Wavelength Dependent Trans to Cis and Quantum Chain Isomerizations of Anthrylethylene Derivatives[†,‡]

V. Raj Gopal, A. Mahipal Reddy, and V. Jayathirtha Rao*

Organic Division II, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Received August 19, 1995[®]

Anthrylethylene derivatives **1**–**4** were synthesized to study their photoisomerization. Interestingly **1** and **2** displayed wavelength dependent trans to cis photoisomerization, whose origin is due to preferential light absorption and excitation of the trans isomer. Triplet sensitization studies revealed that these anthrylethylenes undergo only cis to trans isomerization and not trans to cis isomerization. UV–vis absorption, fluorescence emission, and fluorescence quantum yields were determined for all anthrylethylenes. Dual fluorescence is observed for **1**, **2**, and *cis*-**1**, indicating two different emissive states. The fluorescence solvatochromism displayed by **1**, **2**, and *cis*-**1** is a clear indication of the involvement of a charge transfer excited state. The quantum yield of isomerization was determined in various solvents and also as a function of concentration. We report here the first "quantum chain isomerization" that originates from a singlet excited state. The rationale put forward for the observed quantum chain isomerization process is the involvement of adiabatic isomerization from the singlet excited state and subsequent energy transfer to a ground state molecule.

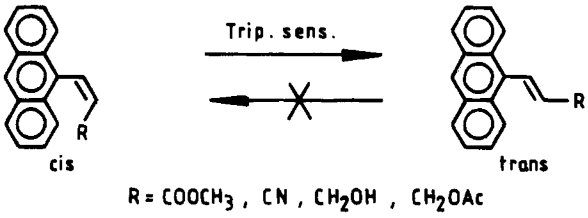
Introduction

Light induced cis–trans isomerization of olefins is of high importance in both biological and technological chemistry. The photoisomerization of stilbenes has been discussed by Saltiel and co-workers and others.[1,2] Recently Becker[3] reviewed the relationship between excited state reactivity and molecular topology in substituted anthracenes. One way photoisomerization of anthrylethylenes[4] from their triplet state has been summarized. However photoisomerization of anthrylethylenes from their singlet excited state has not been well studied. Our continuing interest in photoisomerization[5] leads us now to report our results on anthrylethylene derivatives (Chart 1) which undergo wavelength dependent trans to cis photoisomerization from the singlet state, cis to trans triplet-mediated isomerization, and for the first time, we are reporting a quantum chain isomerization process from the singlet excited state.

Results and Discussion

Photostationary Compositions. Anthrylethylene derivatives **1**–**4** (Chart 1) were synthesized by use of the Horner–Wadsworth–Emmons reaction.[6] The corresponding cis isomers were either generated photochemically or synthesized,[6b] and all the products were characterized by spectral means (Experimental Section). Table 1 gives photostationary compositions of anthrylethylenes in hexane upon direct excitation under different irradiation conditions. Filters and filter solutions[7] were used to achieve different excitation wavelength conditions. Photoisomerization reactions were monitored by HPLC, and the measured product ratios are reported in Table 1. A typical HPLC chromatogram is shown in Figure 1 for ester **1**. Changing the wavelength of irradiation to longer wavelengths (>400 nm) leads to enhanced accumulation of cis isomer to over 94% for **1** and **2** (Table 1). The other two compounds, **3** and **4**, did not undergo photoisomerization upon direct excitation. Photostationary state compositions determined by varying the concentration of **1** in hexane are presented in Table 2.

Triplet-sensitized isomerizations were conducted (Table 3) to differentiate singlet/triplet reactivities in these anthrylethylenes, and the resulting photostationary state compositions are given in Table 3. Triplet sensitizers were employed (Table 3) that differed somewhat in triplet energy. Selective excitation of the sensitizer was achieved by using filter solutions, to avoid direct excitation of anthrylethylenes. Triplet-sensitized isomerization is very effective in bringing cis to trans isomerization (Table 3) but ineffective in the reverse direction (eq 1). Sensitizers with triplet energy of 39 kcal/mol and above are



(1)

[†] This paper is dedicated to Dr. A. V. Rama Rao, Director, on the occasion of his 60th birthday.

[‡] Part of the work was presented at the Trombay Symposium on Radiation and Photochemistry, Bombay, India. *Proc. TSRP* **1994**, *2*, p 386.

[®] Abstract published in *Advance ACS Abstracts,* November 1, 1995.

(1) (a) Saltiel, J.; et al. In *Organic Photochemistry*; Chapman, O. L., Ed.; Marcel Dekker: New York, 1973; Vol. 3, p 1. (b) Saltiel, J.; Charlton, J. L. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 25. (c) Saltiel, J.; Sun, Y.-P. In *Photochromism, Molecules and Systems*; Durr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; p 64.

(2) (a) Allen, M. T.; Whitten, D. G. *Chem. Rev.* **1989**, *89*, 1691. (b) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415.

(3) (a) Becker, H.-D. *Adv. Photochem.* **1990**, *15*, 139. (b) Becker, H.-D. *Chem. Rev.* **1993**, *93*, 145.

(4) (a) Arai, T.; Tokumaru, K. *Chem. Rev.* **1993**, *93*, 23. (b) Arai, T.; et al. *Pure Appl. Chem.* **1988**, *60*, 989. (c) Sundahl, M.; Sandros, K.; Wennerstrom, O.; Arai, T.; Okamoto, H.; Tokumaru, K. *Chem. Phys. Lett.* **1990**, *168*, 395.

(5) (a) Jayathirtha Rao, V.; Fenstemacher, R. J.; Liu, R. S. H. *Tetrahedron Lett.* **1984**, *25*, 1115. (b) Jayathirtha Rao, V.; Bhalerao, U. T. *Tetrahedron Lett.* **1990**, *31*, 3441. (c) Mahipal Reddy, A.; Jayathirtha Rao, V. *J. Org. Chem.* **1992**, *57*, 6727. (d) Jayathirtha Rao, V. *J. Photochem. Photobiol. Chem. A* **1994**, *83*, 211.

(6) (a) Wadsworth, W. S. *Org. React.* **1977**, *25*, 73. (b) Mahipal Reddy, A.; Raj Gopal, V.; Jayathirtha Rao, V. IUPAC Conference, Bangalore, India, December 1994; (c) Vogel A. I. *Text Book of Practical Organic Chemistry*, 4th ed.; ELBS: London, 1978; p 762.

(7) Scaiano, J. C. *Hand Book of Organic Photochemistry*: CRC Press: Boca Raton, FL, 1989; Vol. 1.

