α,ω-Diphenylpolyenes Cabable of Exhibiting Twisted Intramolecular Charge Transfer Fluorescence: A Fluorescence and Fluorescence Probe Study of Nitro- and Nitrocyano-Substituted 1,4-Diphenylbutadienes†

Anil K. Singh,* Manjula Darshi, and Sriram Kanvah

Department of Chemistry, Indian Institute of Technology, Bombay, Powai, Mumbai 400 076, India

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1,4-Diphenylbutadiene compounds, namely 1-*p*-cyanophenyl-4-phenylbuta-1*E*,3*E*-diene (**2**), 1-*p*-nitrophenyl-4-phenylbuta-1*E*,3*E*-diene (**3**), 1-cyano-1,4-diphenylbuta-1*Z*,3*E*-diene (**4**), 1-*p*-cyanophenyl-4-*p*-nitrophenylbuta-1*E*,3*E*-diene (**5**), 1-cyano-1-*p*-nitrophenyl-4-phenylbuta-1*Z*,3*E*-diene (**6**), and 1-cyano-1-phenyl-4-*p*-nitrophenylbuta-1*Z*,3*E*-diene (**7**), have been synthesized and their absorption and fluorescence properties in organic solvents, water−dioxane, and SDS, CTAB, and Triton-X-100 micelles have been investigated. The fluorescence behavior of these dienes has also been examined in ethanol−methanol (1:1) matrix at 298 and 77 K. The dienes with nitro substituents on the aromatic ring are capable of exhibiting dramatically red-shifted fluorescence emission due to twisted intramolecular charge-transfer excited states. The fluorescence properties of nitro-substituted dienes **3**, and **5**−**7** have been utilized to probe the microenvironment of SDS and CTAB micelles in terms of dielectric constant of water−micelle interface, location of the probe molecules in the micelles, and the cmc values. This study has brought out interesting features of the excited state structure and potential energy surface of diphenylpolyenes. It further provides new directions for the development of fluorescence probes as sensors and reporters of microenvironments of organized assemblies.

Introduction

Fluorescence probes as sensors and reporters of microenvironments are of much current interest.[1] However, only a few mechanisms and sensing systems have been described.[1,2] In this context, fluorescence from twisted intramolecular charge transfer (TICT) excited states appears interesting. Since the TICT emission intensity and the peak position are known to be greatly affected by solvent polarity and polarizability, the compounds capable of exhibiting TICT fluorescence may be used as sensors, chromogenic indicators, and reporters of microenvironments. The molecules in TICT excited state have relatively large dipole moment, and, consequently the TICT excited state is influenced by electronic properties of substituents and stabilized in a polar environment. Among many compounds exhibiting TICT emission, the fluorescence of *p*-(*N*,*N*-dimethylamino)benzonitrile and its derivatives have been most extensively studied and form the basis of the discussion on TICT.[2] They show dual fluorescence arising from normal planar and TICT states.

Donor−acceptor α,ω-diphenylpolyenes are interesting models for studies of intramolecular charge transfer in the excited state. These linear polyenes have further attracted a great deal of attention as models of the retinyl polyenes that are related to vitamin A and the opsin family of proteins responsible for biological sensory and energy phototransductions.[3] Consequently, the excited state structure and dynamics of α,ω-diphenylpolyenes have been the subject of many investigations in recent years.[4] However, the exact nature of the excited states of these polyenes and the mechanisms of functions of linear polyene-based photoreceptors are not very clearly known.

