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Wavelength dependent regioselective *E*→*Z* isomerization of 9-anthryldiene derivatives

Majjigapu Janaki Ram Reddy, Perepogu Arun Kumar, Uppalanchi Srinivas, Vummadi Venkat Reddy, Maruthi Janaki Ram Reddy, G Venugopal Rao & Vaidya Jayathirtha Rao*

Organic Division II, Indian Institute of Chemical Technology, Hyderabad 500 007, India
jrao@iict.res.in

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9-Anthryldiene derivatives **1-5** are synthesized to study *E*→*Z* photoisomerization. Photoisomer composition upon direct excitation, and triplet-sensitized isomerization are determined. Quantum yield of isomerization, quantum yield of fluorescence and fluorescence life times are determined for these compounds. Interestingly, upon direct excitation the anthryldiene derivatives **1-3** carrying electron withdrawing end groups (EWG) displayed wavelength dependent regioselective *E*→*Z* isomerization from the singlet excited state. Triplet sensitization studies revealed that these anthryldiene derivatives undergo *Z*→*E* isomerization and not *E*→*Z* isomerization. The dual fluorescence observed for **1**, **2**, **3** and 2*E*, 4*Z*-**1**, indicates the involvement of two different emissive states. The fluorescence solvatochromism displayed by **1**, **2**, **3** and 2*E*, 4*Z*-**1** is a clear indication of the involvement of a highly polarized/charge transfer singlet-excited state and the same is involved in the isomerization process. Fluorescence lifetimes measured for these compounds displayed bi-exponential behavior supporting the presence of two emissive states. A mechanism for photoisomerization is suggested.

Keywords: Anthryldienes, photoisomerization, wavelength dependence, regioselectivity, charge transfer, fluorescence

Photochemical *cis-trans* isomerization is one of the most interesting aspects of the modern molecular photochemistry[1] and photobiology[2]. The photochemical *Z* – *E* isomerization has practical application in industry[3-5] in the process of vitamin A, vitamin D and further it is a likely candidate for the many proposed opto-electrical and opto-mechanical switching and storage devices[6] and also in various types of materials[7-11]. In the above-mentioned systems, regulation of the direction and selectivity of isomerization are major requisites for the utility of desired switching properties. Understanding the relationship between the structures and the behavior of the molecules exhibiting photochemical *Z*/*E* isomerization can yield significant knowledge and clues for the construction of photoswitching molecules, as well as information about the reaction mechanism. The photochemical *cis-trans* isomerization is discussed by several researchers[12-15]. One-way photoisomerization of anthrylethylenes from their triplet state has been summarized[16]. The role of singlet-excited state in the *cis-trans* isomerization is relatively less discussed[17]. The singlet-excited state involved in these photoisomerizations is predicted to have highly polarized/charge transfer character[18,19]. Our continuing interest on isomerization of aryl substituted acrylic compounds[20-22] prompted us to study the 9-anthryldiene derivatives photoisomerization process. To this end several anthryldiene derivatives have been synthesized and studied their photoisomerization process. Interestingly, anthryldiene derivatives (**Chart 1**) carrying electron withdrawing end groups (EWG) displayed wavelength dependent regioselective *E*→*Z* isomerization from their singlet-excited state. Fluorescence studies indicated that highly polarized / charge transfer nature of the singlet excited state involved in the *E*→*Z* isomerization process. Triplet sensitization yields only *Z* to *E* isomerization. Dual

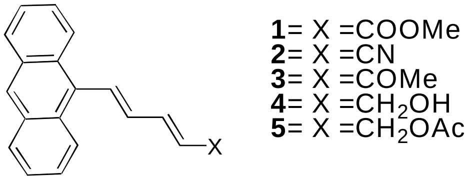


Chart 1

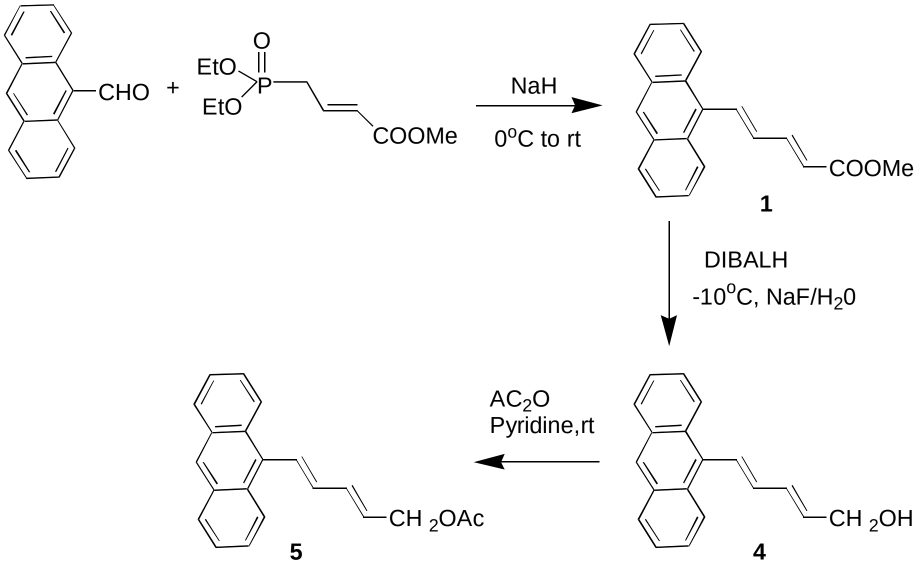
Dedicated to Prof. V Ramamurthy, Dept. of Chemistry, University of Miami, FL, USA, On the occasion of 60th birthday.

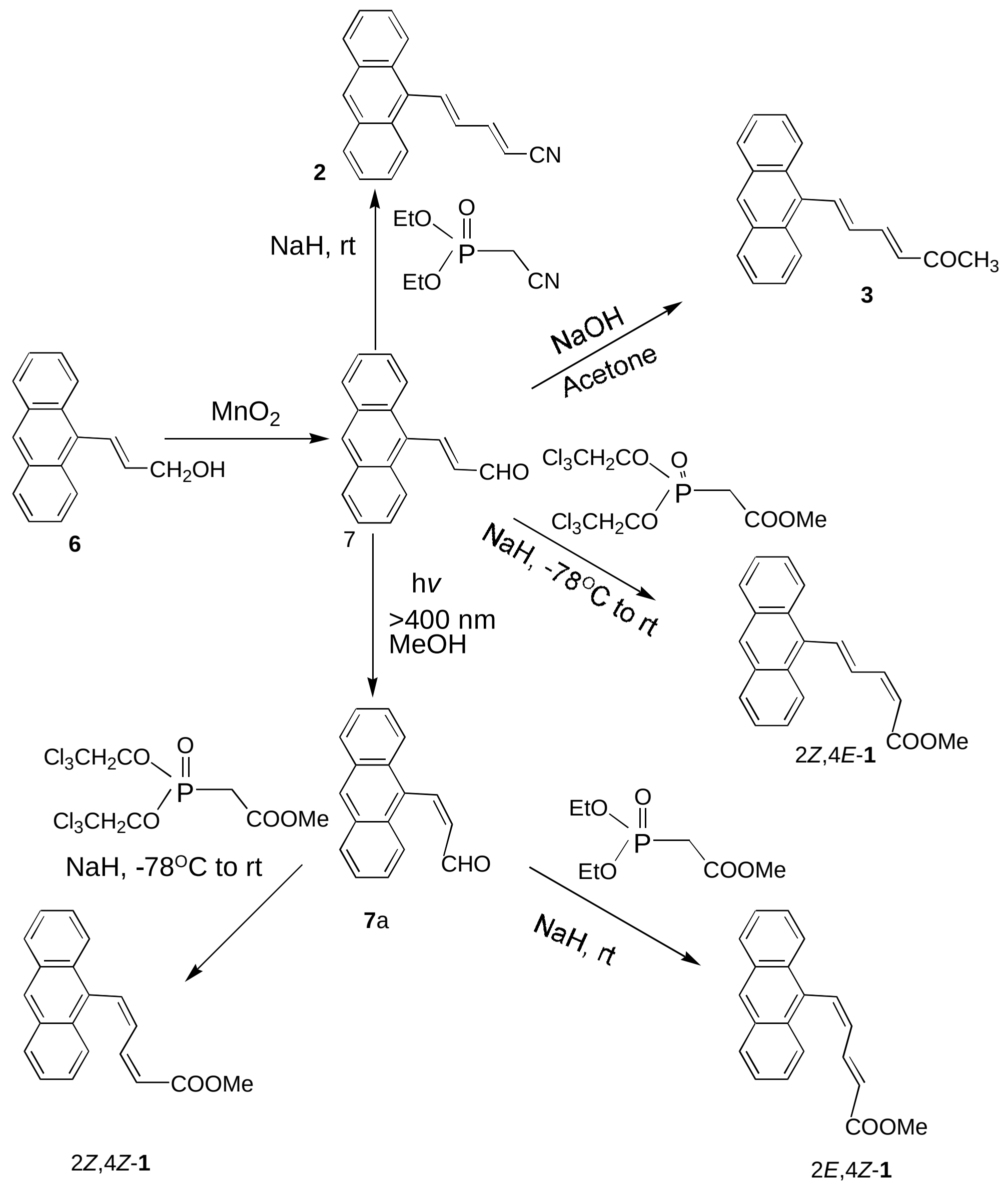
emission indicates two excited states and is supported by the fluorescence lifetimes measured. UV-visible absorption spectra showed that compound **1** has broad absorption spectra and its isomer 2*E*, 4*Z*-**1** has fine structure. Compounds **1**, **2**, **3** and 2*E*, 4*Z*-**1** exhibited fluorescence solvatochromism and these compounds displayed an increase in the quantum yield of isomerization upon changing the solvent polarity, which is attributed to the involvement of intramolecular charge transfer excited state. The fluorescence behavior of compound **4** and **5** is unaffected by solvent polarity.