0022-3263/95/1960-7966$09.00/0 © 1995 American Chemical Society

Chart 1

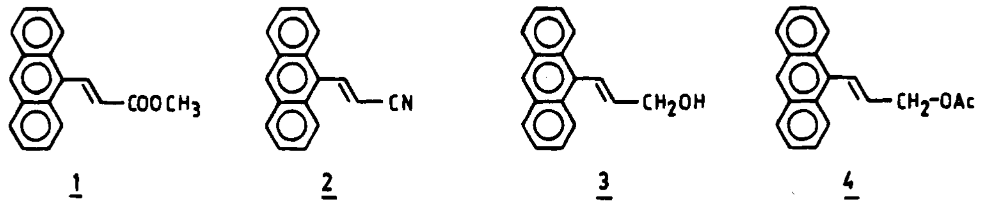


Table 1. Wavelength Dependent Photostationary Compositions of Anthrylethylene Derivatives[a]

compd	light source	excitation wavelength (nm)	cis (%)	trans (%)
1	Rayonet reactor	350 ± 20	48	52
	450 W Hg lamp	>300	67	33
	450 W Hg lamp	>400	94	6
2	Rayonet reactor	350 ± 20	49	51
	450 W Hg lamp	>300	68	32
	450 W Hg lamp	>400	94	6
3		no isomerization		
4		no isomerization		

[a] Pyrex filter for >300 nm; $NaNO_2/CuSO_4$ solution filter for >400 nm; analysis by HPLC; 0.001 M nitrogen-bubbled hexane solutions were used for irradiation; experimental error limit on product ratios is <1.0%.

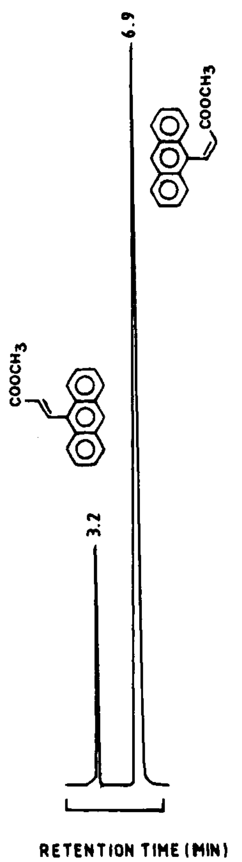


Figure 1. HPLC chromatogram showing **1** at 3.2 min and *cis*-**1** at 6.9 min, (5μm amino silica, 4.5 × 250 mm column; detecting wavelength 380 nm; hexane:dichloromethane, 95:5, mixture as eluent at a rate of 2 mL/min).

Table 2. Photostationary State Compositions of 1 at Various Concentrations Upon Direct Excitation[a]

no.	concentration (M)	cis(%)	trans(%)
1	0.0010	94	6
2	0.0015	94	6
3	0.0030	94	6
4	0.0045	94	6
5	0.0060	94	6

[a] Hexane solvent; all solutions were nitrogen bubbled prior to irradiation; exciting wavelength was >400 nm; analysis by HPLC.

Table 3. Triplet-Sensitized Photostationary Compositions of Anthrylethylene Derivatives[a]

compd	sensitizer	sensitizer A_{max} (nm)	sensitizer E_T (kcal/mol)	cis (%)	trans (%)
cis-1	erythrocin	515	42	2	98
	rose bengal	550	39	2	98
	methyl violet	585	37	no reaction	
	methylene blue	660	32	no reaction	
cis-2	erythrocin	515	42	2	98
	rose bengal	550	39	2	98
cis-3	erythrocin	515	42	2	98
cis-4	erythrocin	515	42	2	98

[a] Nitrogen-bubbled (0.001 M) methanolic solutions containing 0.001 M sensitizer were used for irradiation; solution filters were employed to achieve selective excitation of the sensitizer (refs 7 and 28); analysis by HPLC; experimental error limit is <1.0%; trans isomer is stable under these sensitization conditions.

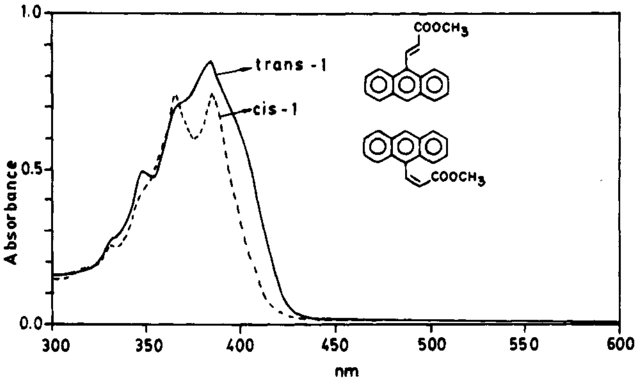


Figure 2. UV−vis absorption spectra of *trans*-**1** (solid line) and *cis*-**1** (broken line) in hexane solvent.

effective in bringing about the cis to trans isomerization process (Table 3), indicating that the triplet energies of these anthrylethylenes are near to this value.

Spectroscopic Studies. To understand the excited state behavior of these anthrylethylene derivatives, we have obtained UV−vis absorption spectra (Figure 2), fluorescence emission and fluorescence excitation spectra (Figures 3−5), and quantum yields of fluorescence (Table 4). Stokes shifts were calculated in various solvents and are shown in Table 4. UV−vis absorption data presented in Table 4 indicate that there is not much change in the absorption properties by changing the solvent polarity. However, there is a dramatic change in the fluorescence behavior of **1**, **2**, and *cis*-**1** as the polarity of the solvent is increased (Table 4) and, accordingly, in the increase in the Stokes shift. The UV−vis absorption spectra are given in Figure 2, and fluorescence emission spectra are given in Figures 3a,b, 4, and Figure 5. Figure 4 clearly indicates the fluorescence solvatochromism exhibited by **1** (see Table 4). Interestingly the dual emission behavior

Table 4. Absorption, Fluorescence, and Quantum Yield of Fluorescence Data of Anthrylethylene Derivatives[a]

compd	solvent	λ_{abs} (nm)	λ_{fluo} (nm)	Stokes shift (cm^{-1})	Φ_{fluo}
1	hexane	384	484	5380	0.116
	benzene	388	500	5773	0.084
	dichloromethane	388	508	6088	0.037
	acetonitrile	385	512	6443	0.023
	methanol	384	520	6811	0.013
2	hexane	384	492	5716	0.201
	benzene	388	504	5932	0.056
	dichloromethane	387	512	6308	0.051
	acetonitrile	385	520	6744	0.031
	methanol	384	526	7030	0.020
cis-1	hexane	385	484	5313	0.101
	methanol	385	520	6744	0.010
3	hexane	367	428	3883	0.66
	methanol	367	428	3883	0.65
4	hexane	366	428	3958	0.97
	methanol	366	428	3958	0.98

[a] Stokes shift was calculated as $\bar{\upsilon}_{abs_{max}} - \bar{\upsilon}_{fluo_{max}}$; 0.00001 M nitrogen-bubbled solutions were used for determining fluorescence at room temperature; quantum yields of fluorescence determined using 9,10-diphenylanthracene fluorescence ($\Phi_f = 0.9$) as the standard (refs 28 and 29); experimental error of Φ_f is ±0.01.