all-trans-Diphenylpolyenes belong to the C_{2h} point group and their ground states are characterized by A_g symmetry while the excited singlet $\pi\pi^*$ state can have either A_g^- or B_u^+ symmetry. Most of the discussions of the excited state properties of diphenylpolyenes center on the relationship between the ground and the two electronically excited states.[4,5] The excited state properties of these polyenes are governed by several factors including the order of symmetry of the two lowest-lying excited state levels, their electronic energy gap and interstate mixing, and the dynamics of isomerization. The A_g excited state is covalent in nature and hence is insensitive to solvent polarity. However, the B_u excited state is ionic and it is stabilized in polar as well as polarizable solvents. For 1,4-diphenylbuta-1*E*,3*E*-diene (DPB, **1**), the energy gap between the two lowest excited states ($2A_g$ and $1B_u$) is rather small and the actual order of the two lowest excited states is not clearly known.[6] In hydrocarbon solvents, allowed emission occurs from a low-lying $1B_u$ state. However, given a small $2A_g$−$1B_u$ splitting, small changes in molecular structure or solvent orientation can affect the relative ordering of the lowest lying excited states of DPB. The trans−cis photoisomerization of ethylenic C═C double bond is believed to occur from a “perpendicular excited state” which is formed after absorption of photon and subsequent 90° twisting of the C═C double bond.[4] It has also been suggested that considerable charge can develop in the excited state upon twisting of C═C double bond to a perpendicular geometry in olefins containing carbons of different electronegativities.[7] This results in the formation of dipolar, zwitterionic perpendicular species from where isomerization products are formed. Such polar excited states are believed to have important role in the photoprocesses of retinal proteins, and their involvement in the photoisomerization of olefins and linear polyenes has been discussed.[8] The fluorescence from S_1 excited state is believed

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* To whom correspondence may be addressed. Fax: (091-22) 576 7152. E-mail: Retinal@ether.chem.iitb.ernet.in.

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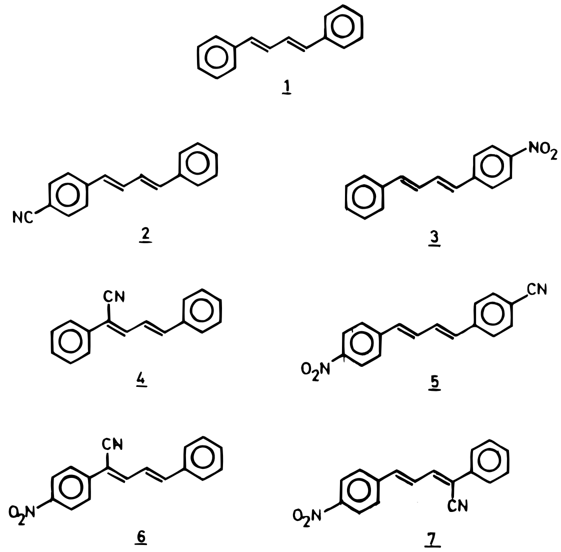

Figure 1. Structure of dienes **1**−**7**.

to compete effectively with the activated twisting of the C═C into the perpendicular geometry. However, the exact shape and nature of the potential energy surface of excited singlet state of DPB and related compounds is not clearly understood.

Excited state properties of some donor−acceptor-substituted diphenylbutadienes have been examined and it has been argued that in the photoprocesses of such compounds other than the "locally" and "perpendicular" excited states, there is one more excited state of twisted nature which is more polar and is of lower energy.[8−12] Thus, donor−acceptor diphenylbutadienes have been found to exhibit solvatochromic behavior attributable to intramolecular charge transfer and TICT state. Further, solvatochromic behavior of diphenylpolyenes in homogeneous and microheterogeneous media have been evaluated, and using photophysics of dipolar ethenes and dienes, attempts have been made to characterize the microenvironment of micelles and vesicles.[10,14] However, such studies are limited and the exact nature of the excited state structure and dynamics of donor−acceptor diphenylpolyenes is far from clear.