Results and Discussion

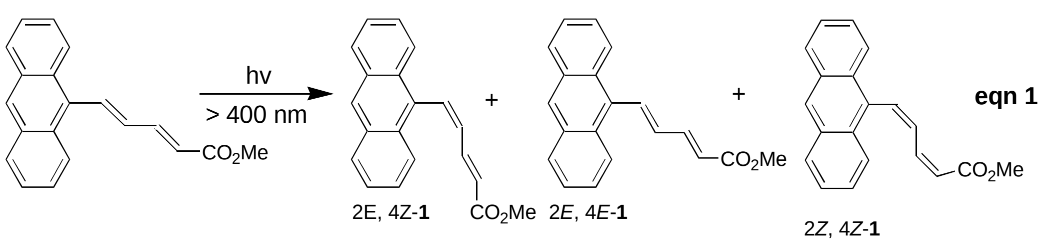
Synthesis 9-anthryldiens derivatives 1-5. The 9-anthryldiene derivatives **1-5** (**Chart 1**) were synthesized starting from 9-anthraldehyde. The 9-anthraldehyde was prepared by adopting known procedure[25a]. Methyldiethylphosphono-2-buteonate, diethylphosphonoacetonitrile and methyl-bis-(2,2,2,trichloroethyl)-phosphonoacetate were prepared according to published procedures[25b,26].Methyl- 5- (9-anthryl)-(2*E*-4*E*)-2,4-pentadienoate **1** was synthesized from 9-anthraldehyde using methyl diethyl phosphono-2-buteonate (Horner-Wadsworth-Emmons reaction; **Scheme I**). Thus synthesized compound **1** was reduced using DIBALH to get compound **4**. Compound **4** was acetylated using Ac_2O/pyridine to make compound **5**. Compound **7** is the key intermediate for the synthesis of **2**, **3** and other *cis* isomers of compound **1**. Compound **7** was synthesized by oxidizing earlier reported[25c] alcohol **6** using MnO_2. The Compound **2** was prepared from **7** using diethylphosphonoacetonitrile (HWE) reaction. Compound **7** was reacted gently with acetone in the presence of base to furnish compound **3** (**Scheme I**). The 2*Z*, 4*E*-**1** isomer was prepared from the corresponding aldehyde **7** using a modified phosphonate (HWE reagent, **Scheme I**)[21]. The compound **7** was photolysed to make **7a** (*Z* isomer of **7**) and thus prepared **7a** served to synthesize 2*E*, 4*Z*-**1** and 2*Z*, 4*Z*-**1** compounds (**Scheme I**).

Photochemical *E*-*Z* isomerization. All the compounds **1-5** were photolysed under different photolytic conditions and also in different solvents (**Table I**). Interestingly compounds **1**, **2** and **3** upon direct excitation using >400 nm light resulted in forming 2*E*, 4*Z*-**1** isomer in >92% (**Table I**) with high regioselectivity. The same compounds **1**, **2** and **3** gave a close to 1:1 mixture of *2E*, 4*E* and 2*E*-4*Z* isomer upon changing the irradiating wavelength to >300 nm (Pyrex filter) or ~350 nm (Rayonet reactor). By changing the wavelength of irradiation, there is a change in the product distribution (**Table I**) indicating the importance of wavelength dependency. All the isomerization reactions were monitored by normal phase HPLC. (**Figure 1**). Solvent polarity did not have any effect on the *E*-*Z* isomer composition but it has effect on the time required to reach the *E*-*Z* isomer composition. The *E*-*Z* isomerization was carried out for **1** at various time intervals (**Table I**) to monitor the reaction closely. It required ~30 min of irradiation to reach maximum selectivity of 92% 2*E*, 4*Z*-**1** isomer, and after 60 min. of irradiation a small amount of 2*Z*, 4*Z*-**1** isomer appeared (Eqn. 1, **Table I**). More interestingly compound **4** and **5** did





Scheme 1



not exhibit *E-Z* isomerization upon direct excitation using >400 nm, ~350 nm, and >300 nm of light source. The compounds **1**, **2**, and **3** carry an electron withdrawing end group (strong acceptor group) where as the compounds **4** and **5** do not carry electron withdrawing end group and this may have effect on the photoisomerization and it is consistent with the earlier observations[27]. Further we have carried out *E-Z*

Table I — Wavelength dependent *E*→*Z* isomer compositions of 9-anthryldiene derivatives[a]

Sl. No	Compd	Light source	Time (min)	λ_{exci} (nm)	2*E*,4*E*-**1** (%)	2*E*,4*Z*-**1** (%)	2*Z*,4*Z*-**1** (%)	2*Z*,4*E*-**1** (%)
1	**1**	450 Hg arc	05	>400	58	42	------	------
2		450 Hg arc	10	>400	20	80	-----	------
3		450 Hg arc	15	>400	08	92	------	------
4		450 Hg arc	20	>400	06	93	01	------
5		450 Hg arc	30	>400	04	94	02	------
6		450 Hg arc	60	>400	04	94	02	------
7		Rayonet	30	~350	40	60	------	------
8		450 Hg arc	30	>300	48	52	------	------
9	**2**	450 Hg arc	30	>400	08	92	------	------
10		Rayonet	30	~350	42	58	------	------
11		450 Hg arc	30	>300	48	52	------	------
12	**3**	450 Hg arc	30	>400	08	92	------	------
13		Rayonet	30	~350	42	58	------	------
14		450 Hg arc	30	>300	48	52	------	------
15	**4 & 5**	450 Hg arc	60	>400		No *E* to *Z* isomerization		
16		Rayonet	60	~350		No *E* to *Z* isomerization		
17		450 Hg arc	60	>300		No *E* to *Z* isomerization		

[a]Pyrex filter for >300 nm; $NaNO_2$ /$CuSO_4$ solution filter[23] for >400 nm; analysis by HPLC; 0.0005 *M* nitrogen bubbled methanol/acetonitrile/hexane solutions were used for irradiation; experimental error limit on product ratio is <1.0%.

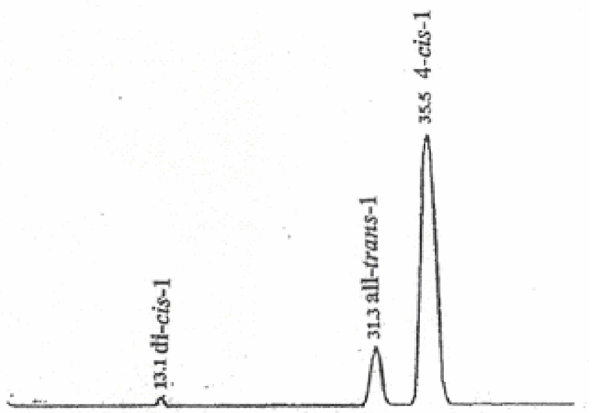


Figure 1 — HPLC chromatogram showing 2*E*, 4*E*-**1** at 31.3 min, 2*E*, 4*Z*,-**1** at 35.5 min and 2*Z*, 4*Z*-**1** at 13.1 min. (5 µm amino silica, 4.5 × 250 mm column; detective wave length 380 nm, hexane/dichloromethane as an eluent; 90:10).