of **1** is especially evident in methanol solvent (Figures 3b and 5), where one emissive state (charge transfer) is affected by solvent polarity and the other state (locally excited) is not (Figure 5). A similar kind of behavior is exhibited by **2** and *cis*-**1** (Table 4). Compounds **3** (Figure 3c) and **4** are highly fluorescent, but their fluorescence behavior is unaffected by solvent polarity (Table 4). Quantum yields of fluorescence were determined for all compounds (Table 4). In the case of **1**, **2**, and *cis*-**1**, the quantum yield of fluorescence decreases as solvent polarity increases, whereas for compounds **3** and **4** the quantum yield of fluorescence is high and unaffected by solvent polarity (Table 4). Fluorescence spectra were recorded for **1** (Figures 6 and 7) and *cis*-**1** at various concentrations to understand the mechanism involved (Table 5). Figure 6 shows that the shorter wavelength emission band, due to locally excited singlet state fluorescence, is quenched as the concentration of the substrate (in the 10^{-4} M range) increases and is totally absent at concentrations of 10^{-3} M and above (Figure 7) in both hexane and methanol. This indicates that the ground state is involved in fluorescence quenching, by a self-quenching process.

Quantum Yields of Isomerization. The quantum yields of isomerization upon direct excitation (366 nm) of these anthrylethylene derivatives determined in various solvents (Table 6) reveal that isomerization is a relatively efficient process upon direct excitation. Interestingly, trans to cis and cis to trans quantum yields of isomerization processes are comparable. More importantly we have determined the concentration dependence of the quantum yields of the trans to cis isomerization for **1** and **2** and cis to trans isomerization for *cis*-**1** (Table 7). All three compounds display an increase in the quantum yield of isomerization as the concentration of the substrate increases. Such increases have been attributed to a "quantum chain" isomerization process, which is discussed below. We have chosen concentrations and wavelength of excitation such that all incident light was completely absorbed during the course of the experiments.

Wavelength Dependent Trans to Cis Isomerization. Scheme 1 describes the efficient photoisomerization processes observed in these anthrylethylenes. Irradiation of **1** or **2** with a pyrex filter (>300 nm) establishes an almost 1:1 cis:trans photostationary (Table 1) isomeric mixture. Most importantly, by changing the wavelength of irradiation to >400 nm, one can achieve a very high "cis" (>94%, Table 1; Figure 1) isomer content starting from the trans isomer. Further, the high-cis isomer (>94%) content of the photostationary state on irradiation above 400 nm is independent of the substrate concentration, as shown in Table 2. The observed wavelength dependency is proposed to be due to preferential light absorption and excitation of the trans isomers

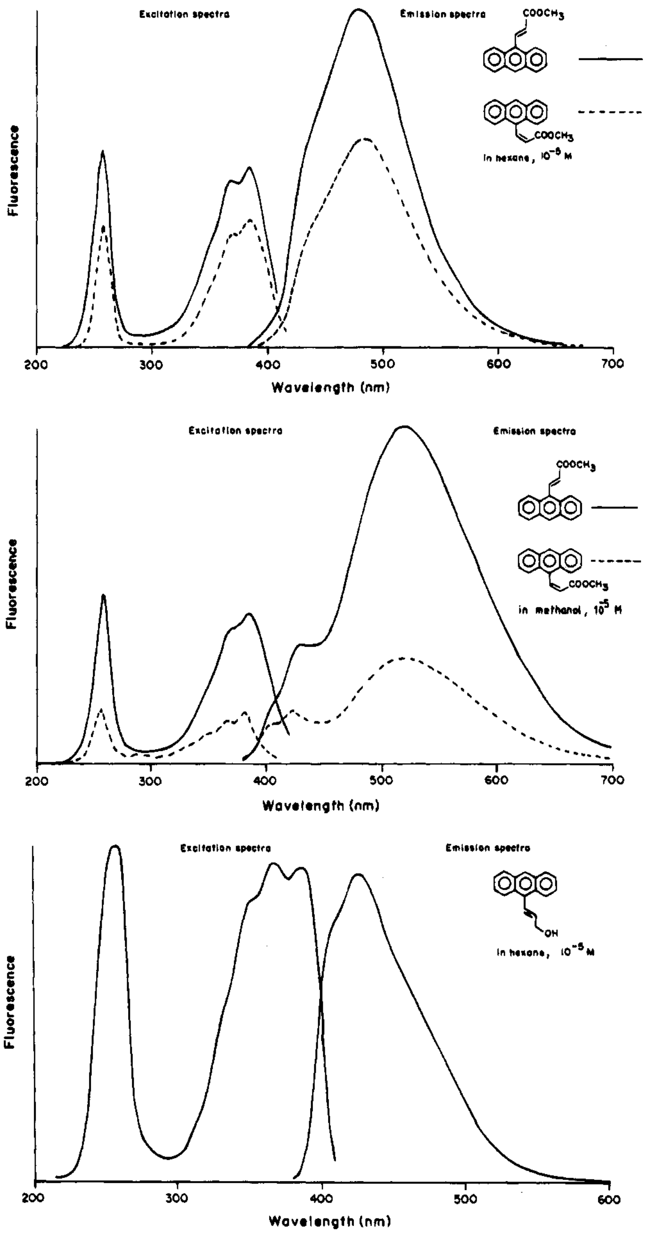


Figure 3. (a) Fluorescence emission and fluorescence excitation spectra of **1** (solid line) and *cis*-**1** (broken line) in hexane (excitation wavelength 360 nm; emission wavelength 430 nm; slit widths 2 × 2 × 2 × 2 mm recorded on a SPEX fluorimeter at room temperature). (b) Fluorescence emission and fluorescence excitation spectra of **1** (solid line) and *cis*-**1** (broken line) in methanol (excitation wavelength 360 nm; emission wavelength 520 nm; slit widths 2 × 2 × 2 × 2 mm; recorded on a SPEX fluorimeter at room temperature). (c) Fluorescence emission and fluorescence excitation spectra of **3** in hexane (excitation wavelength 360 nm; emission wavelength 430 nm; slit widths 2 × 2 × 2 × 2; recorded on a SPEX fluorimeter at room temperature).

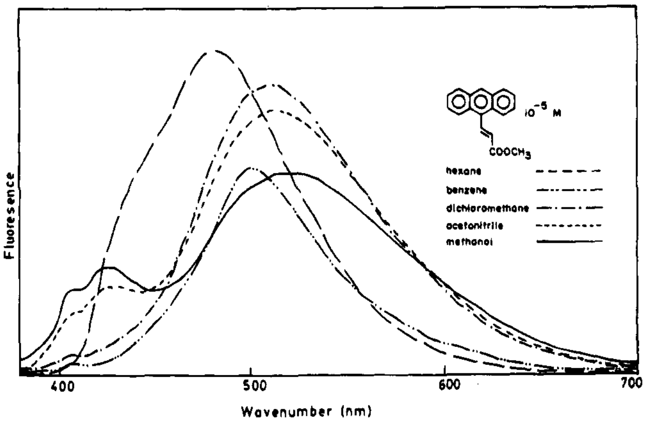


Figure 4. Fluorescence spectra of **1** in various solvents as indicated in the figure. The concentration of **1** is 0.00001 M.