In view of the above facts, we have investigated the photophysical properties of diphenylbutadiene compounds bearing electron-withdrawing cyano and nitro groups on the phenyl ring and on the ethylenic double bond in the diene moiety. Thus, donor−acceptor diphenylbutadiene compounds, namely 1-*p*-cyanophenyl-4-phenylbuta-1*E*,3*E*-diene (**2**), 1-*p*-nitrophenyl-4-phenylbuta-1*E*,3*E*-diene (**3**), 1-cyano-1,4-diphenylbuta-1*Z*,3*E*-diene (**4**), 1-*p*-cyanophenyl-4-*p*-nitrophenylbuta-1*E*,3*E*-diene (**5**), 1-cyano-1-*p*-nitrophenyl-4-phenylbuta-1*Z*,3*E*-diene (**6**), and 1-cyano-1-phenyl-4-*p*-nitrophenylbuta-1*Z*,3*E*-diene (**7**), have been synthesized, and along with the parent 1,4-diphenylbuta-1*E*,3*E*-diene (**1**), their absorption and fluorescence properties investigated in a variety of media including homogeneous organic solvents of varying polarity and microheterogeneous environment of micelles (Figure 1). We now report that the nitro-substituted dienes are capable of exhibiting dramatically red-shifted fluorescence due to TICT excited states and that these dienes exhibit good fluorescence probe properties as indicated by determination of the dielectric constant and the critical micelle concentration (cmc) values of various micelles.

Experimental Section

Materials and General Procedures. Starting materials and reagents for the synthesis of dienes **2**−**7**, 1,4-diphenylbuta-1*E*,3*E*-diene (**1**), SDS, CTAB, Triton-X-100, and quinine sulfate (all Aldrich Chem. Co.) were obtained from local chemical suppliers and used without further purification. For photophysical and spectroscopic studies, UV grade organic solvents were procured from Spectrochem (India) and were used after drying. Deionized and double distilled water was used for preparing the micelle solutions. Chromatography grade silica gel for thin layer and column chromatography was obtained from E. Merck (India). A mixture of 10% ethyl acetate in *n*-hexane and 5% ethyl acetate in *n*-hexane was used for thin layer and column chromatography, respectively.

Melting points were determined on Centrofix melting points apparatus and are uncorrected. UV−vis spectra were recorded on Hitachi U2000 spectrophotometer. IR spectra were measured on Impact 400 Nicolet FTIR spectrophotometer in KBr disks. ^{1}H NMR spectra were measured on a Varian 300 MHz FTNMR spectrometer using TMS as internal standard. Fluorescence studies were performed on Spex Fluorolog spectrofluorimeter. Relative quantum yields of fluorescence (Φ_f) were determined using quinine sulfate as standard.[15] For all electronic spectroscopic (absorption, fluorescence excitation, and emission) studies, 1.0×10^{-5} M solutions of the dienes were used. All the solutions were prepared and handled under protective dim red light condition. Similarly, all the reactions were performed in dim red light conditions.

Synthesis. Dried and freshly distilled solvents were used, and inert (dry N_2) conditions were maintained throughout the reaction. 1-Cyano-1,4-diphenylbuta-1*Z*,3*E*-diene (**4**) was prepared as reported elsewhere.[8,9,12] For the preparation of other dienes, the generalized Emmons−Horner process was employed.[16] Thus, dienes 1-*p*-cyanophenyl-4-phenylbuta-1*E*,3*E*-diene (**2**) and 1-*p*-nitrophenyl-4-phenylbuta-1*E*,3*E*-diene (**3**) were obtained by the reaction of cinnamaldehyde, respectively, with phosphonate esters, p-$\mathrm{CNC_6H_4CH_2P(O)OEt_2}$ and p-$\mathrm{NO_2C_6H_4CH_2P(O)OEt_2}$ in the presence of sodium methoxide in dimethylformamide (DMF). Similarly, reaction of *p*-nitrocinnamaldehyde with p-$\mathrm{CNC_6H_4CH_2P(O)OEt_2}$ in the presence of sodium methoxide in DMF at ambient temperature yielded 1-*p*-cyanophenyl-4-*p*-nitrophenylbuta-1*E*,3*E*-diene (**5**). Condensation of equimolar amounts of *p*-nitrobenzylcyanide and cinnamaldehyde in the presence of 1.5 mol equivalent of sodium methoxide in DMF at ambient temperature yielded 1-cyano-1-*p*-nitrophenyl-4-phenylbuta-1*Z*,3*E*-diene (**6**). Similarly, under similar conditions, the reaction of *p*-nitrocinnamaldehyde with benzylcyanide afforded 1-cyano-1-phenyl-4-*p*-nitrophenylbuta-1*Z*,3*E*-diene (**7**).