Table II — *E*–*Z* isomer compositions of 1 at various concentrations upon direct excitation[a]

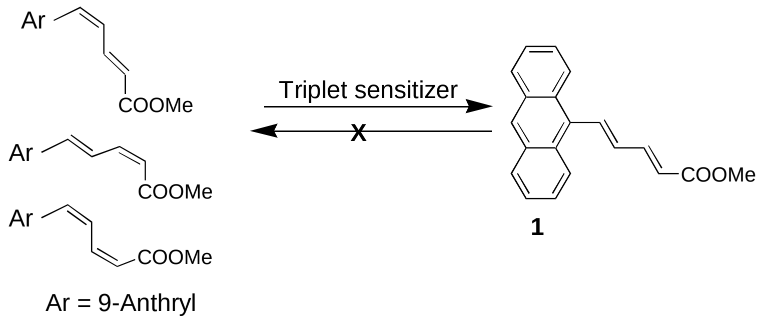
Sl. No	Concn (*M*)	2*E*, 4*E*-**1** (%)	2*E*, 4*Z*-**1** (%)	2*Z*, 4*Z*-**1** (%)	2*Z*, 4*E*-**1** (%)
1	0.0005	04	94	02	------
2	0.0010	04	94	02	------
3	0.0015	04	94	02	------
4	0.0030	04	94	02	------
5	0.0045	04	94	02	------

[a]MeOH solvent; all solutions were nitrogen bubbled prior to irradiation; exciting wavelength was >400 nm; analysis by HPLC; ~30 min of irradiation

photoisomerization for **1** upon direct excitation at >400 nm (**Table II**) at various concentrations and it indicates that the regioselectivity is unaffected by the variation of substrate concentration.

Triplet sensitized isomerization. Triplet sensitized isomerization reactions were carried out for **1-5** and *cis* isomers of **1** to understand the role of multiplicity of excited state on the observed regioselective isomerization. The results of these studies are compiled in **Table III**. All the *cis* isomers (2*E*, 4*Z*-**1**, 2*Z*, 4*Z*-**1**, and 2*Z*, 4*E*-**1**) of compound **1** underwent highly selective One-Way *Z* to *E* isomerization upon triplet sensitization. Triplet sensitization yielded over 98% of *E* isomer (Eqn. 2, **Table III**) irrespective of triplet sensitizer employed. Three triplet sensitizers were used with variable triplet energy for sensitization reactions (**Table III**). Interestingly compounds **1-5** [all *E* isomers] did not yield any *Z* isomer upon triplet sensitization using three different sensitizers (**Table III**).

Absorption and fluorescence properties. We have obtained UV-visible absorption spectra (**Figures 2-4**), fluorescence emission and excitation spectra (**Figures 5-9**) and quantum yield of fluorescence were calculated in various solvents and are shown in **Table IV**, to understand the excited state behavior of these anthryldiene derivatives. UV-visible absorption data (**Table IV**) indicate that the absorption properties are not varied much by changing the solvent polarity. But compound **1** differs in absorption spectra from



eqn 2

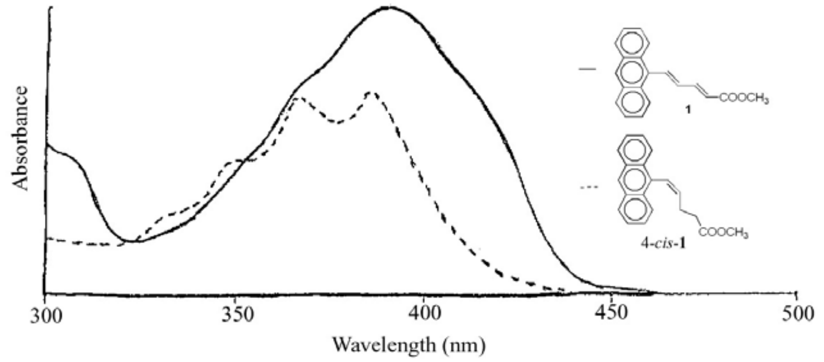


Figure 2 — UV-visible absorption spectrum of compound **1** and 2*E,* 4*Z*-**1** in hexane

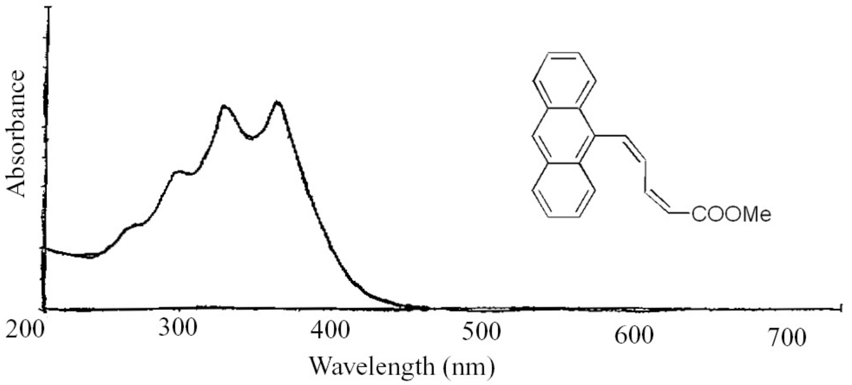


Figure 3 — UV-visible absorption spectrum of compound 2*Z,* 4*Z*-**1** in hexane

its 2*E*, 4*Z*-**1** isomer (**Figure 2**). Compound **1** and 2*Z*, 4*E*-**1** isomers have broad absorption spectra, where as its 2*E*, 4*Z*-**1** and 2*Z*, 4*Z*-**1** isomers show structured absorption spectra (**Figures 2**, **3** and **4**). The same trend is observed for compounds **2** and **3**. Fluorescence data generated for compounds **1-5** and 2*E*, 4*Z*-**1** are arranged in **Table IV**. Unlike UV-visible absorption, the fluorescence responded interestingly towards solvent polarity. There is a dramatic change in the fluorescence behavior of **1**, **2**, **3** and 2*E*, 4*Z*-**1** by changing the solvent polarity (**Table IV**). Fluorescence emission spectra are given in **Figures 5-9**. There is a 32 nm red shift observed in the fluorescence emission maxima of **1** by changing the solvent non-polar hexane to polar methanol and the **Figure 8** clearly indicates the phenomenon of fluorescence solvatochromism exhibited by **3**. Interestingly the dual emission behavior of **1** is

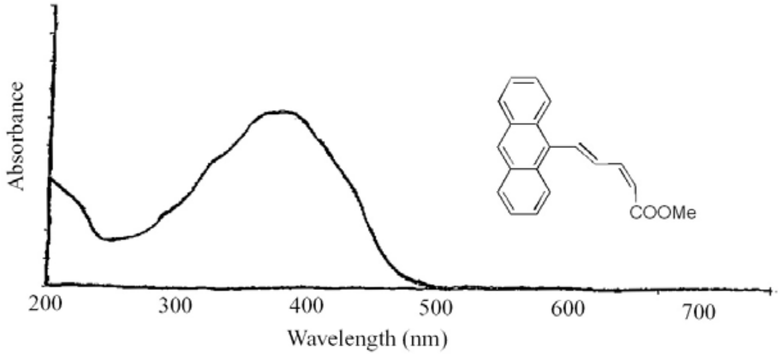


Figure 4 — UV-visible absorption spectrum of compound 2*Z,* 4*E*-**1** in hexane

Table III — Triplet sensitized *E-Z* isomer compositions of 9-anthryldiene derivatives[a]

Sl No.	Compound	Sensitizer	Sensitizer (λ_{max}) nm	E_T K.cal/mol	*trans* (%)	*cis* (%)
1	2*E*, 4*Z*-**1**	Rose Bengal	550	39	98	02
2		Erythrosine	517	42	98	02
3		Eosin	515	43	98	02
4	2*Z*, 4*Z*-**1**	Rose Bengal	550	39	98	02
5		Erythrosine	517	42	98	02
6		Eosin	515	43	98	02
7	2*Z*, 4*E*-**1**	Rose Bengal	550	39	98	02
8		Erythrosine	517	42	98	02
9		Eosin	515	43	98	02
10	**1-5**	Rose Bengal	550	39	No *E* to *Z* isomerization	
11		Erythrosine	517	42	No *E* to *Z* isomerization	
12		Eosin	515	43	No *E* to *Z* isomerization	

[a] Nitrogen-bubbled 0.001 *M* methanolic solutions containing 0.01 *M* sensitizer were used for irradiation; solution filters were employed to achieve selective excitation of the sensitizer[23]; analysis by HPLC; experimental error limit is <1.0%, *trans* isomer is stable under these conditions.

especially evident when the fluorescence spectrum recorded in methanol (**Figure 7**). The quantum yield of fluorescence for all the compounds have been determined. Interestingly the quantum yield of fluorescence is decreasing dramatically from non-polar hexane (0.575) to polar methanol (0.002) for **1** as shown in **Table IV**. The same trend is observed for compounds **2**, **3** and 2*E*, 4*Z*-**1** (**Table IV**). More interestingly the compounds **4** and **5** did not exhibit fluorescence solvatochromism, also there is no change in the quantum yield of fluorescence upon change in solvent polarity and they showed very high quantum yield of fluorescence (>0.8).

