilbene derivatives is still an interesting process to be studied.[15–17] The photochemical *cis–trans* isomerization of diarylethylenes is found to be interesting because of certain compounds exhibiting "one-way" *cis*-to-*trans* isomerization[18] involving a triplet excited state leading to quantum chain isomerization process. Indeed, less attention is being paid towards understanding the *cis-trans* isomerization process in arylethylenes derivatives, carrying electron-withdrawing end groups.[19–22] Here, we prepared several 9-anthraceneacrylic acid esters, arylethylenes carrying electron-withdrawing end groups (Scheme 1), to study photochemical *E–Z* isomerization process. All of the compounds prepared underwent wavelength-dependent *E*-to-*Z* isomerization involving a charge-transfer or polar singlet excited state. Fluorescence studies carried out indicate the polar or chargetransfer nature of the singlet excited state. Photochemical isomerization induced by the triplet sensitizers was found to be *Z*-to-*E* in all the compounds following quantum chain process. Photochemical isomerization carried out in a micelle environment highlights the restrictions imposed on the isomerization process.

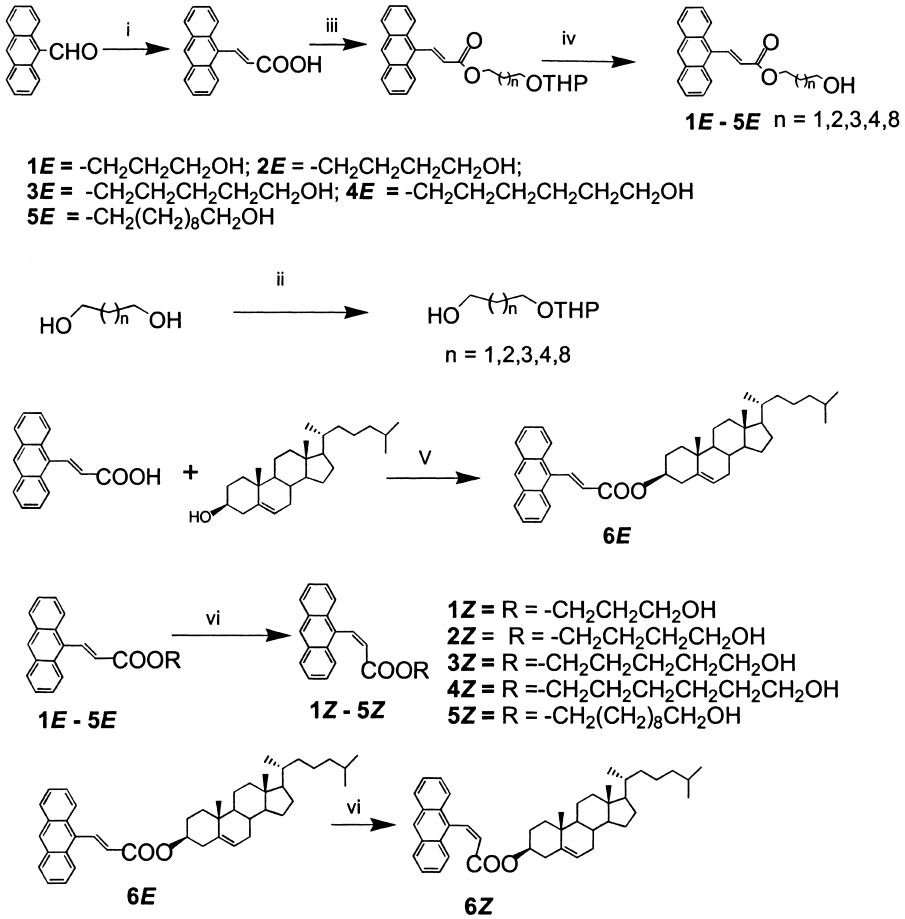
Results and Discussion

Photoisomerization upon Direct Excitation and Triplet Sensitization. All of the compounds **1***E*–**6***E* (Scheme 1) were synthesized and characterized by spectral means (experimental section). Compounds **1***E*–**6***E* were dissolved in a suitable solvent and irradiated using 450 W Hg lamp with filters (> 400 nm) and also with RUL-3500 (~350 nm) in a Rayonet reactor. The obtained results are given in Table 1. The isomer

Table 1. Isomer Composition upon Direct Excitation of **1***E*–**6***E*

Compound	Solvent	Time/min	λ_{ex}/nm	*E*/%	*Z*/%
1*E*	CH_3CN	05	> 400	42	58
		10	> 400	20	80
		20	> 400	04	96
		20	> 300	56	44
		20	~350	52	48
	MeOH	05	> 400	44	66
		20	> 400	04	96
		20	> 300	58	42
		20	~350	56	44
2*E*	CH_3CN	20	> 400	04	96
		20	> 300	56	44
	MeOH	20	> 400	04	96
3*E*	CH_3CN	20	> 400	04	96
		20	> 300	56	44
	MeOH	20	> 400	04	96
4*E*	CH_3CN	20	> 400	04	96
		20	> 300	56	44
	MeOH	20	> 400	04	96
5*E*	CH_3CN	20	> 400	04	96
		20	> 300	56	44
	MeOH	20	> 400	04	96
6*E*	CH_3CN	20	> 400	04	96
		20	> 300	56	44
	MeOH	20	> 400	04	96

Nitrogen bubbled 0.0005 M solutions were irradiated; for > 400 nm, 450 W Hg lamp with filters;[28] for > 300 nm, 450 W Hg lamp with Pyrex filter; for ~350 nm, Rayonet RUL-3500 lamps; analysis by reverse phase HPLC.