In typical procedures, 0.01 mol phosphonates/benzyl cyanides as appropriate, 0.015 mol sodium methoxide, and freshly distilled 10 mL of DMF were taken in a two-necked, rubber-septumed round-bottom flask of 50 mL capacity. The mixture was magnetically stirred at ambient temperature under inert atmosphere for about 1 h after which a solution of the appropriate aldehyde in dry and freshly distilled DMF was syringed in. The stirring was continued until most of the aldehyde had reacted as indicated by thin layer chromatographic analysis. After completion of the reaction, the reaction mixture was quenched with brine and the organic material was taken in diethyl ether. Usual workup followed by removal of diethyl ether on a rotary evaporator yielded yellowish material which was subjected to column chromatography to obtain the desired diene. Further purification of the diene was carried out by repeated crystallization from light petroleum (bp 60−80 °C) when bright yellow crystalline needles of the diene were obtained.

1-*p*-Cyanophenyl-4-phenylbuta-1*E*,3*E*-diene (2). Yield:

50%; mp: 158−159 °C; UV−vis (THF): λ_{max}, 343 nm (ϵ, 54 000 mol L^{-1} cm^{-1}); ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.65 (1H, d, *J* = 15.01 Hz, C_6H_5−C*H*═CH−CH−), 6.77 (1H, d, *J* = 14.65 Hz, *p*-NC−C_6H_4−C*H*═CH−), 6.96 (1H, dd, *J* = 14.83/10.62 Hz, *p*-NC−C_6H_4−CH═CH−C*H*═CH−), 7.05 (1H, dd, *J* = 14.83/10.62 Hz, *p*-NC−C_6H_4−CH═C*H*−CH═), 7.27−7.47 (5H, m, phenyl protons), 7.50 (2H, dd of AB quartet, *J* = 8.43/1.83 Hz, *p*-NC−C_6H_4−), 7.60 (2H, dd of AB quartet, *J* = 8.42/1.83 Hz, *p*-NC−C_6H_4−).

1-*p*-Nitrophenyl-4-phenylbuta-1*E*,3*E*-diene (3). Yield: 60%; mp: 166−168 °C; UV−vis (THF): λ_{max}, 375 nm (ϵ, 56 235 mol L^{-1} cm^{-1}); ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.70 (1H, d, *J* = 15.20 Hz, C_6H_5−C*H*═CH−), 6.80 (1H, d, *J* = 15.17 Hz, *p*-NO_2−C_6H_4−C*H*═CH−), 7.00 (1H, dd, *J* = 15.20/10.44 Hz, C_6H_5−CH═C*H*−CH═), 7.13 (1H, dd, *J* = 15.35/10.44 Hz, *p*-NO_2−C_6H_4−CH═C*H*-CH═), 7.28−7.48 (5H, m, phenyl protons), 7.55 (2H, dd of AB quartet, *J* = 8.61/2.83 Hz, *p*-NO_2−C_6H_4−), 8.20 (2H, dd of AB quartet, *J* = 8.61/2.83 Hz, *p*-NO_2−C_6H_4−).

1-*p*-Cyanophenyl-4-*p*-nitrophenylbuta-1*E*,3*E*-diene (5). Yield: 60%; mp: 228−229 °C; UV−vis (THF): λ_{max}, 373 nm (ϵ, 50 000 mol L^{-1} cm^{-1}); ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.79 (1H, dd, *J* = 14.65/10.25 Hz, *p*-NO_2−C_6H_4−CH═C*H*), 6.93 (1H, dd, *J* = 14.65/10.25 Hz, *p*-CN−C_6H_4−CH═C*H*−CH═), 7.13 (1H, d, *J* = 14.83 Hz, *p*-NO_2−C_6H_4−C*H*═CH−), 7.04 (1H, d, *J* = 14.83 Hz, *p*-NC−C_6H_4−C*H*═), 7.54 (2H, dd of AB quartet, *J* = 8.42/1.64 Hz, *p*-CN−C_6H_4−), 7.64 (2H, dd of AB quartet, *J* = 8.42/1.64 Hz, *p*-CN−C_6H_4−), 7.58 (2H, dd of AB quartet, *J* = 8.79/1.83 Hz, *p*-NO_2−C_6H_4−), 8.21 (2H, dd of AB quartet, *J* = 8.79/1.83 Hz, *p*-NO_2−C_6H_4−).