Fluorescence lifetimes were measured for these 9-anthryldiene derivatives in selected solvents, and the results are arranged in **Table V**. Decay profiles were obtained by using a time correlated single photon counting apparatus[28]. Satisfactory fits to a bi-exponential were obtained for **1** and **3**, and satisfactory fits to a single exponential were obtained for **4** and **5**. The χ^2 values and the pre-exponentials are listed. The bi exponential behavior indicates that two singlet-excited states are involved, these may be Locally Excited (LE) and Charge Transfer (CT) singlet excited states. The dual emission behavior of these compounds **1** and **3** is explained involving LE and CT excited singlet states. It is proposed that long-lived excited state may be LE singlet state; the other short-lived may be CT state. Interestingly compounds **4** and **5** displayed mono-exponential behavior, *i.e.* involvement of only one excited state and this may be LE singlet state. The short-lived singlet is found to contribute more fluorescence compared to the long-lived singlet in **1** and **3**.

Quantum yield of isomerization. The quantum yield of isomerization upon direct excitation (366 nm) for these anthryldiene derivatives **1**, **2**, **3** and 2*E*, 4*Z*-**1**, determined in hexane and acetonitrile solvents (**Table VI**). The data indicate that photoisomerization is a relatively efficient process upon direct excitation. Interestingly, *E*→*Z* and *Z*→*E* quantum yield of isomerization are comparable (**Table VI**). All these

Table IV — Absorption and fluorescence data of 9-anthryldiene derivatives[a]

Sl. No .	Compd	Solvent	λ_{abs} (nm)	λ_{fluo} (nm)	Φ_{flu}
1	**1**	Hexane	388	520	0.575
2		Benzene	394	536	0.087
3		Dichloromethane	394	540	0.016
4		Acetonitrile	388	548	0.008
5		Methanol	388	552	0.002
6	2*E*, 4*Z*-**1**	Hexane	388	524	0.325
7		Methanol	388	552	0.001
8	**2**	Hexane	388	520	0.518
9		Methanol	388	552	0.002
10	**3**	Hexane	382	492	0.194
11		Benzene	388	508	0.04
12		Dichloromethane	388	520	0.008
13		Acetonitrile	386	524	0.001
14	**4**	Hexane	384	484	0.84
15		Acetonitrile	384	488	0.82
16	**5**	Hexane	384	484	0.865
17		Acetonitrile	384	488	0.826

[a] Nitrogen-bubbled 0.00001 *M* solutions were used for measuring the fluorescence at room temperature; quantum yields of fluorescence were determined using 9,10-diphenyl anthracene (Φ_{flu} = 0.9) as standard[38], experimental error is ± 10.0%.

Table V — Fluorescence life times of various compounds in different solvents[a]

Compd	Solvent	τ_1 (ns)	τ_2 (ns)	χ^2
1	Hexane	2.329(0.34)	1.73(0.66)	1.106
	CH_3CN	0.493(0.996)	3.45(0.004)	0.947
3	CH_3CN	0.176(0.99)	4.216(0.01)	1.276
4	Hexane	4.431	-----	1.126
	CH_3CN	4.641	-----	0.970
5	Hexane	4.741	-----	1.045
	CH_3CN	5.273	-----	0.990

[a] The quantities in brackets indicate the relative weightage of individual components present in the decay curves. Life times are measured at 10^{-4} *M* concentration of compounds.

Table VI — Quantum yield isomerization of **1**, **2**, **3** and 2*E*, 4*Z*-**1** upon direct excitation[a]

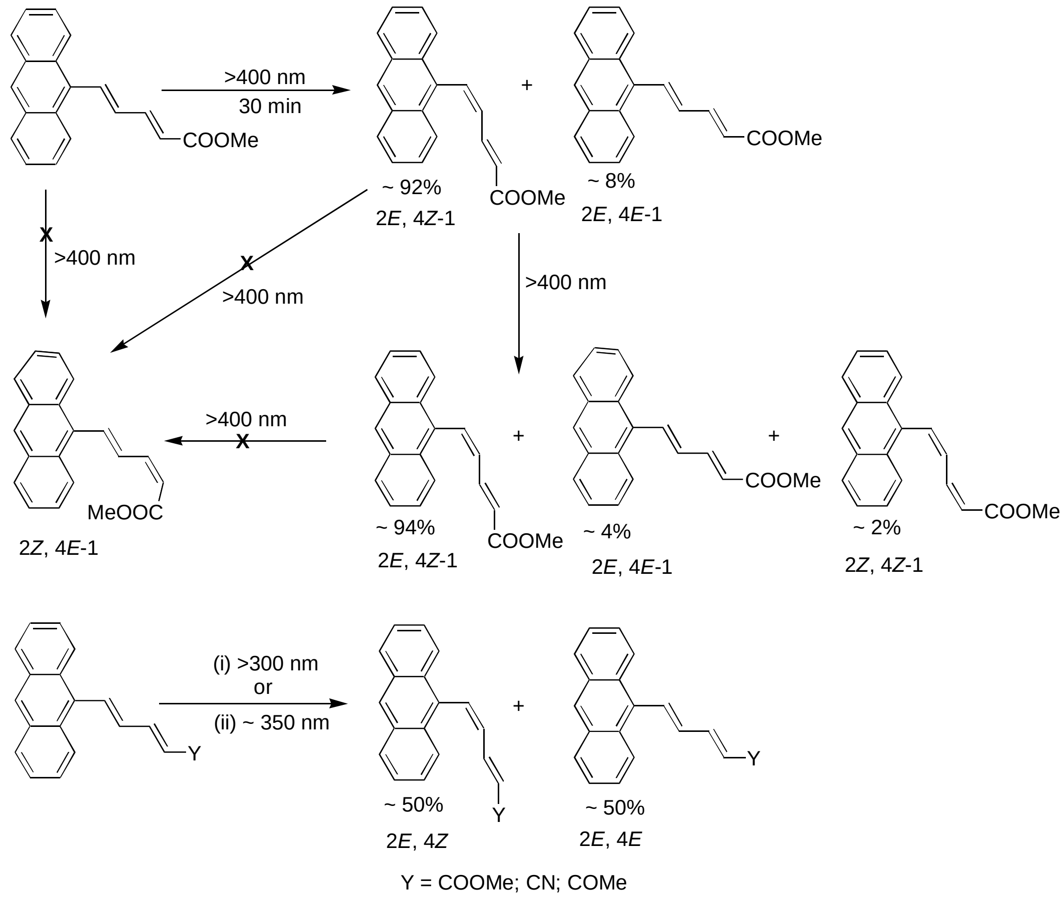
Compd	Φ_{Iso} in Hexane	Φ_{Iso} in Acetonitrile
1	0.220	0.438
2	0.280	0.480
3	0.192	0.382
2*E*, 4*Z*-**1**	0.314	0.45

[a] Nitrogen bubbled solutions were irradiated; the 366 nm line of Hg lamp was isolated using solution filters[23]; potassium ferrioxalate was used for counting photons; for **1**, **2** and **3** the reaction is *E* to *Z* isomerization, and for 2*E*, 4*Z*-**1** the reaction is *Z* to *E*.

compounds displayed an increase in the quantum yield of isomerization upon changing the solvent polarity.