Scheme 1. Reagents and conditions: i) malonic acid, pyridine and piperidine at steam bath for 4 h, 125–130 °C for 1 h and at 180–190 °C for 30 min; ii) 3,4-dihydropyran, $CHCl_3$, 0.01 mol $SnCl_2{\cdot}2H_2O$ at r.t. for 24 h; iii) monoprotected diol, DCC, DMAP, dry CH_2Cl_2, under N_2 atmosphere for 3 h; iv) I_2/MeOH reflux for 5 h; v) DCC, DMAP, dry CH_2Cl_2, under N_2 atmosphere for 3 h; vi) hv, N_2 bubbled and irradiated using 450 W Hg arc lamp with suitable filters ($>$ 400 nm) for 45 min.

composition was monitored by HPLC. All of the compounds, **1***E*–**6***E* underwent very efficient *E*-to-*Z* isomerization upon direct excitation using $>$ 400 nm radiation (Table 1). The isomer composition was found to be different under ~350 nm (RUL-3500; Rayonet reactor) and $>$ 300 nm (450 W Hg lamp; pyrex filter) irradiations (Table 1). The photoisomerization of **1***E* was monitored at various time intervals ($>$ 400 nm irradiation), and the result is the accumulation of $>$ 96% of the *Z isomer*. These studies indicate that the *E*-to-*Z* selectivity is wavelength dependent. The reported isomer composition also reflects the photostationary state composition under the given photolytic conditions. Photochemical *E*–*Z* isomerization was conducted in CTAB and SDS micellar environments. The photostationary state composition was 30:70 (*E*:*Z*) upon direct excitation, ($>$ 400 nm; Table 2) in a micellar environment. The wavelength ($>$ 400 nm) dependent *E*-to-*Z* selectivity noticed in organic solvents (Table 1) is not observable in a micellar environment (Table 2).

Triplet sensitized reactions were planned so as to understand and differentiate the triplet/singlet reactivities. The triplet sensitizers employed were visible absorbing dyes, and could be selectively excited in the presence of substrates **1***E*–**6***E*. The triplet energy of the selected sensitizers (Table 3) fell in the region of 163–180 kJ/mol. The triplet sensitization studies conducted on **1***E*–**6***E* were found to be ineffective and there was no *E*- to-*Z* isomerization observed. The *Z* isomers of **1***Z*–**6***Z* were found to undergo efficient, almost complete one-way conversion to the *E* isomer (Table 3). Triplet sensitized isomerization studies establishes that the triplet energy of the substrates are in the range of $>$ 163 kJ/mol, and that it is effective in bringing *Z*-to-*E* conversion only.

The quantum yields of the isomerizations were determined for *E*-to-*Z*, *Z*-to-*E* upon direct excitation and triplet sensitized *Z*-to-*E* (Table 4) in methanol solvent, and also for **1***E*-to-*Z* and **6***E*-to-*Z*. The quantum yield of isomerization upon direct excitation is fairly fine, and represents that it is efficient. The quantum yield of *Z*-to-*E* isomerization upon triplet sensitization is interesting because the values are well above unity, which is consistent with the one-way isomerization concept developed earlier.[27]

Absorption and Fluorescence Studies. Absorption and fluorescence studies were conducted to understand the nature of the excited state. Absorption spectra were recorded for all of the compounds in various solvents, CTAB & SDS micelles. The generated data are compiled in Table 5. The absorption maximum did not change upon changing the medium (Table

Table 2. Isomer Composition Upon Direct Excitation of **1***E*–**6***E* in Micelles

Compound	Micelle	λ_{ex}/nm	*E*/%	*Z*/%
1*E*	CTAB	> 400	22	78
		> 300	55	45
	SDS	> 400	26	74
		> 300	52	48
2*E*	CTAB	> 400	24	76
		> 300	56	44
	SDS	> 400	25	75
		> 300	55	45
3*E*	CTAB	> 400	23	77
		> 300	54	46
	SDS	> 400	22	78
		> 300	56	44
4*E*	CTAB	> 400	26	74
		> 300	58	42
	SDS	> 400	24	76
		> 300	54	46
5*E*	CTAB	> 400	27	73
		> 300	55	45
	SDS	> 400	26	74
		> 300	54	46
6*E*	CTAB	> 400	22	78
		> 300	58	42
	SDS	> 400	23	77
		> 300	57	43

Nitrogen bubbled 0.001 M solutions were irradiated for 45 min; for > 400 nm, 450 W Hg lamp with filters;[28] for > 300 nm, 450 W Hg lamp with pyrex filter; analysis by reverse phase HPLC; the concentration of CTAB & SDS was kept well above the corresponding CMCs.

Table 3. Isomer Composition Upon Triplet Sensitization of **1***Z*–**6***Z*, **1***E* and **6***E*

Com-pound	Sensitizer	λ_{max}/nm	ET-Sens. kJ/mol	*E*/%	*Z*/%
1*Z*	Rose Bengal	550	~163	98	02
	Eosin	515	~180	98	02
2*Z*	Rose Bengal	550	~163	98	02
	Eosin	515	~180	98	02
3*Z*	Rose Bengal	550	~163	98	02
	Eosin	515	~180	98	02
4*Z*	Rose Bengal	550	~163	98	02
	Eosin	515	~180	98	02
5*Z*	Rose Bengal	550	~163	98	02
	Eosin	515	~180	98	02
6*Z*	Rose Bengal	550	~163	98	02
	Eosin	515	~180	98	02
1*E*	Rose Bengal	550	~163	No isomerization	
	Eosin	515	~180	No isomerization	
6*E*	Rose Bengal	550	~163	No isomerization	
	Eosin	515	~180	No isomerization	

Nitrogen bubbled 0.001 M methanol solutions with 0.001 M sensitizer were irradiated for 15 min using 450 W Hg lamp with filters, > 500 nm; analysis by reverse phase HPLC.

5), which informs that there is not much ground- state and medium interaction.

Table 4. Quantum Yield of Photoisomerization of **1***E*–**6***E* and **1***Z*–**6***Z*

Compound	Φ_{iso}	Φ_{iso}	Φ_{iso} Triplet Sens.
	E Z	*Z E*	*Z E*
1	0.21	0.22	1.64
2	0.22	0.23	1.82
3	0.21	0.23	1.56
4	0.22	0.24	1.66
5	0.22	0.25	1.72
6	0.23	0.26	1.86
1	0.11 (hexane)	—	—
	0.14 (benzene)	—	—
6	0.12 (hexane)	—	—
	0.16 (benzene)	—	—

Nitrogen bubbled 0.001 M methanol solutions with 0.001 M sensitizer were irradiated in a merry-go-round of QYR-20 quantum yield reactor; the 366 nm line of the 200 W Hg arc lamp was isolated to irradiate; analysis by reverse phase HPLC.