1-Cyano-1-*p*-nitrophenyl-4-phenylbuta-1*Z*,3*E*-diene (6). Yield: 25%; mp: 205−207 °C; UV−vis (THF): λ_{max}, 373 nm (ϵ, 42 500 mol L^{-1} cm^{-1}); ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.17 (1H, d, *J* = 15.00 Hz, C_6H_5−C*H*═CH−), 7.38−7.44 (5H, m, phenyl protons), 7.52 (1H, dd, *J* = 15.00/11.00 Hz, C_6H_5−CH═C*H*-CH═), 7.59 (1H, d, *J* = 11.00 Hz, C_6H_5−CH═CH−C*H*-C(CN)−), 7.79 (2H, dd of AB quartet, *J* = 8.79/1.83 Hz, *p*-NO_2−C_6H_4−), 8.29 (2H, dd of AB quartet, *J* = 8.79/1.83 Hz, *p*-NO_2−C_6H_4−).

1-Cyano-1-phenyl-4-*p*-nitrophenylbuta-1*Z*,3*E*-diene (7). Yield: 40%; mp: 172−173 °C; UV−vis (THF): λ_{max}, 366 nm (ϵ, 44 000 mol L^{-1} cm^{-1}); ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.17 (1H, d, *J* = 15.02 Hz, *p*-NO_2−C_6H_4−C*H*═CH−), 7.38−7.44 (5H, m, phenyl protons), 7.52 (1H, dd, *J* = 15.02/11.00 Hz, *p*-NO_2−C_6H_4−CH═C*H*-CH═), 7.59 (1H, d, *J* = 11.00 Hz, C_6H_5−C(CN)═C*H*-CH═), 7.79 (2H, dd of AB quartet, *J* = 9.15/2.19 Hz, *p*-NO_2−C_6H_4−), 8.31 (2H, dd of AB quartet, *J* = 9.15/2.19 Hz, *p*-NO_2−C_6H_4−).

Results and Discussion

Solvent-Induced Shifts of Absorption and Fluorescence. The absorption and fluorescence spectral data of compounds **1**−**4** and **5**−**7** in solvents of different polarity are summarized respectively in Tables 1 and 2. While the absorption maximum of parent 1,4-diphenylbuta-1*E*,3*E*-diene (**1**) is insensitive to solvent polarity, monosubstituted dienes **2** and **4** bearing cyano group either on the ethylenic bond or on the aromatic ring show a very moderate red shift of ∼5 nm in polar solvents. Diene **3** with *p*-nitro substituent on the phenyl ring shows a red shift of 13 nm in its absorption maximum in going from nonpolar *n*-heptane to polar DMF. Similarly, only moderate red shift of ∼10−19 nm, depending on the position of the substituent is observed in the absorption maximum of disubstituted dienes **5**−**7**. The maximum red shift is observed for diene **5** in which the electron-withdrawing substituents are on the para position of the aromatic ring. The red shift in the absorption maximum of these compounds is attributed to the increased conjugation due to the presence of substituent on the para position of the aromatic ring. The excitation spectra of these dienes are similar to their absorption spectra, except that the λ_{max} of excitation spectra of nitro-substituted dienes **3** and **5**−**7** is slightly red-shifted by about 5 nm.