Photoisomerization. Compounds **1**, **2**, and **3** underwent wavelength dependent photisomerization upon photolysis at >400 nm of light giving regioselectively 2*E*, 4*Z*-**1** isomer (**Table I**, **Scheme II**). The observed regioselectivity is rationalized based on the absorption properties of these compounds. Compound **1** and its 2*Z*, 4*E*-**1** isomer have similar absorption properties compared to 2*E*, 4*Z*-**1** and 2*Z*, 4*Z*-**1** isomers (**Figures 2-4**) and hence they (**1** and 2Z, 4E-**1**) absorb light differentially under the same photolytic conditions. The formation of highly selective 2*E*, 4*Z*-**1** isomer is attributed to the higher light absorption capability of 2*E*, 4*E*-**1** and 2*Z*, 4*E*-**1** isomer (**Figures 2-4**) at the given >400 nm irradiation conditions giving 94% of the isomer. Further irradiation gives formation of 2*Z*, 4*Z*-**1** isomer from 2*E*, 4*Z*-**1** but not from 2*E*, 4*E*-**1** or 2*Z*, 4*E*-**1**. This is supported by the time dependent isomer distribution data provided in **Table I**. The non-formation of 2*Z*, 4*E*-**1** isomer (**Scheme II**) also be explained because of the higher light absorption property (**Figure IV**) at the given wavelength of irradiation (>400 nm). The same compounds **1**, **2**, and **3** upon photolysis at >300 nm (Pyrex filter) or ~350 (Rayonet reactor) gave almost 1:1 mixture of 2*E*, 4*E* and 2*E*, 4*Z* isomer (**Table I**), as both the *E* and *Z* isomers can absorb light at that particular wavelength of irradiation. These observations indicate that 2*E*, 4*Z* formation is regioselective and is wavelength dependent.

Compounds **1-5** upon irradiation using various triplet sensitizers (**Table III** with selective excitation of sensitizer) did not yield *Z* isomer, but the *cis* isomers of **1** underwent *'One-Way' Z*→*E* photoisomerization when the same triplet sensitizers employed. This indicates that the *E*→*Z* photoisomerization is taking place from singlet excited state but not from the triplet state as may be the intersystem crossing is not taking place from singlet excited manifold. *Z*→*E* Isomerization is effective from triplet state (Eqn 2) indicating that the triplet energies of these compounds are in the range of 38-45 kcal/mole. Compounds **4** and **5** lack electron withdrawing end group (EWG) and did not undergo photoisomerization, but exhibit high fluorescence[29]. This observation supports that an electron withdrawing group is essential in the formation of charge transfer excited state and also responsible for the observed *E*→*Z* isomerization.



Scheme II

Compounds **1**, **2**, **3** and 2*E*, 4*Z*-**1** displayed an increase in the quantum yield of isomerization upon changing the solvent polarity (**Table VI**). These compounds get highly polarized upon excitation, forming a charge transfer singlet excited state and this polarized/charge transfer excited state interacts with polar solvent leading to an increase in the quantum yield of isomerization.

Charge transfer nature of the singlet excited state. We have obtained absorption and fluorescence data for these anthryldiene derivatives to understand the involvement and nature of the highly polarized/charge transfer excited state. Absorption and fluorescence data are arranged in **Table IV**. The absorption maximum for all the compounds is unaffected by the solvent polarity indicating that there is no ground state level interaction. Fluorescence studies indicate the involvement of a charge transfer/polar nature of singlet-excited state (fluorescence solvatochromism; **Figure 8**, **Table IV**). The solvent polarity induced (solvatochromism) red shift of the fluorescence maximum and decrease in the quantum yield of emission is a definite indication of the involvement of an intramolecular charge transfer[30-33] excited state. Upon absorption of light, the molecule is excited to a "locally excited (LE) singlet excited state and subsequently it is transformed into 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 7**. The fluorescence of **1** in hexane shows a small shoulder in the lower wavelength region corresponding to Locally Excited state (LE state) and this LE state becomes prominent in the methanol solvent (**Figure 7**). Compounds **4** and **5** did not exhibit fluorescence solvatochromism but exhibits high fluorescence from the LE state indicating the non-involvement of charge transfer excited state due to lack of acceptor group or electron withdrawing group. Additionally, the fluorescence spectra of the *trans* and *cis* isomers of **1** are nearly identical[34] as shown in **Figure 5** and **Figure 6**, supporting the hypothesis that singlet excited states of **1** and 2*E*, 4*Z*-**1** have same nature of

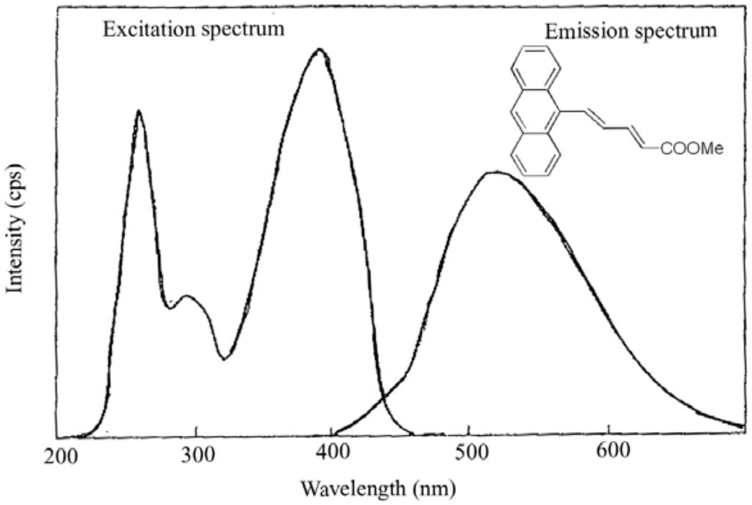


Figure 5 — Fluorescence excitation and emission spectra of compound **1** in hexane

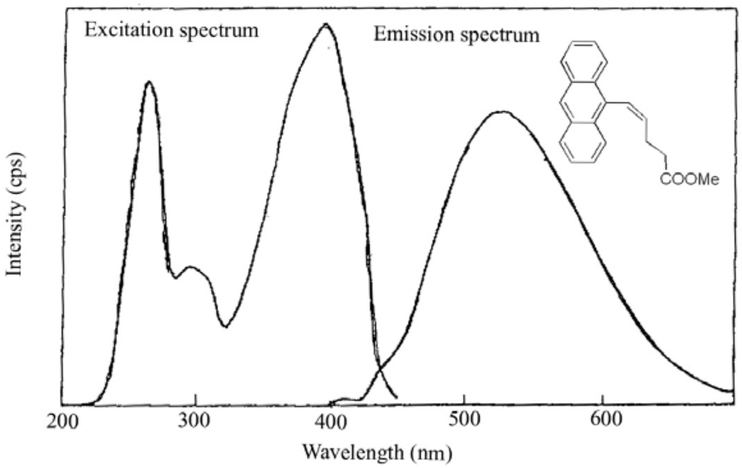


Figure 6 — Fluorescence excitation and emission spectra of compound 2*E*, 4*Z*-**1** in hexane