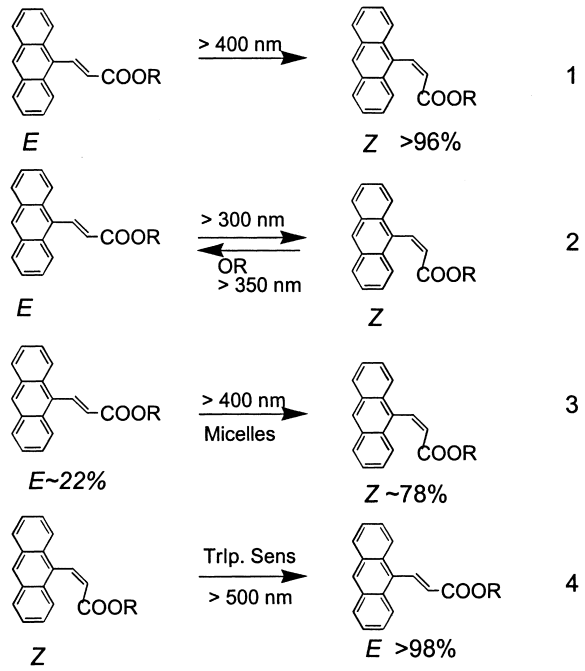
The *E* isomer has broad absorption in the 340 to 400 nm region,. and the *Z* isomer has relatively structured absorption in the same region (Figs. 1 & 2). Fluorescence was recorded at room temperature for all of the compounds. The fluorescence emission maxima and quantum yield of fluorescence data are given in Table 5, and the fluorescence spectra for three compounds are displayed in Figs. 3–5. The fluorescence emission maximum showed a red shift of ~20 nm (Table 5) upon changing the nonpolar solvent hexane to polar solvent acetonitrile/methanol/micelles. There was a decrease in the quantum yield of fluorescence upon changing the nonpolar hexane solvent to polar acetonitrile/methanol/micelles. The red shift observed in the emission maxima and the decrease in the quantum yield of the fluorescence upon changing the solvent polarity throws light on the singlet excited state as being charge-transfer or polar in nature. There was a slight increase in the fluorescence quantum yield for all compounds in CTAB & SDS micelles compare to polar solvents acetonitrile/methanol. There was not much change observed in the fluorescence spectrum of *Z* isomers (Figs. 3–5) compared to *E* isomers.

Photoisomerization and Nature of the Singlet Excited State. Table 1 reveals that all of the compounds **1***E*–**6***E* upon direct excitation using > 400 nm radiation produced the thermodynamically less stable *Z* isomer > 96% (Scheme 2, reaction. 1). The highly selective *E*-to-*Z* isomerization is attributed to the higher light absorption capabilities of the *E* isomer under the irradiation conditions.[30–32] This explanation becomes more clear by saying that upon changing the wavelength of irradiation, both isomers absorb light and give almost a 1:1 photostationary state mixture (Table 1; Scheme 2, reaction. 2; Fig. 1 and 2). The quantum yield of the isomerization data (Table 4) also suggests that both *E*-to-*Z* and *Z*-to-*E* are equally efficient processes from the singlet excited manifold. The *E*-to-*Z* isomerization originates from the singlet excited state, since the triplet excitation is ineffective in producing the *Z* isomer from the *E* isomer. Triplet sensitization is effective in converting the *Z* isomer to the *E* isomer only (Scheme 2, reaction. 4; Table 3). The quantum yield of isomerization from the triplet

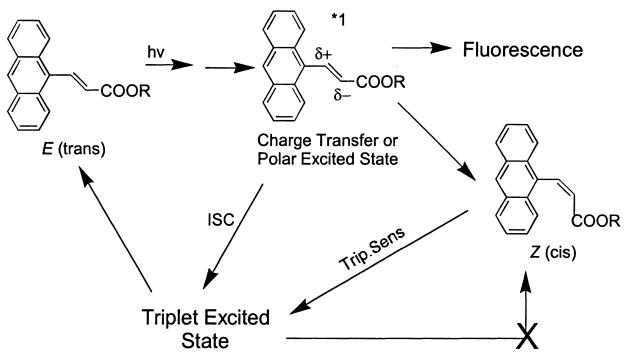
Table 5. Absorption and Fluorescence Data for **1***E*–**6***E* and **1***Z*, **3***Z*, **6***Z*

Compound	Solvent	λ_{abs}/nm	λ_{fluo}/nm	Φ_{flu}
1*E*	Hexane	388	488	0.51
	MeOH	388	508	0.08
	CH_3CN	388	508	0.09
	SDS	388	508	0.16
	CTAB	388	508	0.12
1*Z*	Hexane	385	488	0.34
	CH_3CN	385	508	0.04
2*E*	Hexane	387	492	0.49
	MeOH	387	512	0.09
	CH_3CN	387	516	0.07
	SDS	387	512	0.26
	CTAB	387	516	0.22
3*E*	Hexane	388	484	0.56
	MeOH	388	508	0.14
	CH_3CN	388	508	0.11
	SDS	388	508	0.28
	CTAB	388	508	0.21
3*Z*	Hexane	385	484	0.32
	CH_3CN	385	508	0.08
4*E*	Hexane	386	488	0.50
	MeOH	386	512	0.11
	CH_3CN	386	512	0.09
	SDS	386	512	0.18
	CTAB	386	512	0.17
5*E*	Hexane	388	488	0.47
	MeOH	388	508	0.12
	CH_3CN	388	508	0.09
	SDS	388	508	0.19
	CTAB	388	508	0.12
6*E*	Hexane	389	488	0.70
	MeOH	389	520	0.11
	CH_3CN	389	520	0.12
	SDS	389	512	0.18
	CTAB	389	512	0.16
6*Z*	Hexane	385	488	0.49
	CH_3CN	385	520	0.08

0.00001 M Solutions were used for measuring the fluorescence at room Temperature; quantum yield of fluorescence were determined using 9,10-diphenylanthracene (Φ_{flu} = 0.9) as standard,[29] experimental error ±10%.



Scheme 2.