TABLE 1: Absorption and Fluorescence Data for Dienes 1−4 in Homogeneous Media of Organic Solvents at 298 K

diene[a]	solvent	λ_{max} (nm) abs	emi	exi	Stokes' shift (cm^{-1})	Φ_f (±0.0001)
2	*n*-heptane	344	406	344	4439	0.031
	dioxane	347	407	345	4248	0.007
	THF	346	418	346	4978	0.007
	AcCN	344	420	343	5260	0.003
	MeOH	344	420	343	5260	0.004
	DMF	349	422	345	4956	0.014
3	*n*-heptane	370	470	334	6000	0.002
	dioxane	375	495	389	6464	0.006
	THF	374	508	383	6875	0.003
	AcCN	378	574	377	8998	0.274
	MeOH	379	606	378	9848	0.003
	DMF	383	567	386	9000	0.295
4	*n*-heptane	341	421	340	5572	<0.001
	dioxane	343	421	340	5401	<0.001
	THF	343	422	346	5457	<0.001
	AcCN	343	421	340	5401	<0.001
	MeOH	343	419	342	5288	<0.001
	DMF	349	424	348	5068	0.002

[a] **1** in *n*-heptane and AcCN: absorption λ_{max}, 315, 330, 350 nm; fluorescence λ_{max} 360, 380, 390 nm; excitation λ_{max}, 331 nm; Stokes' shift 4000 cm^{-1}; Φ_f, 0.22 (*n*-heptane), 0.01 (AcCN).

TABLE 2: Absorption and Fluorescence Data for Dienes 5−7 in Homogeneous Media of Organic Solvents at 298 K

diene	solvent	λ_{max} (nm) abs	emi	exi	Stokes' shift (cm^{-1})	Φ_f (±0.0001)
5	*n*-heptane	362	400	343	2620	0.012
	dioxane	368	463	351	5575	0.001
	THF	378	485	384	6190	0.001
	AcCN	374	539	376	8400	0.078
	MeOH	375	588	377	9950	0.003
	DMF	381	540	385	7730	0.148
6	*n*-heptane	366	456	370	5393	0.001
	dioxane	371	484	376	6335	0.001
	THF	373	486	371	5970	0.001
	AcCN	374	540	378	8509	0.001
	MeOH	375	557	373	9220	0.001
	DMF	376	522	392	7438	0.018
7	*n*-heptane	356	399	357	3020	0.002
	dioxane	364	430	384	4217	0.001
	THF	366	473	383	6181	0.001
	AcCN	368	523	375	8202	0.021
	MeOH	368	573	377	10020	0.004
	DMF	373	517	385	7462	0.045

In contrast to a very moderate solvent polarity effect on the absorption maxima of dienes **2**−**7**, marked influence of solvent polarity on the fluorescence maxima, particularly of nitro dienes **3** and **5**−**7**, is observed (Figures 2 and 3). The maximum red shift of 188 nm in the fluorescence maxima of **5** (in *n*-heptane 400 nm and in methanol 588 nm) is observed when the nitro and cyano groups are on the para position of the aromatic ring. The cyano group exerts a slightly destabilizing effect on the excited state fluorescent species in polar solvent. The Stokes' shifts of nitro-substituted dienes are relatively large and increase with solvent polarity. The fluorescence λ_{max} of the dienes was not affected by increasing concentration of the dienes in the range of 1.0×10^{-3} to 1.0×10^{-5} M.

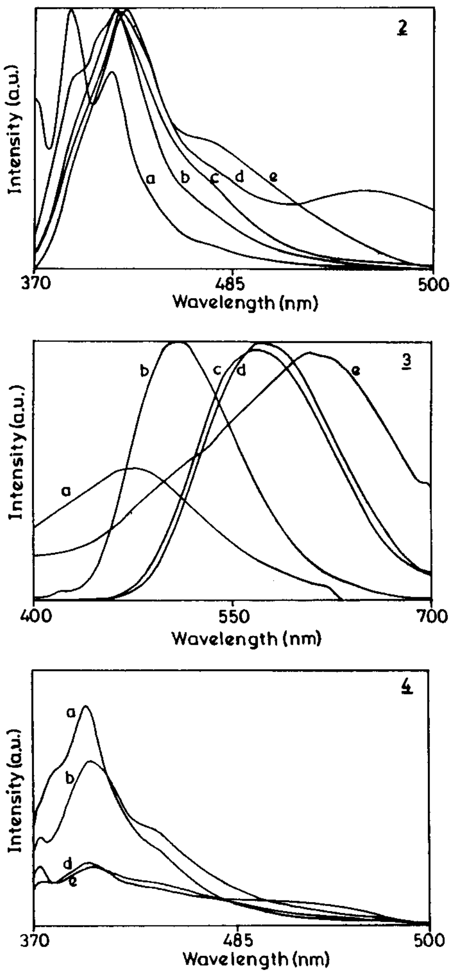

Figure 2. Fluorescence spectra of **2**−**4** in organic solvents at 298 K: (a) *n*-heptane, (b) dioxane, (c) tetrahydrofuran, (d) acetonitrile, (e) methanol.