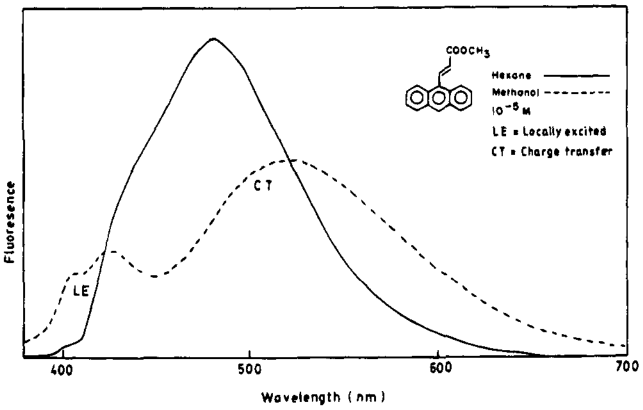


Figure 5. Fluorescence spectra of **1** in hexane (solid line) and methanol (broken line) solvents (LE = locally excited state; CT = charge transfer excited state). The concentration of **1** is 0.00001 M.

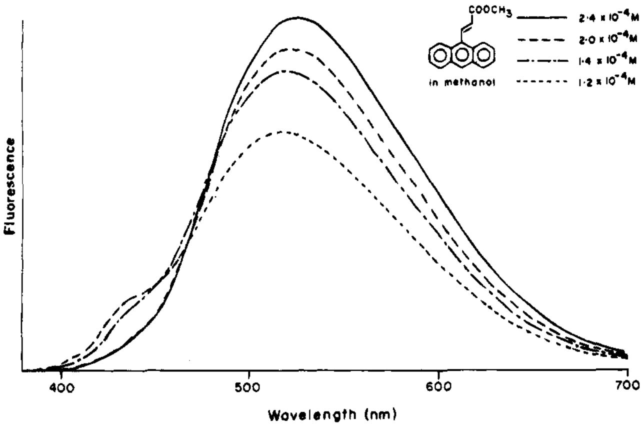


Figure 6. Fluorescence emission of **1** at various concentrations in methanol at room temperature showing quenching of the LE state (excitation wavelength 360 nm; slit widths 2 × 2 × 1 × 1 mm). Concentrations employed are indicated in the figure.

Table 5. Concentration Dependent Fluorescence of 1 and *cis*-1 in Hexane and Methanol Solvents[a]

no.	concentration (M)	fluorescence intensity 1 hexane	1 methanol	*cis*-1 hexane	*cis*-1 methanol
1	0.0015	142	27	80	10.6
2	0.0030	108	19	42	8.1
3	0.0045	65	11	27	5.1
4	0.0060	44	5.5	18	1.4

[a] Excitation wavelength 360 nm; 2 × 2 × 1 × 1 slit widths; measured at room temperature; 380–700 nm spectral width; fluorescence intensity is given as the area under the fluorescence curve.

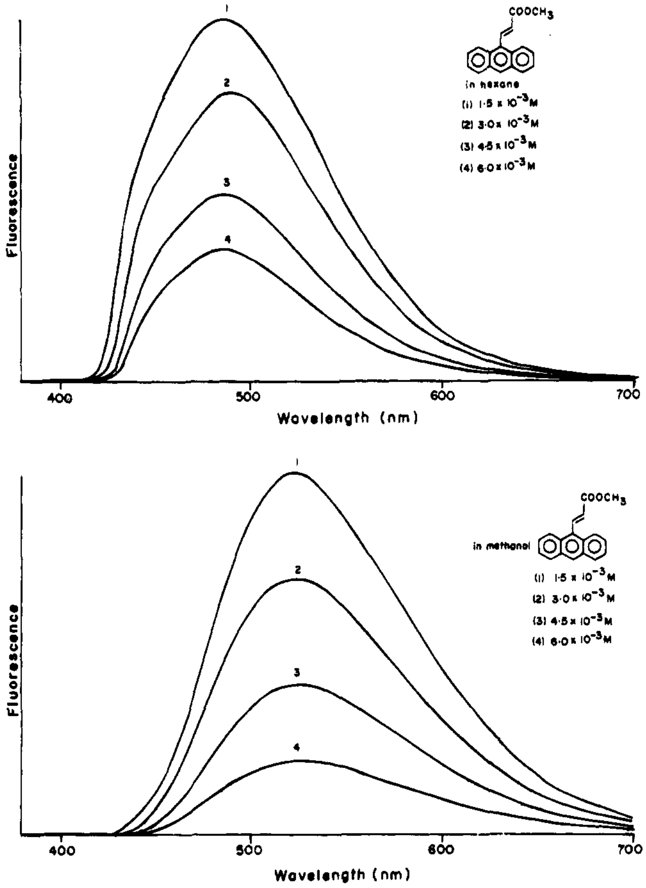


Figure 7. (a) Fluorescence emission of **1** at various concentrations in hexane at room temperature showing self quenching process (excitation wavelength 360 nm; slit widths 2 × 2 × 1 × 1 mm). Concentrations employed were 1.5×10^{-3}, 3.0×10^{-3}, 4.5×10^{-3}, and 6.0×10^{-3} M, corresponding to decreasing order of fluorescence intensity. (b) Fluorescence emission of **1** at various concentrations in methanol at room temperature showing self-quenching process (excitation wavelength 360 nm; slit widths 2 × 2 × 1 × 1 mm). Concentrations employed were 1.5×10^{-3}, 3.0×10^{-3}, 4.5×10^{-3}, and 6.0×10^{-3} M, corresponding respectively to decreasing order of fluorescence intensity.

and is consistent with earlier observations.[8-10] Evidence for this rationale is seen in the UV–vis absorption spectra of cis and trans isomers of **1** (shown in Figure 2), where it is clear that the trans isomer preferentially absorbs light in the longer wavelength region. Triplet sensitization (eq 1) established that on the lowest triplet energy surface only the cis isomer undergoes isomerization to the trans isomer and not vice versa.[11]

Charge Transfer Nature of the Singlet Excited State. To understand the mechanism of the isomerization and the possible involvement of charge transfer

---

[8] (a) Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978**, *78*, 125. (b) Jacobs, H. J. C.; Havinga, E. *Adv. Photochem.* **1979**, *11*, 305.

[9] Dauben, W. G.; Phillips, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 355.

[10] Saltiel, J.; Marinari, A.; David, W. L.; Mitchener, J. C.; Dennis Megarity, E. *J. Am. Chem. Soc.* **1979**, *101*, 2982.

[11] Arai, T.; Tokumaru, K. *Adv. Photochem.* **1995**, *20*, 1.