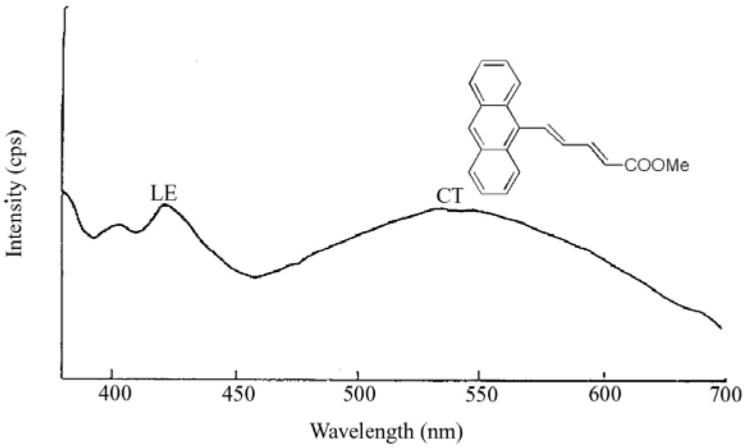


Figure 7 — Fluorescence emission spectra of compound **1** in methanol

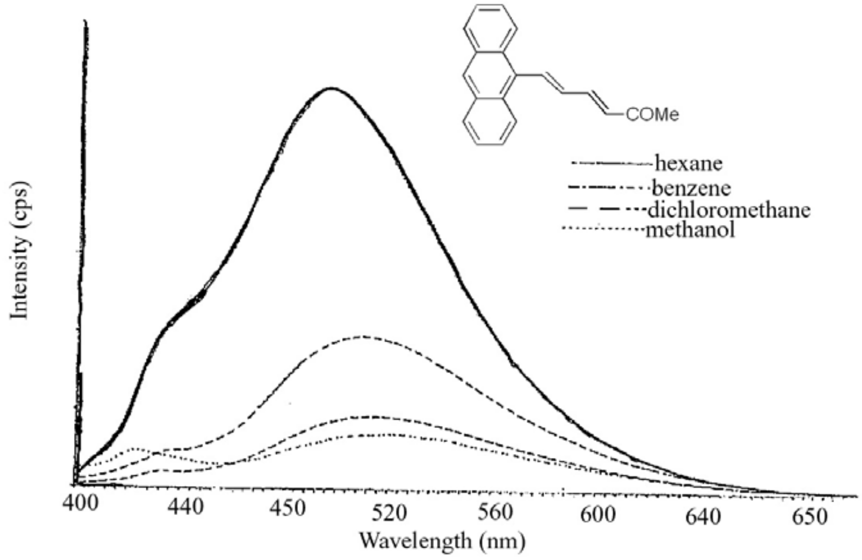


Figure 8 — Fluorescence emission spectra of compound **3** in different solvents

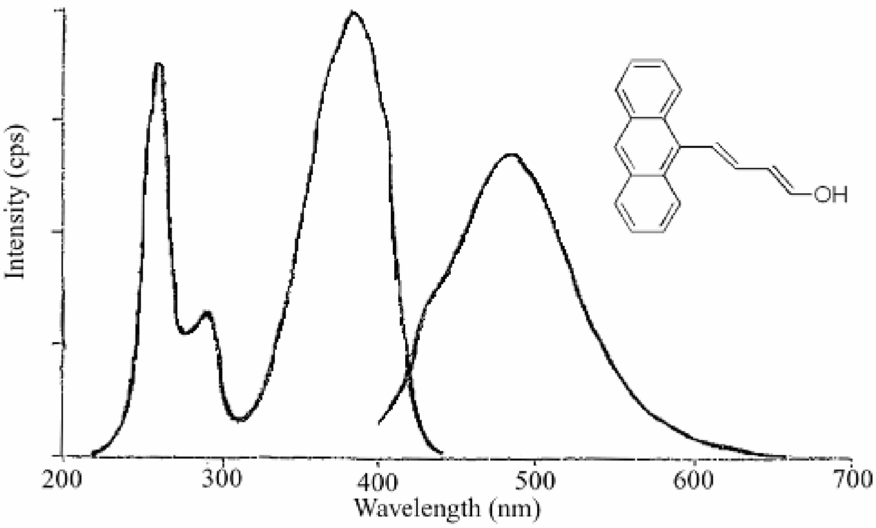
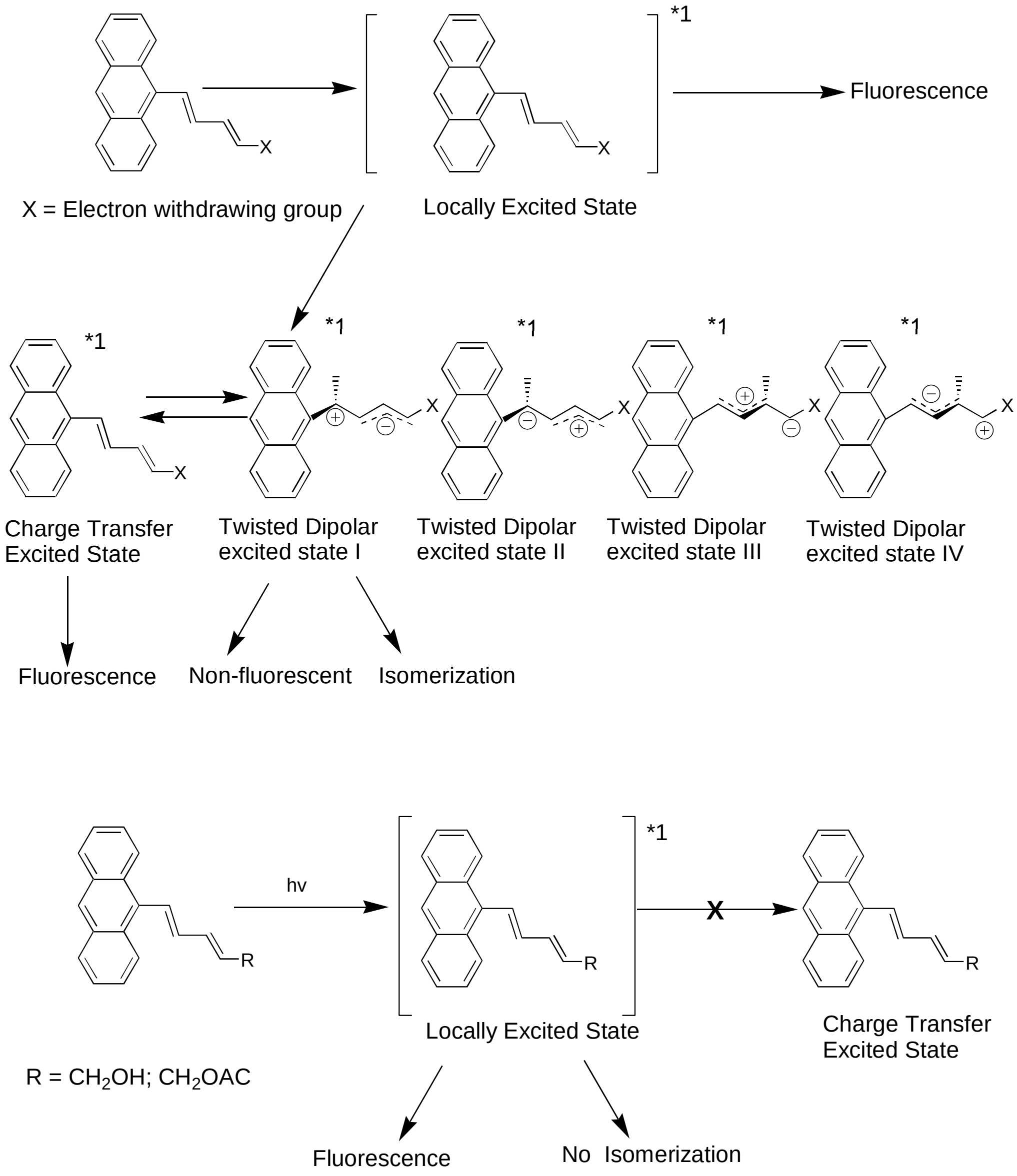


Figure 9 — Fluorescence excitation and emission spectra of compound **4** in hexane

charge transfer character[35,36]. The fluorescence life time data (**Table V**) for compounds **1** and **3** is found to be bi-exponential and for compounds **4** and **5** it is single exponential. The bi-exponential behavior indicate that there are two singlet excited states are involved, these may be Locally Excited State (LE) and Charge Transfer (CT) State. Dual emission behavior of these compounds (**1** and **3**) is explained involving LE and CT excited singlet state. It is proposed that long-lived singlet may be LE singlet state; the other short-lived may be the CT state. Compounds **4** and **5** have monoexponential decay indicating only one excited state and this may be LE state since there is no solvent polarity effect observed on their fluorescence (**Table IV**).

Mechanism. The proposed mechanism of photochemical *E*→*Z* isomerization for these anthryldiene derivatives is depicted in **Scheme III**. Initial light absorption results in the molecule being in the locally excited (LE) singlet state, transforms into a charge transfer (CT) state. The two LE and CT states proposed are supported by the dual fluorescence and fluorescence life times measured. The same two-state model proposed here is also consistent with the earlier reports[37], where multiple adiabaticity was formulated. Theoretically four possible twisted dipolar excited states are possible (**Scheme III**). Out of which two excited states (I, II) are formed by the twisting of 4–5 double bond of anthryldiene moiety and the other two are formed by the twisting of 2–3 double bond (III, IV, **Scheme III**). As the compound **1** is substituted with electron withdrawing end group (EWG, COOMe), the excited state in which the negative charge is localized towards electron withdrawing end group is more stable, and hence III and IV can be ruled out. Twisting/rotation (+ 90°) of twisted excited state I gives 2*E*, 4*Z*-**1** isomer and excited state III gives 2*Z*, 4*E*-**1** isomer. From our experimental studies 2*E*, 4*Z*-**1** isomer is formed in 94% exclusively. This indicates that the "twisted dipolar" excited state I (Dauben intermediate; **Scheme III**) is the most probable and it is the possible twisted excited state leading to the formation of 2*E*, 4*Z*-**1** isomer achieving regioselectivity. The next process for the excited state is further twisting, which ultimately leads to *Z* isomer. The twisted dipolar excited state may be non-fluorescent (**Scheme III**) because of perturbation introduced in the molecule due to twisting. Interestingly, the anthryldienes without electron withdrawing groups shows high fluorescence, no *E* to *Z* isomerization and no charge transfer excited state formation.