Scheme 3.

state for all compounds was found to be higher than unity (Table 4). This is consistent with an earlier observation[33] that the triplet state in anthrylethylenes induces a quantum chain process leading to higher quantum-yield values. More interestingly, the *E*-to-*Z* selectivity observed (Table 1; Scheme 2, reaction. 1) for all compounds **1***E*–**6***E* in the organic solvent phase is not the case when a micellar (CTAB, SDS; Table 2; Scheme 2, reaction. 3) medium was introduced. Although *Z* is the preferred isomer (Scheme 2, reaction. 3), the % of *Z* isomer formed was less (Scheme 2, reaction. 3; Table 2). The decrease in the selectivity of *E*-to-*Z* isomerization may be due to restrictions imposed by the micellar environment, exerting a hindrance for rotation of the double bond, or it may promote the possible formation of a triplet state. UV–visible absorption and fluorescence studies were carried out (Table 5) in order to understand the nature of the singlet excited state. The UV–visible absorption data indicate that there is not much ground state and medium interactions in all of the substrates (Table 5). The red shift observed in the emission maxima (fluorescence solvatochromism)[34] for all of compounds **1***E*–**6***E* (Table 5) by changing the solvent polarity and solvent polarity dependent quantum yield of *E*-to-*Z* photoisomerization indicates that the singlet excited state has a considerable amount of charge-transfer or polar character,[35–36] and is responsible for the *E*-to-*Z* photoisomerization. The very high *Z* isomer formation also suggests that the charge-transfer or polar singlet excited state may not undergo intersystem crossing[37] to form a triplet state.

Mechanism. The proposed mechanism for photochemical *E*–*Z* isomerization studies conducted for **1***E*–**6***E* is depicted in Scheme 3. The light absorption (> 400 nm) by the *E* substrate, followed by structural changes in the molecule, leads to the formation of a charge-transfer (CT) or polar singlet excited state. The formation of a CT state was confirmed by fluorescence studies (Table 5). The thus-formed CT or polar excited state would undergo rotation around the double bond to give

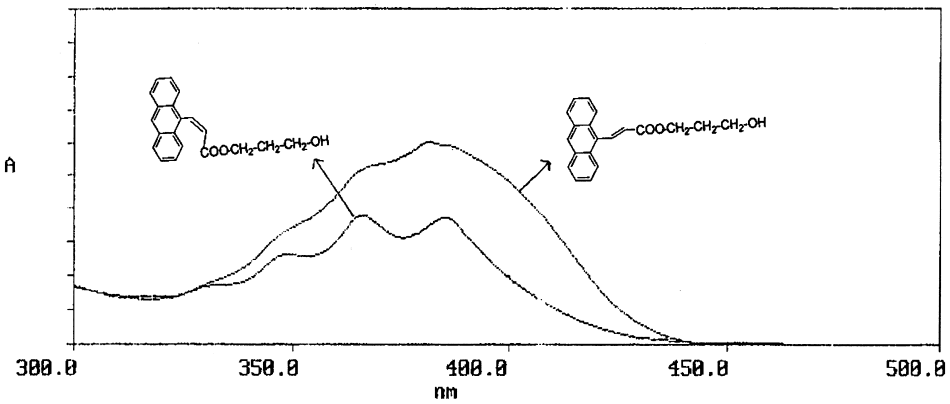


Fig. 1. UV-visible absorption spectra of **1***E* and **1***Z* in hexane, at 10^{-5} M.

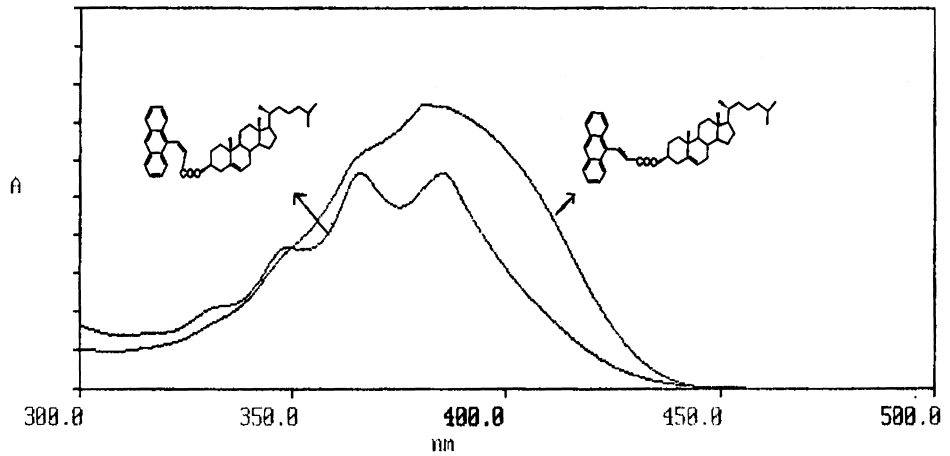


Fig. 2. UV-visible absorption spectra of **6***E* and **6***Z* in hexane, at 10^{-5} M.

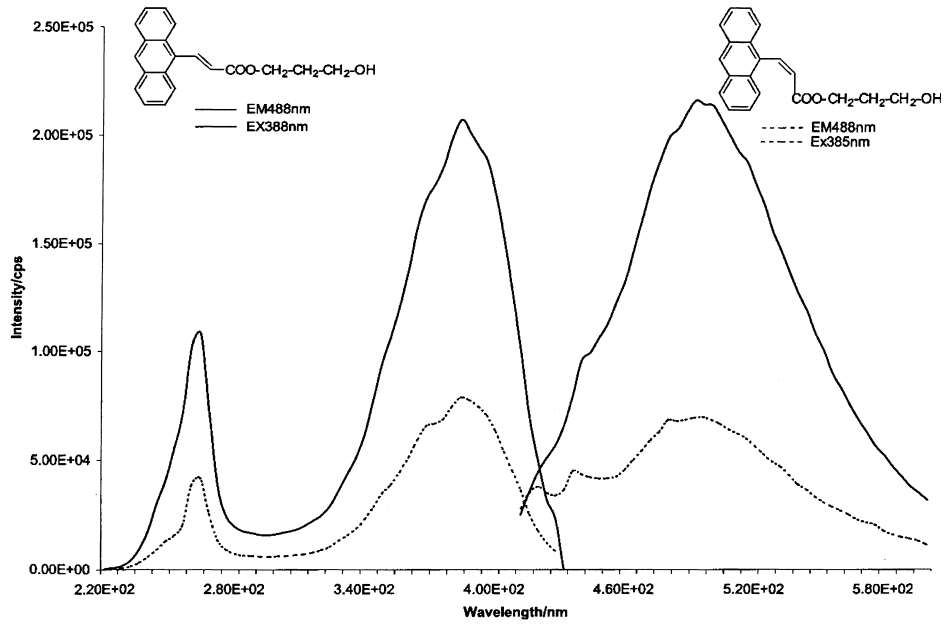


Fig. 3. Fluorescence and fluorescence excitation spectra of **1***E* (——) and **1***Z* (·····) in hexane, at 10^{-5} M.

the *Z* isomer. The formation of a triplet state from the CT or polar state may not be possible,[37] since very high *E*-to-*Z* selectivity was observed, and the *E* triplet did not give the *Z* isomer.[19,27,33] The *Z* isomer was found to undergo efficient one-way *Z*-to-*E* isomerization from the triplet state.