Table 6. Quantum Yield of Photoisomerization of Anthrylethylene Derivatives in Various Solvents[a]

	quantum yield of isomerization				
compd	hexane	benzene	dichloromethane	acetonitrile	methanol
1	0.138	0.229	0.234	0.203	0.193
2	0.188	0.307	0.328	0.283	0.234
cis-**1**	0.197	0.289	0.238	0.257	0.231

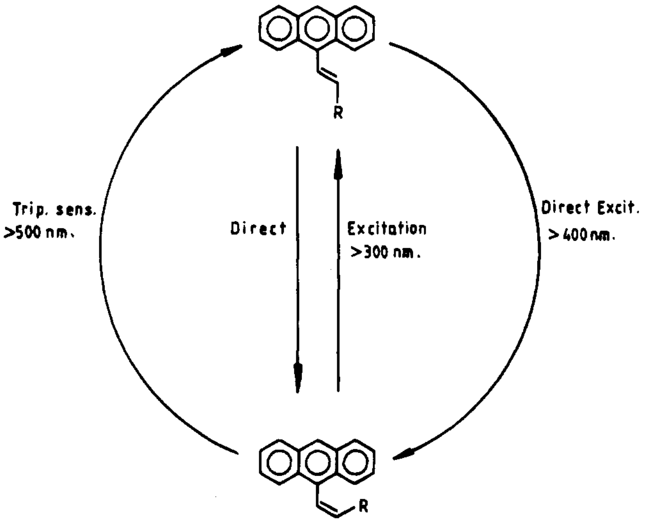
[a] Nitrogen-bubbled 0.0005 M solutions were irradiated; the 366 nm line of Hg lamp was isolated using solution filters; potassium ferrioxalate was used for counting photons; for **1** and **2** the reaction is trans to cis isomerization, and for *cis*-**1** the isomerization is from cis to trans; experimental error is ±0.01.

Table 7. Concentration Dependent Quantum Yield of Photoisomerization of 1, 2, and *cis*-1 upon Direct Excitation[a]

	Φ_{iso}					
concn	**1**		**2**		*cis*-**1**	
(M)	hexane	methanol	hexane	methanol	hexane	methanol
0.0005	0.138	0.193	0.188	0.234	0.197	0.231
0.0010	0.164	0.245	0.261	0.352	0.243	0.277
0.0015	0.217	0.282	0.29	0.465	0.255	0.324
0.0030	0.270	0.365	0.401	0.701	0.303	0.413
0.0045	0.316	0.517	0.488	0.903	0.363	0.620
0.0060	0.414	0.624	0.766	0.959	0.469	0.651

[a] Nitrogen-bubbled solutions were irradiated using 366 nm light; potassium ferrioxalate was used for counting photons; experimental error is ±0.01.

Scheme 1



excited states, absorption and fluorescence data were obtained for these anthrylethylenes. Scheme 2 illustrates the mechanism involving two singlet excited states. Upon absorption of light, the molecule is excited to a "locally excited" (LE) singlet state, and subsequently the initially formed LE state leads to formation of a "charge transfer" (CT) singlet excited state. Support for the involvement of two singlet excited states, LE and CT, stems from the dual emission behavior of **1** as shown in Figure 5. Fluorescence solvatochromism exhibited by **1**, **2**, and *cis*-**1** (Table 4, Figure 4) is a clear indication of the charge transfer nature[12-14] of the singlet excited state. There are quite a few molecules which show anomalous fluorescence behavior,[15] and the present systems (**1**, **2**, and *cis*-**1**) fall into the same category, as well as exhibiting fluorescence solvatochromism. The CT singlet excited state undergoes twisting resulting in trans−cis isomerization. Interestingly compounds **3** and **4** did not exhibit fluorescence solvatochromism (Table 4), indicating noninvolvement of CT excited state (Scheme 2), presumably because they lack an electron-withdrawing group (acceptor group). Compounds **3** (Figure 3c) and **4** exhibit high fluorescence[16] from the LE state and do not undergo isomerization (Scheme 2), supporting the role of the CT state in the trans−cis isomerization. Additionally, the fluorescence spectra of the trans and cis isomers of **1** are nearly identical,[17] as shown in Figure 3, supporting the hypothesis that singlet excited states of **1** and *cis*-**1** have similar zwitterionic character[18-21] as represented by structure **5** in Scheme 2. This zwitterionic excited state **5** is suggested to be responsible for the fluorescence solvatochromism (Figure 4).

Quantum Chain Isomerization Process. Quantum yields of photoisomerization were determined for the anthrylethylenes (Table 6) in various solvents. The trend shows that the isomerization process is very efficient in these systems. More interestingly, the quantum yield of photoisomerization of **1**, **2**, and *cis*-**1** increases as the substrate concentration increases (Table 7). An increase in the quantum yield of isomerization as the substrate concentration increases is known as a "quantum chain isomerization" process and was first postulated by Hammond[22] and co-workers and later demonstrated by other groups[23-26] for triplet excited states of olefin. In the present case, **1**, **2**, and *cis*-**1** all displayed quantum chain isomerization processes originating from the singlet excited state. The rationale given for the observed quantum chain isomerization process involves adiabatic isomerization from the singlet excited state and subsequent energy transfer to a ground state molecule and is summarized in Scheme 3. Absorption of a photon by anthrylethylene (AE) elevates it to a LE singlet state, (Scheme 3, step 1). This LE state exhibits fluorescence (step 2; Figures 3 and 5) or can lead adiabatically to a CT singlet excited state (step 3). The CT excited singlet state exhibits fluorescence (step 4; Figures 3−5) or can isomerize to the cis isomer (step 5). Most importantly, it is proposed that the AE(CT)^{*1} state leads to the cis isomer in the excited state (adiabatic reaction; step 6). The excited cis isomer can transfer excitation to a ground

---

(12) Barbara, P. F.; Jarzeba, W. *Adv. Photochem.* **1990**, *15*, 1.

(13) (a) Lippert, E. *Z. Naturforsch.* **1955**, *109*, 541. (b) Lippert, E.; Rettig, W.; Bonacic-Koutecky, V.; Heisel, F.; Meihe, J. A. *Adv.* Chem.Phys. **1987**, *68*, 1.

(14) Kosower, E. M.; Huppert, D. *Annu. Rev. Phys. Chem.* **1986**, *37*, 127.

(15) (a) Rettig, W. *Angew. Chem., Intl. Ed. Engl.* **1986**, *25*, 971. (b) Rettig, W. *Topics in Current Chemistry*; Springler Verlag: New York, 1994; Vol. 169, p 253. (c) Bhattacharya, K.; Chowdhury, M.*Chem.* Rev. **1993**, *93*, 507.

(16) Similar types of compounds exhibit very high fluorescence quantum yield; see: Bhattacharya, K.; Chattopadhyay, S. K.; Baral Tosh, S.; Das, P. K. *J. Phys. Chem.* **1986**, *90*, 2646.

(17) Sandros, K.; Becker, H.-D. *J. Photochem.* **1987**, *39*, 301.