Scheme III

Materials and Methods

All solvents were freshly distilled and dried before use according to the standard procedures. Reagents were of analytical grade. Solvents for spectral measurements were of UV-infrared (IR) spectral grade. ^{1}H and ^{13}C NMR spectra were recorded using Gemini 200 MHz Varian instrument and Avance 300 MHz Bruker UX-NMR instrument. All chemical shifts were referenced to tetramethylsilane (TMS) as an internal standard. UV-visible absorption spectra were recorded on Perkin-Elmer Lambda-2 spectrophotometer and values are given in nanometers (nm). HPLC analysis were carried out on a Shimadzu LC-6A amino silica column with UV-visible detector and Shimadzu LC-8 with CR-8 integrator by using a C-18 reverse phase 5μ, 0.5 cm/25 cm column.

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[23] 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 for **1-5** and *cis* isomers of **1** (0.001 *M*) by using sensitizer (0.01 *M*) in MeOH (10 mL), N_2 bubbled, which was irradiated for 1 hr 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 hr; the reaction was monitored by HPLC and the *Z* isomer was isolated by column chromatography using silica gel (100-200 mesh). Prolonged irradiation, ~14 hr, 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, ref. 24).

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[23]. Conversions were kept below 7% in all measurements, and all experiments were conducted at room temperature.

Experimental Section

Methyl- 5- (9-anthryl)-(2*E*-4*E*)-2,4-pentadienoate 1

Methyl diethyl phosphono-2-buteonate (3 g, 14.5 mmole) was added slowly to a solution containing NaH (345 mg, 14.5 mmole) in dry *N*, *N*'-dimethylformamide (15 mL) under $N_{2,}$ at 0°C temperature. The phosphoryl-stabilized carbanion was treated with 9-anthraldehyde (2.7 g, 13 mmole) in 10 mL of dry *N*, *N'*-dimethylformamide slowly. After addition, the reaction- mixture was brought to room temperature and stirred for 3 hr. The reaction was quenched with water and the reaction mixture was extracted with ether and the organic layer was dried over anhydrous sodium sulfate, the ether was evaporated, and the compound was purified by column chromatography (EtOAc/hexane 1:4) to afford **1** (3 g, 80%) as a solid; m.p. 145°C ^{1}H NMR (200 MHz, $CDCl_{3,}$ 25°C): δ (ppm): 3.75 (s, 3H), 5.9-6.05 (d, 1H, *J*=15.5 Hz), 6.6-6.75 (dd, 1H, *J*=15.8 Hz), 7.3-7.45 (m, 5H), 7.65-7.8 (d, 1H, *J*=15.5 Hz), 7.85-7.95 (m, 2H), 8.05-8.15 (m, 2H), 8.35 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 51.5, 121.5, 125.3, 125.9, 127.5, 128.8, 129.4, 130.8, 131.3, 135, 137, 144.4, 167.4; IR: 3300, 1706, 1624, 1430 cm^{-1}; UV-vis: 388 nm (hexane at $10^{-5}M$); $\varepsilon = 6184\ cm^{-1}M^{-1}$; emission maxima (hexane) = 520 nm, quantum yield of fluorescence = 0.575; Mass (EI): *m*/*z* 288(M^+), 255, 277, 202, 114, 82; HRMS (EI): *m*/*z* Calcd for $C_{20}H_{16}0_2$ (M^+) 288.115030, Found: 288.114281.

2.5.2. 5-(9-Anthryl)-(2*E*-4*E*)-2,4-pentadienenitrile 2

Methyl diethyl phosphonoacetonitrile (2 g, 11 mmole) in dry *N*, *N*'-dimethylformamide (15 mL) was added slowly to a solution containing NaH (264 mg, 11 mmole) in dry *N*, *N*'-dimethylformamide (20 mL) at room temp. the phosphoryl-stabilized carbanion was treated with **7** (2.3 g, 10 mmole) in 10 mL of dry *N*, *N*'-dimethylformamide slowly. After 3 hr of stirring, the reaction was quenched with water and the reaction mixture was extracted with ether and the organic layer was dried over anhydrous sodium sulfate, the ether was evaporated, and the compound was purified by column chromatography (EtOAc/hexane 1:4) to afford 2 (1.53 g, 60%) as a solid; m.p. 168°C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 ^{o}C): δ 5.4-5.55 (d, 1H, *J*=16.1 Hz), 6.6-6.8 (dd, 1H, *J*=16 Hz), 7.4-7.55 (m, 5H), 7.7-7.85 (d, 1H, *J*=16.1 Hz), 7.9-8.05 (m, 2H), 8.1-8.2 (m, 2H), 8.4 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 99, 125.1, 126.3, 127.1, 128.5, 129, 131.6, 134.3, 138, 150; IR: 3300, 1690, 1620, 1435 cm^{-1}; UV-vis: 388 nm (hexane at $10^{-5}M$); ε = 5665 cm$^{-1}M^{-1}$; emission maxima (hexane) = 520 nm, quantum yield of fluorescence = 0.518; mass (EI): *m*/*z* 255(M+), 229, 215, 202, 113, 101; HRMS (EI): *m*/*z* Calcd for $C_{19}H_{13}N$ (M^+) 255.104800, Found: 255.104801.

5-(9-Anthryl)-(2*E*-4*Z*)-2,4-pentadienenitrile (2*E*,4*Z*-2)

Solid; m.p. 156°C. ^{1}H NMR (200 MHz, $CDCl_3$, 25^{o}C): δ 5.45-5.6 (d, 1H, *J*=16 Hz), 6.85-7.0 (m, 2H), 7.4-7.55 (m, 4H), 8.1-8.2 (m, 5H), 8.45 (s, 1H); UV-vis: 386 nm (hexane at $10^{-5}M$); ε = 5163 cm$^{-1}M^{-1}$; mass (EI): 255(M^+), 229, 215, 202, 113, 101.

5-(9-Anthryl)-(2*E*-4*E*)-2,4-hexadien-1-one 3

Sodium hydroxide solution (5 mL 1 *M*) was added drops wise to a mixture of **7** (2.3 g, 10 mmole) and acetone (50 mL) while stirring at room temp. Stirring was continued for 1hr and the reaction was quenched with water (30 mL) and extracted with ether (3 × 30 mL), organic layer was washed with water (2 × 20 mL), brine solution (20 mL) and dried over anhydrous sodium sulfate, the ether was evaporated, and the compound was purified by column chromatography (EtOAc/hexane 1:3) to afford **3** (2.17 g, 80%) as a solid; m.p. 109°C. ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): δ 2.35 (s, 3H), 6.2-6.35 (d, 1H, *J*=16.5 Hz), 6.6-6.8 (dd, 1H, *J*=16.3 Hz), 7.4-7.6 (m, 5H), 7.75-7.85 (d, 1H, *J*=16.5 Hz), 7.9-8.05 (m, 2H), 8.1-8.25 (m, 2H), 8.4 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 27.5, 125.2, 126, 127.6, 128.8, 129.3, 130.8, 131.3, 135.4, 137.8, 142.8, 198.3; IR: 3426, 3027, 1664, 1440 cm^{-1}; UV-vis: 382 nm (hexane at $10^{-5}M$); ε = 6296 cm$^{-1}M^{-1}$; emission maxima (hexane) = 492 nm, quantum yield of fluorescence = 0.194; mass (EI): 272(M^+), 253, 239, 229, 215, 202, 101; HRMS (EI): *m*/*z* Calcd for $C_{20}H_{16}O$ 272.120825, Found: 272.120825.

5-(9-Anthryl)-(2*E*-4*Z*)-2,4-hexadien-1-one (2*E*,4*Z*-3)

Solid; m.p. 101°C. ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): δ 1.9 (s, 3H), 6.15-6.25 (d, 1H, *J*=16.2 Hz), 6.6-6.8 (m, 2H), 7.4-7.55 (m, 4H), 7.8-7.9 (d, 1H, *J*=16.2 Hz), 7.95-8.1 (m, 4H), 8.45 (s, 1H); UV-vis: 380 nm (hexane at $10^{-5}M$); ε = 5694 cm$^{-1}M^{-1}$; mass (EI): 272 (M^+), 253, 239, 229, 215, 202, 101.

5-(9-Anthryl)-(2*E*-4*E*)-2,4-pentadiene-1-ol 4

Compound **1** (1.2 g, 4.19 mmole) was taken up in to hexane and cooled to –10°C, DIBALH (4.5 mL of 1.9 *M*, in hexane 8.39 mmole) was then added slowly with stirring. After 30 min. at room temp. the reaction mixture 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 and the organic layer was dried over anhydrous sodium sulfate, the ether was evaporated, to get pure alcohol 4 (0.98 g, 90%) as a solid; m.p. 90°C. ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): δ 4.25-4.4 (m, 2H), 5.9-6.05 (m, 1H), 6.5-6.7 (m, 2H), 7.4-7.55 (m, 5H), 7.9-8.05 (m, 2H), 8.2-8.35 (m, 2H), 8.4 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 63.4, 125.2, 125.5, 126.3, 127.5, 129.7, 130, 132.2, 133.4, 137.5; IR: 3240, 2918, 2364 cm^{-1}; UV-vis: 384 nm (hexane at $10^{-5}M$); ε = 6749 cm$^{-1}M^{-1}$, emission maxima (hexane) = 484 nm, quantum yield of fluorescence = 0.84; mass (EI): *m*/*z* 260(M^+), 241, 251, 203; HRMS (EI): *m*/*z* Calcd for $C_{19}H_{21}O_2$ 260.120115, Found: 260.120376.