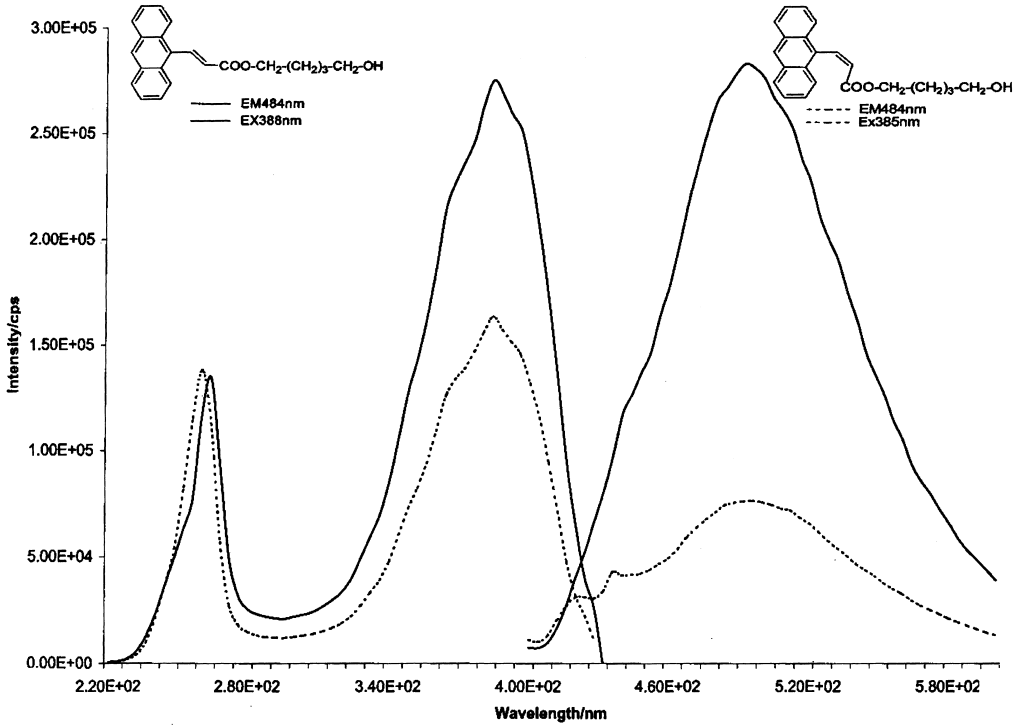


Fig. 4. Fluorescence and fluorescence excitation spectra of **3***E* (——) and **3***Z* (·····) in hexane, at 10^{-5} M.

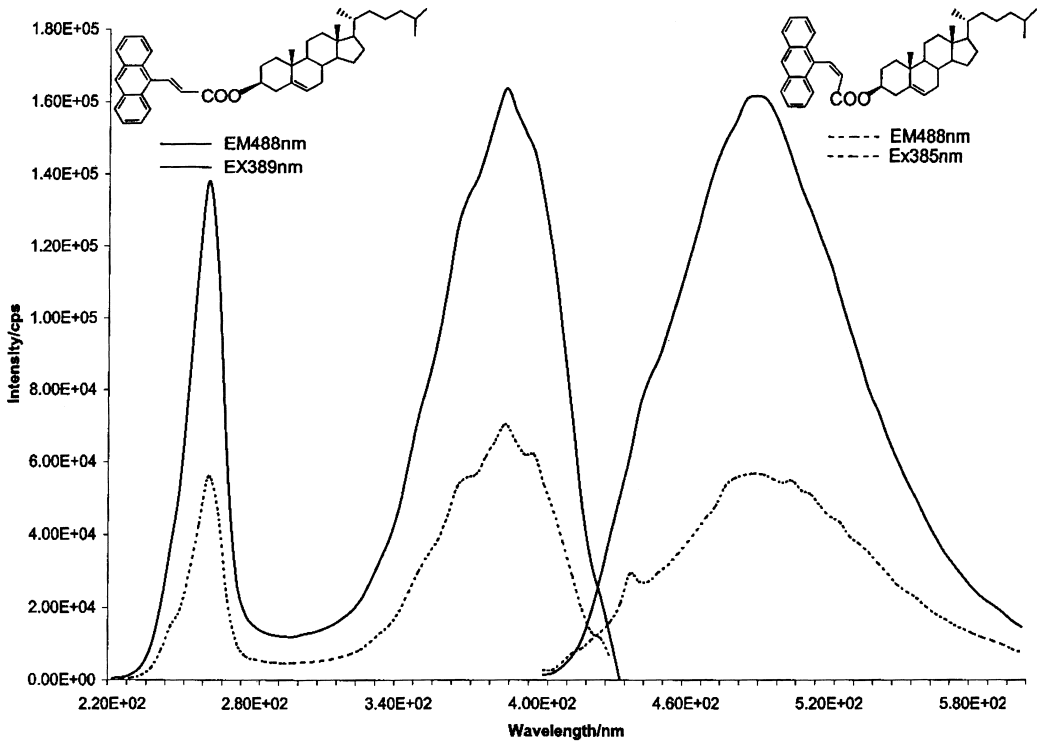


Fig. 5. Fluorescence and fluorescence excitation spectra of **6***E* (——) and **6***Z* (·····) in hexane, at 10^{-5} M.

Conclusions

In conclusion, we synthesized several (**1***E*–**6***E*) 9-anthraceneacrylic esters to study photochemical *E*–*Z* isomerization. All of compounds **1***E*–**6***E* underwent selective *E*-to-*Z* isomerization upon direct excitation ($>$ 400 nm). Changing the wavelength of irradiation to $>$ 300 nm or $\sim$350 nm led to the photo stationary state equilibration of two isomers. Triplet sensitization produces only *Z*-to-*E* isomerization. The higher quantum yields observed in the triplet induced isomerization process is indicative that quantum chain isomerization is in operation. Fluorescence studies carried out on compounds **1***E*–

6*E* showed that a charge-transfer or polar excited state is involved in the direct excitation reactions. Photochemical isomerization studies carried out in a micellar environment are interesting.