The solvatochromic fluorescence shifts of these dienes were further analyzed using the Lippert−Mataga equation:[17] $\nu_a - \nu_f = \{[(2(\mu_e - \mu_g)^2/hca^3]F(D,n)\}$, where $\nu_a - \nu_f$ is the Stokes' shift, $\mu_e - \mu_g = \Delta\mu$ is change in the dipole moment, *h* is Planck's constant, *c* is velocity of light, *a* is Onsager radius, and $F(D,n) = \Delta_f$ is the polarity determining factor. $\Delta f = (D - 1)/(2D + 1) - (n^2 - 1)/(2n^2 + 1)$, where *D* is dielectric constant and *n* is refractive index of the solvent. The Onsager radius for these dienes was taken as 9 Å which is a known value for a similar diphenylbutadiene compound, namely, 1-*p*-(*N*,*N*-dimethylamino)phenyl-4-*p*-nitrophenylbuta-1*E*,3*E*-diene.[18] The plots of Stokes' shifts vs solvent parameter, Δ*f*, are shown in Figure 4. The change in dipole moment (Δ*μ*) upon excitation for various dienes were obtained as follows: **3**, 20.9 D; **5**, 19.7 D; **6**, 17.5 D; **7**, 20.5 D. The Lippert−Mataga plots clearly demonstrate the solvent polarity sensitive fluorescent behavior of **3** and **5**−**7**, which is further well supported by the large excited state dipole moment changes (Δ*μ*) observed. In terms of Lippert−Mataga parameters used here, no appreciable change in excited state dipole moment was observed in the case of dienes **1**, **2**, and **4**. These fluorescence data for **3** and **5**−**7** mean that the fluorescent state is not the initially prepared excited state, and it is more polar. Such an excited state can be dipolar in nature and formed due to intramolecular charge transfer.

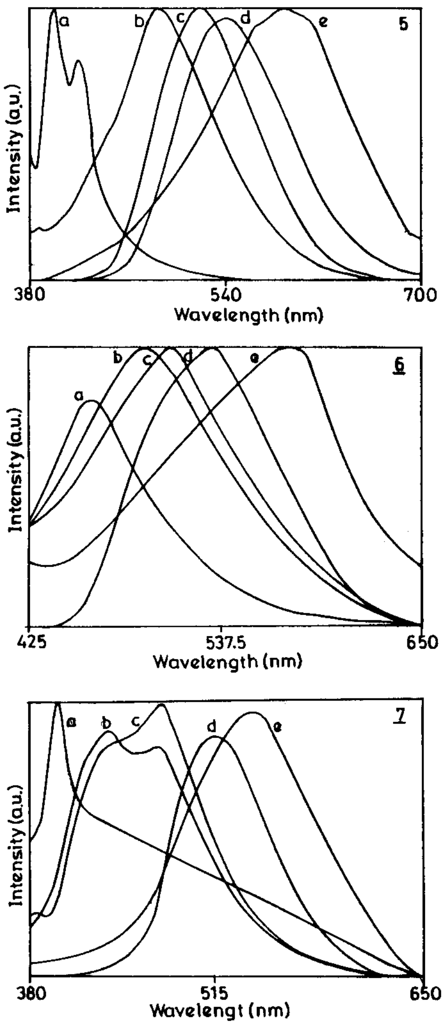

Figure 3. Fluorescence spectra of **5**−**7** in organic solvents at 298 K: (a) *n*-heptane, (b) dioxane, (c) tetrahydrofuran, (d) acetonitrile, (e) methanol.