(18) Sun, Y.-P.; Fox, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 747.

(19) Schuddeboom, W.; Jonker, S. A.; Warman, J. M.; deHass, M. P.; Vermulen, M. J. W.; Jager, W. F.; deLange, B.; Feringa, B. L.; Fessemden, R. W. *J. Am. Chem. Soc.* **1993**, *115*, 3286.

(20) Morias, J.; Ma, J.; Zimmt, M. B. *J. Phys. Chem.*. **1991**, *95*, 3885.

(21) Schilling, C. L.; Hilinski, E. F. *J. Am. Chem. Soc.* **1988**, *110*, 2296.

(22) Hyndman, H. L.; Monroe, B. M.; Hammond, G. S. *J. Am. Chem. Soc.* **196**, *91*, 2852.

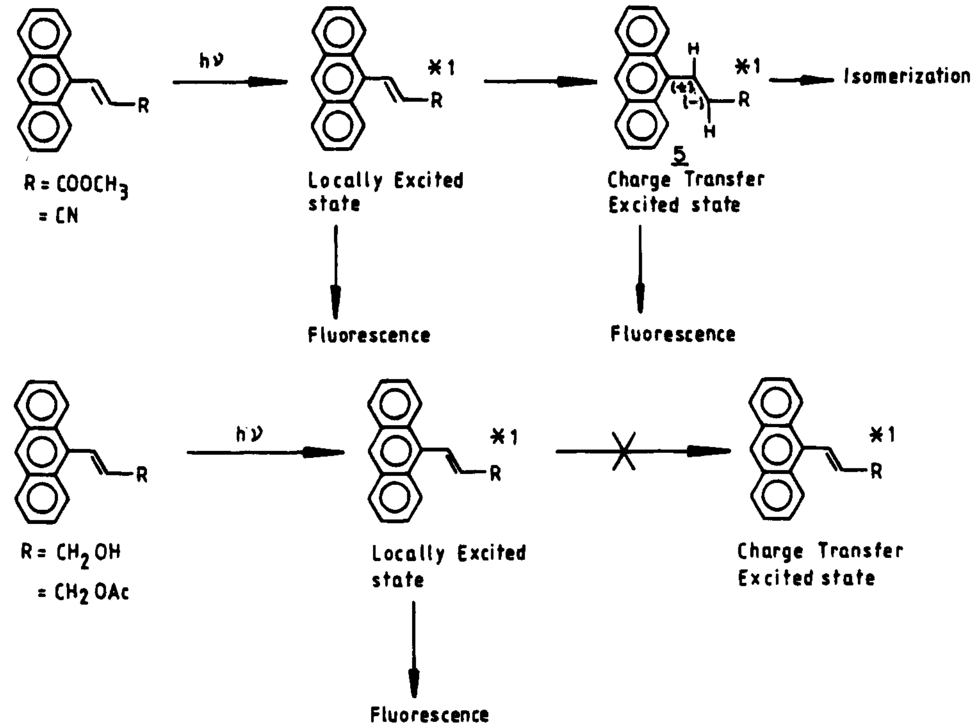
(23) Saltiel, J.; Townsend, T. E.; Sykes, A. *J. Am. Chem. Soc.* **1973**, *95*, 5968.

(24) (a) Butt, Y. C. C.; Singh, A. K.; Baretz, B. H.; Liu, R. S. H. *J. Phys. Chem.* **1981**, *85*, 2091. (b) Ganapathy, S.; Liu, R. S. H. *J. Am. Chem. Soc.* **1992**, *114*, 345.

(25) Whitten, D. G.; Wildes, P. D.; Deroier, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 7811.

(26) Hurley, R.; Testa, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 211.

Scheme 2



Scheme 3[a]

$$\mathrm{AE} \xrightarrow{h\nu} \mathrm{AE}^{*1}_{(\mathrm{LE})} \tag{1}$$

$$\mathrm{AE}^{*1}_{(\mathrm{LE})} \longrightarrow \mathrm{AE{+}Fluorescence} \tag{2}$$

$$\mathrm{AE}^{*1}_{(\mathrm{LE})} \rightleftharpoons \mathrm{AE}^{*1}_{(\mathrm{CT})} \tag{3}$$

$$\mathrm{AE}^{*1}_{(\mathrm{CT})} \longrightarrow \mathrm{AE{+}Fluorescence} \tag{4}$$

$$\mathrm{AE}^{*1}_{(\mathrm{CT})} \longrightarrow \mathrm{AE{-}cis} \tag{5}$$

$$\mathrm{AE}^{*1}_{(\mathrm{CT})} \longrightarrow \mathrm{AE{-}cis}^{*1}_{(\mathrm{CT})} \tag{6}$$

$$\mathrm{AE{-}cis}^{*1}_{(\mathrm{CT})} + \mathrm{AE} \longrightarrow \mathrm{AE}^{*1}_{(\mathrm{CT})} + \mathrm{AE{-}cis} \tag{7}$$

$$\mathrm{AE{-}cis}^{*1}_{(\mathrm{CT})} \rightleftharpoons \mathrm{AE{-}cis}^{*1}_{(\mathrm{LE})} \tag{8}$$

$$\mathrm{AE{-}cis}^{*1}_{(\mathrm{LE})} + \mathrm{AE} \longrightarrow \mathrm{AE}^{*1}_{(\mathrm{CT})} + \mathrm{AE{-}cis} \tag{9}$$

$$\mathrm{AE}^{*1}_{(\mathrm{LE})} \xrightarrow{\mathrm{ISC}} \mathrm{AE}^{*3} \tag{10}$$

$$\mathrm{AE}^{*1}_{(\mathrm{CT})} \xrightarrow{\mathrm{ISC}} \mathrm{AE}^{*3} \tag{11}$$

$$2\mathrm{AE}^{*3} \longrightarrow \mathrm{AE}^{*1} + \mathrm{AE} \tag{12}$$

[a] AE, anthrylethylene derivative; LE, locally excited singlet state; CT, charge transfer singlet state; ISC, intersystem crossing.

state trans AE molecule (step 7 or 9) thereby propagating quanta. These two steps, formation of an excited state after isomerization (adiabatic photoisomerization) and its involvement in energy transfer, together provide a rationale for the observed quantum chain isomerization in **1**, **2**, and *cis*-**1** as shown in Table 7.