Experimental

General Procedures. A Perkin-Elmer Lambda-2 UV-visible spectrometer was used to obtain the absorption spectra. A SPEX Fluorolog 0.22 m fluorimeter was used for fluorescence measurements. Mass spectra were recorded on a VG Micro Mass 7070H instrument. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a FT-200 MHz instrument in a $CDCl_3$ solvent. A Shimadzu LC-8 HPLC system with a CR-8 integrator was used for HPLC analysis. An Applied Photo Physics QYR-20 Quantum Yield Reactor coupled with a 200 W Hg lamp was used to determine the quantum yields. All other chemicals were purchased locally and also from Aldrich/Fluka.

Photolysis. A Rayonet reactor equipped with RUL-3500 (~350 nm) lamps and a 450 W medium pressure Hg arc lamp along with suitable filters were used for irradiation. All reactions were monitored by HPLC using a C-18 reverse-phase 5μ, 0.5 cm/25 cm column. In a typical experiment 10 mL of a 0.0005 M N_2 bubbled solution of **1***E*–**6***E* was used for irradiation. After irradiation the products were characterized by comparing with authentic samples. Triplet sensitized reactions were carried out using a mixture of a sensitizer (0.001 M) and a substrate (0.001 M) in a solvent (N_2 bubbled), which was irradiated using a 450 W Hg lamp with suitable filters (> 500 nm).

Preparative photoisomerization was carried out using 100 mg of **1***E*–**6***E* in 150 ml methanol or acetonitrile solvent, bubbled nitrogen and irradiated using a 450 W Hg lamp with suitable filters (> 400 nm) for 45 min; the reaction was monitored by HPLC and the *Z* isomer was isolated by silica-gel column chromatography. The product was characterized by ^{1}H NMR and other spectral data.

Fluorescence: A SPEX-Fluorolog fluorimeter equipped with a 450 W Xenon lamp was used to generate fluorescence data. Dry solvents were used, identical conditions were employed for all of the fluorescence measurements and 9,10-diphenyl anthracene was used as fluorescence standard (Φ_{flu} = 0.9) for determining the quantum yield of the fluorescence. The slit widths were 2 × 2 × 2 × 2 and the emission spectral range was 400–700 nm. All operations were carried out at room temperature.

Preparation of 9-Anthraceneacrylic Acid.[23] A mixture of 2.06 g 9-Antraldehyde, 1.4 g of malonic acid, 0.5 mL of piperdine and 3 ml of pyridine was heated on a steam bath for four hours; the solution was then refluxed for one hour in an oil-bath at 125–135 °C. The mixture was cooled, diluted with 20 mL of water and soon solidified. The orange solid weighed 3.08 g. When dry and it began to melt with decomposition at about 145 °C, it evidently consisted rarely of the substituted malonicacid. The material was heated for 30 min. at 180–190 °C to eliminate any carbon dioxide. The dark-red melt solidified upon cooling, and was purified by recrystalization from 12 mL of chlorobenzene containing 0.5 mL of glacial acetic acid. 9-Anthraceneacrylic acid formed as bright-yellow needles (mp 235.5–237.5 °C, yields 2.05 g (82.6%)). A second recrystalization gave a first crop of 1.80 g, mp 246–247 °C. Spectral data: ^{1}H-NMR δ 6.3–6.45 (d, 1H, J = 15.4 Hz), 7.4–7.6 (m, 4H), 7.9–8.1 (m, 2H), 8.2–8.35 (m, 2H), 8.4–8.45 (s, H), 8.5–8.65 (d, 1H, J = 15.4 Hz); MS *m*/*z* 248 (M^+), 203, 101, 83.

Preparation of Monoprotected Diols.[24] The diol (100 mmol) and 3,4 di-hydropyran (100 mmol) were stirred in solvent $CHCl_3$ (200 mL), followed by the addition of 0.001 mole (1 mole%) of $SnCl_2{\cdot}2H_2O$ at room temperature for 24 hours. The $CHCl_3$ layer was separated by decantation and concentrated under reduced pressure. The product was separated by column chromatography over silica gel while eluting with pet ether for the diprotected tetra hydro pyrenyl ether (yield 20–25%) and pet ether, EtOAc (80:20) for a monoprotected diol yield of 75–80%.

Esterification of 9-Anthraceneacrylic Acid.[25] After a mixture of 9-anthraceneacrylic acid (10 mmol), dichloromethane (dry; 10 mL) 2 drops of dry DMF, DMAP (30–90 mg) and monoprotected diol (20–30 mmol) was cooled to 0 °C, DCC (10 mmol) was added and the mixture was stirred at 0 °C for 5 min and then 3h at rt. The filtered and dichloromethane solution was washed thrice with 0.5 M HCl, then with $NaHCO_3$ solution and dried over Na_2SO_4. The solvent was removed and the residue was purified by silica-gel column chromatography using 1:1 CH_2Cl_2/Hexane to 100% CH_2Cl_2 to obtain protected ester in 80% yield.

Deprotection of 9-Anthraceneacrylic Acid Protected Ester.[26] A mixture of protected 9-anthraceneacrylic ester (10 mmol), methanol (20 mL) and iodine (0.1 mmol) was heated under reflux for 5 h. After methanol was removed, the residue was taken in ethyl acetate and washed with hypo, brine and water and dried over Na_2SO_4. The solvent was removed and the product was purified by silica-gel column chromatography using hexane/EtOAc (50:50) to obtain 9-anthraceneacrylic ester, yield 75%.

The above procedures were repeated to synthesize other derivatives (Scheme 1). The cholesterol derivative **6***E* was synthesized by adopting an esterification procedure. *Z* isomers were prepared (**1***Z*–**6***Z*) by the preparative photoisomerization procedure (experimental section, photolysis) and isolated by silica-gel column chromatography. The product was characterized by ^{1}H-NMR and other spectral data. The spectral data for **1***E*–**6***E* & **1***Z*–**6***Z* are given below.

3-Hydroxypropyl (*E*)-9-Anthraceneprop-2-enoate (1*E*). A Semisolid; ^{1}H NMR ($CDCl_3$) δ 2.1 (m, 2H), 3.8 (t, 2H), 4.5 (t, 2H), 6.4–6.5 (d, 1H, J = 16.5 Hz), 7.4–7.6 (m, 4H), 8.05 (m, 2H), 8.2–8.3 (m, 2H), 8.4–8.5 (s, 1H), 8.7 (d, 1H, J = 16.5 Hz); MS 306 (M^+), 231 202, 99; HRMS *m*/*z* calculated for $C_{20}H_{18}O_3$ 306.125595, found 306.125634; UV 388 nm (ε 6400).