5-(9-Anthryl)-(2*E*-4*E*)-2,4-pentadienylacetate 5

Acetate 5 was synthesized by a standard procedure by treating alcohol **4** (1.1 g, 4.7 mmole) with acetic anhydride/DMAP (5 mmole/cat. amount) in 10 mL of dichloromethane stirred at room temp. for 12 hr, to afford 5 (1.08 g, 90%) as a solid; m.p. 103°C. ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): δ 2.13 (s, 3H), 4.75 (m, 2H), 5.8-6.0 (m, 1H), 6.6-6.8 (m, 2H), 7.35-7.5 (m, 5H), 7.9-8.05 (m, 2H), 8.15-8.25 (m, 2H), 8.35 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 20.8, 64.5, 124.7, 125.3, 126.5, 126.8, 127.3, 128.5, 129.6, 131.3, 132, 134, 136.2; IR: 2925, 1717, 1440, 1249 cm^{-1}; UV-vis: 384 nm (hexane at $10^{-5}M$); ε = 5949 cm$^{-1}M^{-1}$, emission maxima (hexane) = 484 nm, quantum yield of fluorescence = 0.865; mass (EI): 302 (M^+), 242, 216, 204, 43; HRMS (EI): *m*/*z* Calcd for $C_{21}H_{18}O_2$ 302.1313, Found: 302.13018.

Methyl-5-(9-Anthryl)-(2*E*-4*Z*)-2,4-pentadienoate (2*E*,4*Z*-1)

Methyldiethylphosphono- acetate (1 g, 5.5 mmole) in dry DMF (15 mL) was added slowly to a solution containing NaH (132 mg, 5.5 mmole) in dry DMF (20 mL) at room temp. The phosphoryl-stabilized carbanion was treated with **7a** (1.15 g, 5 mmole) in 10 mL of dry DMF slowly. After 3 hr of stirring, the reaction was quenched with water and the reaction-mixture was extracted with ether and the organic layer was dried over anhydrous sodium sulfate, the ether was evaporated, and the compound was purified by column chromatography (EtOAc/hexane 1:4) to afford 2*E*,4*Z*-**1** (1.15 g, 80%) as a solid; m.p. 134°C. ^{1}H NMR (200 MHz, CDCl$_3$, 25°C): δ 3.55 (s, 3H), 5.95-6.10 (d, 1H, J=16.1 Hz), 6.8-7.0 (m, 2H), 7.4-7.55 (m, 5H), 7.9-8.05 (m, 4H), 8.45 (s, 1H); ^{13}C NMR (CDCl$_3$): δ 52.3, 121.4, 125.6, 126.8, 127.4, 129, 130.3, 132.4, 135,137.7, 144.1, 167.5; IR: 2944, 1710, 1630, 1430 cm^{-1}; UV-vis: 388 nm (hexane at 10^{-5}M); ε = 3952 cm^{-1}M^{-1}; emission maxima (hexane) = 524 nm, quantum yield of fluorescence = 0.325; mass (EI): *m*/*z* 288(M$^+$), 255, 277, 202, 114, 82.

Methyl-5-(9-Anthryl)-(2*Z*-4*Z*)-2,4-pentadienoate (2*Z*,4*Z*-1)

Bis-(2,2,2-trichloroethyl)-methylphosphonoacetate (5.5 mmole) in dry DMF (15 mL) was added slowly to a solution containing NaH (132 mg, 11 mmole) in dry DMF (20 mL) at room temp. and stirred it for 15 min. Then reaction mixture was cooled to –78°C and the phosphoryl-stabilized carbanion was treated with **7a** (1.15 g, 10 mmole) in 10 mL of dry DMF slowly. After complete addition, the reaction was brought to room temp. and stirred for 1 hr. The reaction was quenched with water and the reaction mixture was extracted with ether and the organic layer was dried over anhydrous sodium sulfate, the ether was evaporated, and the compound was purified by column chromatography (EtOAc/hexane 1:4) to afford 2*Z*,4*Z*-**1** (0.864 g, 60%) as a solid; m.p. 132°C. ^{1}H NMR (200 MHz, CDCl$_3$, 25°C): δ 3.7 (s, 3H), 5.35-5.45 (d, 1H, J=11.4 Hz), 6.05-6.25 (m, 2H), 7.3-7.45 (m, 4H), 7.85-7.95 (m, 5H), 8.35 (s, 1H); ^{13}C NMR (CDCl$_3$): δ 51.9, 121.4, 125, 126.3, 127.2, 129.1, 130.7, 132.9, 135, 137, 144.4, 166.5; UV-vis: 388 nm (hexane at 10^{-5}M); ε = 3292 cm^{-1}M^{-1}; mass (EI): *m*/*z* 288(M$^+$), 255, 277, 202, 114, 82.

Methyl-5-(9-Anthryl)-(2*Z*-4*E*)-2,4-pentadienoate (2*Z*,4*E*-1)

Bis-(2,2,2-trichloroethyl)-methylphosphonoacetate (5.5 mmole) in dry DMF (15 mL) was added slowly to a solution containing NaH (132 mg, 11 mmole) in dry DMF (20 mL) at room temp. and stirred for 15 min. Then reaction was cooled to –78°C and the phosphoryl-stabilized carbanion was treated with **7a** (1.15 g, 10 mmole) in 10 mL of dry DMF slowly. After complete addition, the reaction was brought to room temperature and stirred for 1 hr. The reaction was quenched with water and the reaction-mixture was extracted with ether and the organic layer was dried over anhydrous sodium sulfate, the ether was evaporated, and the compound was purified by column chromatography (EtOAc/hexane 1:4) to afford 2*Z*,4*E*-1 (1 g, 70%) as a solid; m.p. 141°C. ^{1}H NMR (200 MHz, CDCl$_3$, 25°C): δ 3.75 (s, 3H), 5.8-6.95 (d, 1H, J=12 Hz), 7.3-7.5 (m, 1H), 7.3-7.5 (m, 5H), 7.6-7.75 (d, 1H, J=16.4 Hz), 7.9-8.05 (m, 2H), 8.2-8.3 (m, 2H), 8.4 (s, 1H); ^{13}C NMR (CDCl$_3$): δ 51.9, 97.9, 121.4, 125.1, 126.4, 127.5, 129.6, 130, 132.4, 135,137.6, 144.1, 167.2; UV-vis: 394 nm (hexane at 10^{-5}M); ε = 5826 cm^{-1}M^{-1}; mass (EI): *m*/*z* 288(M$^+$), 255, 277, 202, 114, 82.

(*E*)-3-Anthracene-9-yl-propenal 7

A mixture of compound **6** (2.1 g, 9 mmole) in hexane (20 mL) and MnO$_2$ (4 g, 20 mmole) was stirred at room temp. for 18 hr, and filtered the reaction mixture, and washed with dichloromethane (5 × 20 mL), filtrate was washed with water, concentrated the organic layer and the compound was purified by column chromatography (EtOAc/hexane 1:3) to afford **7** (1.66 g, 80%) as a solid.

Conclusion

In conclusion, substituted 9-anthryldiene derivatives have been synthesized to study their photoisomerization process. These derivatives underwent wavelength dependent *E*→*Z* isomerization with very high regioselectivity and high efficiency. The wavelength dependent *E*→*Z* photoisomer 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 *Z*→*E* isomerization process only. Compounds **1**, **2**, **3** and 2*E,*4*Z*-**1** exhibited fluorescence solvatochromism and thus clearly indicating the involvement of CT singlet excited state. Dual fluorescence behavior of **1**, **2**, **3** and 2*E*,4*Z*-**1** indicates the involvement of two emissive states. Compounds **4** and **5** did not exhibit fluorescence solvatochromism as they lack an electron withdrawing end group indicating non-involvement of CT excited state. Fluorescence lifetime measurements suggests the presence of two singlets *viz* LE state and CT state. Quantum yield of photoisomerization is increased on changing the solvent polarity from hexane to acetonitrile and it is relatively an efficient process upon direct excitation.

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