The data for fluorescence of **1** (Figures 6 and 7) and *cis*-**1** in hexane and methanol solvents as a function of substrate concentration, in the same concentration range where the quantum chain isomerization experiments were conducted, are given in Table 5. A decrease in the fluorescence intensity as the substrate concentration increases (Table 5; Figure 7) was observed, thereby indicating that a ground state molecule is involved in quenching the fluorescence (self-quenching process). This quenching process becomes efficient as the substrate concentration increases, thus supporting the rationale that an adiabatically formed excited cis isomer is involved in the energy transfer process. In this energy transfer process, it is reasonable to say that it is the LE singlet state involved (step 9) rather than the CT excited state (step 7), since the LE state emission is at a shorter wavelength region and a more feasible process. Figure 5 displays emission behavior of **1**, and the emitting states are shown as LE singlet state (shorter wavelength band) and CT singlet excited state (longer wavelength band). The LE state emission is present only in dilute solutions (Figures 3b and 5), and at higher concentrations it is totally absent (Figures 6 and 7b). This clearly indicates that the emission originating from the LE singlet state is being quenched by the ground state molecule, when the concentration of the substrate increases. This observation clearly supports involvement of the LE state in the energy transfer process.

Erythrocin, a triplet sensitizer (with 42 kcal/mol triplet energy), is unable to produce "cis" isomer when sensitized isomerization was carried out, and this clearly ruled out the possibility of triplet state involvement. Further ruled out was the possibility of triplet–triplet annihilation (step 12) when the isomerizations were conducted using aerated solutions, where the oxygen effect was not observed on the isomerization process. In all these isomerization processes, it is the CT singlet excited state which is involved and not the LE singlet state because compounds **3** and **4** are capable of forming LE state only, do not form CT state, do not undergo isomerization (Table 1) process, and do not exhibit fluorescence solvatochromism (Table 4). The adiabatic nature of a CT singlet state was recently proposed in the case of stilbene derivatives[27] to explain their photophysical and fluorescence behavior. The results of this investigation also suggest the involvement of adiabatically derived CT singlet excited state.

Conclusion

Anthrylethylene derivatives undergo wavelength dependent trans to cis isomerization with very high efficiency. The wavelength dependent trans to cis photostationary state composition is explained by preferential light absorption and excitation of the trans isomer at longer wavelength only. Triplet sensitization is found to be effective in bringing the cis to trans isomerization process only. Dual fluorescence emission behavior of **1**, **2**, and *cis*-**1** indicates the involvement of two fluorescing states. The involvement of CT singlet excited state is clearly indicated by the fluorescence solvatochromism studies conducted with **1**, **2**, and *cis*-**1**. A "quantum chain" isomerization process originating in the singlet excited state of these anthrylethylenes is reported for the first time. The rationale put forward is the involvement of adiabatic isomerization, and subsequent energy transfer processes are responsible for the observed quantum chain isomerization process. Further studies, like time-resolved fluorescence, are in progress to unravel the isomerization mechanism.

Experimental Section

The analytical instruments employed have been described in a previous paper.[5c] Solvents were distilled prior to use. Other chemicals are commercially available. Methyl dimethylphosphonoacetate and dimethylphosphonoacetonitrile were prepared according to published procedures.[6] 9-Anthraldehyde was prepared according to Vogel.[6c] Methyl bis(trichloroethyl)-phosphonoacetate (modified phosphonate) was prepared from the corresponding dichloride $Cl_2P(O)CH_2COOCH_3$, by treating it with trichloroethanol/triethylamine. In turn the dichloride $Cl_2P(O)CH_2COOCH_3$ was prepared from the corresponding phosphonate and phosphorus pentachloride.

Synthesis of 1. Methyl dimethylphosphonoacetate (2.0 g, 11 mmol) in dry DMF (15 mL) was added slowly to a solution containing NaH (264 mg, 11 mmol) in dry DMF (20 mL) at room temperature. The phosphoryl-stabilized carbanion was treated with 9-anthraldehyde (2.06 g, 10 mmol) in 10 mL of DMF slowly. After 30 min of stirring, the reaction was quenched with water and the mixture extracted with ether. The product was purified by silica gel column chromatography to get pure *trans*-**1** in 70% yield (1.83 g): Solid; mp 114 °C; ^{1}H-NMR δ 3.9 (s, 3H), 6.45 (d, 1H, J = 15.0 Hz), 7.4–7.6 (m, 4H), 7.95–8.1 (m, 2H), 8.15–8.3 (m, 2H), 8.45 (s, 1H), 8.65 (d, 1H, J = 15.0 Hz); ^{13}C-NMR δ 51.8, 125.06, 125.2, 126.2, 126.6, 128.1, 128.7, 131.1, 142.1, 166.7; IR (cm^{-1}) 3000, 1690, 1620, 1420, 1260; UV max = 384 nm, ϵ = 6088 cm^{-1} M^{-1}; emission max (hexane) = 484 nm, quantum yield of fluorescence = 0.116; mass fragments 262 (M$^+$), 204, 203, 178, 101. Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.37. Found: C, 82.79; H, 5.33.

cis-**1**: solid; mp 132 °C; ^{1}H-NMR δ 3.3 (s, 3H), 6.6 (d, 1H, J = 11.1 Hz), 7.3–7.5 (m, 4H), 7.75 (d, 1H, J = 11.1 Hz), 7.9–8.1 (m, 4H), 8.4 (s, 1H); ^{13}C-NMR δ 51.1, 125.0, 125.2, 125.6, 126.9, 128.3, 128.6, 131.0, 141.7, 165.4; IR (cm^{-1}) 3000, 1700, 1620, 1430, 1280; UV max = 385 nm, ϵ = 4170 cm^{-1} M^{-1}; emission max (hexane) = 482 nm, quantum yield of fluorescence = 0.101; mass fragments 262 (M$^+$), 204, 203, 178, 101.

Synthesis of 2. A similar procedure as mentioned above was adopted using dimethylphosphonoacetonitrile to synthesize **2**: yield 68% (1.55 g); solid; mp 180 °C; ^{1}H-NMR δ 5.9 (d, 1H, J = 16.2 Hz), 7.4–7.6 (m, 4H), 7.95–8.2 (m, 4H), 8.4 (d, 1H, J = 16.2 Hz), 8.5 (s, 1H); ^{13}C-NMR δ 105.5, 124.3, 125.5, 126.9, 128, 129.2, 131, 148.4; IR (cm^{-1}) 3000, 2210, 1610, 1450; UV max = 384 nm, ϵ = 6820 cm^{-1} M^{-1}; emission max (hexane) = 492 nm, quantum yield of fluorescence = 0.201; mass fragments 229 (M$^+$), 203, 201, 177, 101, 91. Anal. Calcd for $C_{17}H_{11}N$: C, 89.05; H, 4.83; N, 6.10. Found: C, 89.57; H, 4.86; N, 5.45.

cis-**2**: solid; mp 171 °C; ^{1}H-NMR δ 6.2 (d, 1H, J = 11.62 Hz), 7.45–7.65 (m, 4H), 7.95–8.2 (m, 5H), 8.54 (s, 1H); ^{13}C-NMR δ 105.3, 124.7, 125.4, 126, 129, 148.4; IR (cm^{-1}) 3000, 2210, 1610, 1450; UV max = 384 nm, ϵ = 5080 cm^{-1} M^{-1}; mass fragments 229 (M$^+$), 203, 201, 177, 101, 91.