3-Hydroxypropyl (*Z*)-9-Anthraceneprop-2-enoate (1*Z*). A semisolid; ^{1}H NMR ($CDCl_3$) δ 1.15 (m, 2H), 2.7 (t, 2H), 3.8 (t, 2H), 6.65 (d, 1H, J = 14.28 Hz), 7.4–7.5 (m, 4H), 8 (m, 4H), 8.4 (s, 1H), 7.8 (d, 1H, J = 14.28 Hz); Mass: 306 (M^+), 231, 202, 99; UV 385 nm (ε 5500).

4-Hydroxybutyl (*E*)-9-Anthraceneprop-2-enoate (2*E*). A semisolid; ^{1}H NMR ($CDCl_3$) δ 1.7–2 (m, 4H), 3.8 (t, 2H), 4.4 (t, 2H), 6.4–6.5 (d, 1H, J = 15 Hz), 7.4–7.6 (m, 4H), 8–8.1 (m, 2H), 8.2–8.35 (m, 2H), 8.5 (s, 1H), 8.6–8.8 (d, 1H, J = 15 Hz); MS *m*/*z* 320 (M^+), 248, 231, 203, 143, 101; HRMS *m*/*z* calculated for $C_{21}H_{20}O_3$ 320.141245, found 320.142461; UV 387 nm (ε 6400).

4-Hydroxybutyl (*Z*)-9-Anthraceneprop-2-enoate (2*Z*). A semisolid; ^{1}H NMR ($CDCl_3$) δ 0.5–0.7 (m, 2H), 0.7–0.9 (m, 2H), 3–3.2 (t, 2H), 3.5–3.7 (t, 2H), 6.5–6.7 (d, 1H, J = 14.3 Hz), 7.4–7.6 (m, 4H), 7.9–8.1 (m, 4H), 8.4 (s, 1H), 7.8–7.9 (d, 1H, J = 14.3 Hz); MS *m*/*z* 320 (M^+), 248, 231, 203, 143, 101; UV 385 nm (ε 5500).

5-Hydroxypentyl (*E*)-9-Anthraceneprop-2-enoate (3*E*). A semisolid; ^{1}H NMR ($CDCl_3$) δ 1.4–1.9 (m, 6H), 3.5–3.7 (t, 2H), 4.2–4.4 (t, 2H), 6.3–6.5 (d, 1H, J = 16 Hz), 7.35–7.55 (m, 4H),

7.9–8 (m, 2H), 8.1–8.3 (m, 2H), 8.3–8.4 (s, 1H), 8.5–8.7 (d, 1H, J = 16 Hz); MS *m/z* 334 (M^+), 248, 231,204, 99; HRMS *m/z* calculated for $C_{22}H_{22}O_3$ 334.156895, found 334.158432; UV 388 nm (ε 6100).

5-Hydroxypentyl (*Z*)-9-Anthraceneprop-2-enoate (3*Z*). A semisolid; ^{1}H NMR ($CDCl_3$) δ 0.4–0.5 (m, 2H), 0.7–0.85 (m, 2H), 1–1.2 (m, 2H), 3.15–3.3 (t, 2H), 3.5–3.7 (m, 2H), 6.5–6.65 (d, 1H, J = 10.7 Hz), 7.4–7.55 (m, 4H), 7.7–7.8 (m, 4H), 8.45 (s, 1H), 7.7–7.8 (d, 1H, J = 10.7 Hz); MS *m/z* 334 (M^+), 248, 231,204, 99; UV 385 nm (ε 5400).

6-Hydroxyhexyl (*E*)-9-Anthraceneprop-2-enoate (4*E*). A semisolid; ^{1}H NMR ($CDCl_3$) δ 1.2–1.9 (m, 8H), 3.6–3.75 (t, 2H), 4.3–4.4 (t, 2H), 6.3–6.5 (d, 1H, J = 15.4 Hz), 7.4–7.6 (m, 4H), 7.9–8.1 (m, 2H), 8.3–8.3 (m, 2H), 8.4–8.5 (s, 1H), 8.5–8.7 (d, 1H, J = 15.4 Hz); MS 348 (M^+), 231, 203, and 99; HRMS *m/z* calculated for $C_{23}H_{24}O_3$ 348.172545, found 348.171221; UV 386 nm (ε 6200).

6-Hydroxyhexyl (*Z*)-9-Anthraceneprop-2-enoate (4*Z*). A Semisolid; ^{1}H NMR ($CDCl_3$) δ 0.4–0.8 (m, 8H), 3.4–3.5 (t, 2H), 3.6–3.7 (m, 2H), 6.6–6.7 (d, 1H, J = 12.5 Hz), 7.4–7.6 (m, 4H), 7.7–7.8 (d, 1H, J = 10.7 Hz), 8–8.1 (m, 4H), 8.4 (s, 1H); MS *m/z* 348 (M^+), 231, 203, and 99; UV 385 nm (ε 5300).

10-Hydroxydecyl (*E*)-9-Anthraceneprop-2-enoate (5*E*). A solid mp 121 °C; ^{1}H NMR ($CDCl_3$) δ 1.2–1.9 (m, 16H), 3.6–3.7 (t, 2H), 4.3–4.4 (t, 2H), 6.4–6.55 (d, 1H, J = 16.3 Hz), 7.47–7.65 (m, 4H), 8–8.15 (m, 2H), 8.22–8.35 (m, 2H), 8.5 (s, 1H), 8.6–8.75 (d, 1H, J = 16.3 Hz), MS 404 (M^+), 249, 232, 204, 55; HRMS *m/z* calculated for $C_{27}H_{32}O_3$ 404.235788 found 404.235788; UV 388 nm (ε 6700).

10-Hydroxydecyl (*Z*)-9-Anthraceneprop-2-enoate (5*Z*). A solid mp 110 °C ; ^{1}H NMR ($CDCl_3$) δ 0.1–1.85 (m, 18H), 2.4–2.7 (t, 2H), 6.5–6.7 (d, 1H, J = 14.28 Hz), 7.4–7.55 (m, 4H), 7.8–7.9 (d, 1H, J = 14.28 Hz), 7.9–8.15 (m, 4H), 8.4 (s, 1H); MS 404 (M^+), 249, 232, 204, 55; UV 385 nm (ε 5800).