Synthesis of 3. Compound **1** (1.1 g, 4.19 mmol) was taken up in hexane and cooled to −10 °C; DIBALH (4.5 mL of 1.9 M in hexane, 8.39 mmol) was then added slowly with stirring. After 30 min at room temperature, the reaction was quenched at −50 °C with NaF/H_2O with stirring. The hexane layer was decanted, and the remaining solid was extracted thrice with ether. The combined organic layer was washed with water, dried, evaporated, and chromatographed to get pure alcohol **3** in 85% yield (833 mg): solid; mp 115 °C; ^{1}H-NMR δ 4.6 (d, 2H, J = 4.6 Hz), 6.1–6.3 (m, 1H), 7.3–7.5 (m, 5H), 7.9–8.0 (m, 2H), 8.2–8.3 (m, 2H), 8.35 (s, 1H); ^{13}C-NMR δ 63.6, 124.9, 125.2, 125.7, 126.2, 126.4, 128.5, 129.3, 131.2, 132, 137; IR (cm^{-1}) 3390, 3000, 1600, 1610, 1080; UV max = 367 nm, ϵ = 7503 cm^{-1} M^{-1}; emission max (hexane) = 428 nm, quantum yield of fluorescence = 0.660; mass fragments 234 (M$^+$), 215, 203, 202, 178, 101, 91. Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.01. Found: C, 85.11; H, 6.01.

cis-**3**: solid; mp 148 °C; ^{1}H-NMR δ 3.85 (d, 2H, J = 4.6 Hz), 6.38–6.51 (m, 1H), 7.15 (d, 1H, J = 11.6 Hz), 7.35–7.5 (m, 4H), 7.9–8.2 (m, 4H), 8.38 (s, 1H); ^{13}C-NMR δ 60.2, 125.2, 125.6, 125.9, 126.6, 127.2, 128.7, 131.3, 134.9; IR (cm^{-1}) 3400, 3000, 1610, 1010; UV max = 365 nm, ϵ = 7803 cm^{-1} M^{-1}; mass fragments 234 (M$^+$), 215, 203, 202, 178, 101, 91.

Synthesis of 4. Acetate **4** was synthesized by a standard procedure by treating alcohol **3** (1.1 g, 4.7 mmol) with acetic anhydride/pyridine, in 80% yield (1.03 g): solid; mp 105 °C; ^{1}H-NMR δ 2.18 (s, 3H), 5.0 (d, 2H, J = 4.4 Hz), 6–6.2 (m, 1H), 7.35–7.55 (m, 5H), 7.9–8.0 (m, 2H), 8.15–8.25 (m, 2H), 8.35 (s, 1H); ^{13}C-NMR δ 20.9, 64.9, 125, 125.2, 125.4, 125.6, 126.5, 128.5, 129.3, 129.6, 131.2, 131.9, 171; IR (cm^{-1}) 3000, 1730, 1620, 1220; UV max = 366 nm; ϵ = 4530 cm^{-1} M^{-1}; emission max (hexane) = 428 nm, quantum yield of fluorescence = 0.970; mass fragments 276 (M$^+$), 233, 215, 202, 201, 178, 101, 91. Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.32; H, 6.13. Found: C, 82.32; H, 6.09.

cis-**4**: solid; mp 85 °C; ^{1}H-NMR δ 1.8 (s, 3H), 4.2 (d, 2H, J = 4.6 Hz), 6.2–6.4 (m, 1H), 7.15 (d, 1H, J = 11.6 Hz), 7.3–7.45 (m, 4H), 7.8–8.15 (m, 4H), 8.3 (s, 1H); ^{13}C-NMR δ 20.5, 61.8, 125.08, 125.2, 125.6, 126.7, 128.5, 129.4, 129.8, 131.1, 170.4; IR (cm^{-1}) 3000, 1720, 1620, 1220; UV max = 365 nm, ϵ = 8584 cm^{-1} M^{-1}; mass fragments 276 (M$^+$), 233, 215, 202, 201, 178, 101, 91.

Photolysis. A Rayonet reactor equipped with RUL-3500 (350 nm) lamps was used for irradiation. A 450 W medium pressure Hg arc lamp along with suitable solution ($NaNO_2$/$CuSO_4$ and $K_2Cr_2O_7$/$CuSO_4$) filters[7,28] was also used for irradiation. All reactions were monitored by HPLC. A Shimadzu LC-6A HPLC system with a UV–vis detector coupled with a CR-3A integrator was used. An amino silica 5 μm, 4.6 × 250 mm column was used for HPLC analysis. In a typical experiment, 10 mL of a 0.003 M solution of **1–4**, N_2 bubbled, was used for irradiation. After irradiation, products were characterized by comparison with authentic materials. Prolonged irradiation leads to other products (mostly dimers).[3a]

Preparative photoisomerization was conducted as follows: 200 mg of **1** or **2** in 250 mL of benzene (0.003 M) was N_2 bubbled and irradiated using a 450 W Hg lamp with $NaNO_2$/$CuSO_4$ solution filter (excitation above 400 nm). Reaction was monitored by HPLC. The reaction was complete in 1 h, and the cis isomer (94%) was isolated by silica gel column chro-

---

(27) (a) Letard, J. F.; Lapouyade, R.; Rettig, W. *J. Am. Chem. Soc.* **1993**, *115*, 2441. (b) Lapouyade, R.; Czeschka, K.; Majenz, W.; Rettig, W.; Gilabert, E.; Rulliere, C. *J. Phys. Chem.* **1992**, *96*, 9643.

(28) Calvert, J. G., Pitts, J. N., Jr., Eds. *Photochemistry*; John Wiley: New York, 1966; Chapter 7.

matography. Both *cis*-**1** and *cis*-**2** were prepared in this way. Thus prepared, *cis*-**1** isomer was used to make *cis*-**3** alcohol and *cis*-**4** acetate.

A SPEX-Fluorolog fluorimeter equipped with a 450 W Xe lamp was used for fluorescence studies. Solvents used were of analytical grade. Identical conditions were maintained for all the fluorescence measurements. The excitation wavelength was 360 nm, the slit width was 2 × 2 × 2 × 2 mm, and the emission spectral range was 380–700 nm; all operations were at room temperature. Quantum yields of fluorescence were determined relative to that of 9,10-diphenylanthracene (0.9).[28,29]

Quantum yields of isomerization were 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 the 360 nm band. Potassium ferrioxalate was used as an actinometer. Conversions were kept below 7% in all measurements, and all experiments were conducted at room temperature.

Acknowledgment. We thank the referees for helpful comments on the mechanism. We thank Dr. U. T. Bhalerao, Head Division and Incharge Director, for encouraging support in these investigations. V.R. thanks UGC and A.M.R. thanks CSIR for fellowships. This is IICT Communication No. 3559.

Supporting Information Available: Copies of ^{1}H-NMR, ^{13}C-NMR, mass, and UV–vis spectra of **1**–**4** and *cis*-**1**–*cis*–**4** (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9501203

---

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