Cholest-5-en-3β-yl (*E*)-9-Anthraceneprop-2-enoate (6*E*). A solid mp 163.5 °C ; ^{1}H NMR ($CDCl_3$) δ 0.6–2.1 (m, 39 Hs), 2.4–2.55 (m, 2H), 3.1–3.3 (m, H), 4.75–4.95 (m, 2H), 5.4–5.5 (m, H), 6.3–6.45 (d, 1H, J = 15.78 Hz), 7.4–7.6 (m, 4H), 7.9–8.05 (m, 2H), 8.2–8.3 (m, 2H), 8.4 (s, 1H), 8.55–8.7 (d, 1H, J = 15.78 Hz); FAB MS *m/z* 617 (M^+), 369, 281, 245, 231, 202; UV 389 nm (ε 6900).

Cholest-5-en-3β-yl (*Z*)-9-Anthraceneprop-2-enoate (6*Z*). A solid mp 154 °C; ^{1}H NMR ($CDCl_3$) δ 0.4–1.9 (m, 42 Hs), 4.1–4.2 (m, H), 5.1 (m, 2H), 6.6 (d, 1H, J = 12.3 Hz), 7.4–7.5 (m, 4H), 7.8 (d, 1H, J = 12.3 Hz), 8–8.1 (m, 4H), 8.45 (s, 1H); FAB MS *m/z* 617 (M^+), 369, 281, 245, 231, 202; UV 385 nm (ε 5700).

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References

1 a) J. Saltiel et al., in "Org. Photochemsitry," ed by O. L. Chapman, Marcel Dekker, New York (1973), vol. 3, p. 1. b) J. Saltiel, and J. L. Charlton, in "Rearrangements in Ground and Excited States," ed by P. Demayo, Academic press, New York (1980), vol. 3, p. 5.

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

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

4 H. Garner and H. J. Kuhn, *Adv. Photochem.*, **19**, 1 (1995).

5 L. Zechmeister, *Experientia*, **10**, 1 (1954).

6 J. Saltiel and Y. P. Sun, in "Photochromism: Molecules, and Systems," ed by H. Durr and H. Bonos-Laurent, Elsevier, Amsterdam (1990), p. 64.

7 G. Orlando, F. Zerbetto, and M. Zgierski, *Chem. Rev.*, **91**, 867 (1991).

8 R. S. H. Liu, and A. E. Asato, *Tetrahedron*, **40**, 1931 (1984).

9 M. Mouseron-Canet, *Methods Enzymol.*, **58**, 591 (1971).

10 R. S. H. Liu and Y. Schichida, in "Photochemistry in Organized and Constrained Media," ed by Ramamurthy, VCH Publishers (1991), Chapter 18, p. 18.

11 A. M. Braun, M. J. Maurette, and E. Oliveror, "Photochemical Technology," Wiley (1991), Chapter 12, p. 500.

12 Kirk-Other Encyclopedia of Chemical Technology, 4th ed, Wiley (1996), vol. 18, p. 799.

13 "Photochromism: Molecules and Systems," ed by H. Durr and H. Bous-Laurent, Elsevier, Amsterdam (1990).

14 B. L. Feringa, *Tetrahedron*, **49**, 8267 (1993).

15 F. D. Lewis, and R. S. Kalgutkar, *J. Phys. Chem. A*, **105**, 285 (2001).

16 K. L. Wieners and J. F. Kaufman, *J. Phys. Chem. A*, **105**, 823 (2001).

17 P. Rademaches, A. L. Marzinzik, K. Kowski, and M. E. Weiss, *Eur. J. Org. Chem.*, **1**, 121 (2001).

18 T. Arai and K. Tokumaru, *Adv. Photochem.*, **20**, 1 (1995).

19 K. Mani Bushan, G. Venugopal Rao, T. Soujanya, V. Jayathirtha Rao, S. Saha, and A. Samantha, *J. Org. Chem.*, **66**, 681 (2001).

20 F. D. Lewis and J. M. Denari, *J. Photochem. Photobiol. A*, **105**, 151 (1996).

21 H. Tanaka, K. Honda, and N. Suzuki, *J. Chem. Soc. Chem. Commun.*, **1977**, 506.

22 V. Jayathirtha Rao, in "Organic Photochemistry: Molecular & Supramolecular Photochemistry," ed by, V. Ramamurthy, and K. Schanze, Marcel Dekker, New York (1999), vol. 3, Chapter IV, p. 169.

23 C. H. Davis, and M. Karmack, *J. Org. Chem.*, **12**, 76 (1947).

24 J. Davies, U. T. Bhalerao, and B. V. Rao, *Synth. Commun.*, **29**, 1679 (1999).

25 B. Neiser, and W. Steglich, *Angew. Chem. Intl. Ed. Eng.*, **17**, 522 (1978).

26 J. S. Yadav, and B. V. S. Reddy, *Chem. Lett.* **1999**, 857.

27 T. Arai, T. Karatsu, H. Sakuragi, and K. Tokumary, *Tetrahedron Lett.*, **24**, 2873 (1983).

28 J. C. Scaiano, "Hand Book of Organic Photochemistry," CRC press, Boca Raton, FL (1989).

29 A. Maciejewski and R. P. Steer, *J. Photochem*, **35**, 59 (1986).

30 N. J. Turro and V. Ramamurthy, *Chem. Rev.*, **78**, 125 (1979).

31 H. J. C. Jacobs, and E. Havinga, *Adv. Photochem.* **11**, 305 (1979).

32 W. G. Dauben and R. B. Philips, *J. Am. Chem. Soc.*, **104**, 355 (1982).

33 K. Tokumaru and T. Arai, *Bull. Chem. Soc. Jpn.*, **68**, 1065 (1995).
34 C. Reichhardt, "Solvents and Solvent Effects in Organic Chemistry," VCH, Weinhein (1988).
35 P. F. Barbara and W. Jarzeba, *Adv. Photochem.*, **15**, 1 (1990).
36 E. Z. Lippert, W. Rettig, V. Banacic-Kontecky, F. Heisel, and J. Meihe, *Adv. Chem. Phys.*, **68**, 1 (1987).
37 K. Bhattacharya and M. Choudhary, *Chem. Rev.*, **93**, 507 (1993).