Fluorescence Quantum Yields (Φ_f) 2−7 in Organic Solvents. These dienes show rather very weak fluorescent emission. In general, the solvent polarity and the type of substituent and its position appear to influence the fluorescence quantum yields. In protic polar solvents like methanol, the fluorescence quantum yields (Φ_f) are very low. Aprotic polar solvents and electronegative substituents can cause some increase in the Φ_f. Increase in Φ_f with increase in solvent polarity can partly be attributed to the possible state reversals of the lowest excited states of the dienes. In nonpolar solvent, the fluorescent excited state can be of A_g^- nature. Since $A_g^{-*} \rightarrow A_g$ transition is symmetry forbidden, the resulting emission is very weak. In polar solvents, however, there is reversal of states from A_g^{*-} to B_u^{*+}, which gives rise to allowed $B_u^{*-} \rightarrow A_g$ transition responsible for relatively increased Φ_f.

1-Cyano-substituted diene **4** has the least Φ_f. Apparently, the cyano group has a destabilizing effect on the fluorescent excited state. It is known that considerable charge separation may occur upon twisting out of plane of an ethylenic C=C chromophore during the formation of perpendicular species in the excited state.[4] Appropriate substituents can stabilize the resulting dipolar "perpendicular excited state". This effect can decrease the energy barrier for the formation of perpendicular state facilitating trans−cis photoisomerization and diminishing fluorescence.[9,12,13] The low Φ_f can be attributed to the enhanced stability of perpendicular dipolar species due to cyano group in the excited state. Thus, while the cyano group in the ethylenic bond renders the diene less fluorescent by lowering the barrier between the fluorescent excited state and the perpendicular state, the nitro group on the phenyl ring makes the diene fluorescence efficient

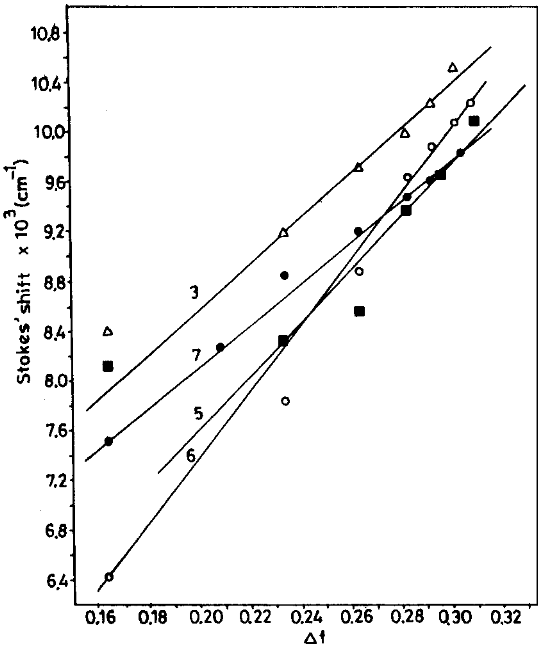

Figure 4. Lippert–Mataga plots for dienes **3** (△), **5** (◆), **6** (○), and **7** (●).

TABLE 3: Fluorescence Data of 1–7 in 1:1 Methanol–Ethanol Matrix at 298 and 77 K

	fluorescence at 298 K			fluorescence at 77 K			
diene	λ_{em} (nm)	λ_{ex} (nm)	Φ_f	λ_{em} (nm)	λ_{ex} (nm)	Φ_f	$\Delta\lambda_{em}$ (nm)
1	375	334	0.018	379	334	1	4
2	418	347	0.007	412	328	1	6
3	600	385	0.003	492	403	0.288	108
4	420	339	0.001	424	339	0.520	4
5	576	387	0.005	480	398	0.075	96
6	569	379	0.002	480	400	0.022	89
7	567	391	0.005	484	400	0.055	83

by increasing the activation barrier for the formation of perpendicular species. The aprotic polar solvents appear to affect the excited state of nitro-dienes much before the formation of perpendicular state.

A relatively higher Φ_f and large red-shifted fluorescence of nitrodienes (e.g., **3** and **5**) in aprotic polar solvents further indicate that the fluorescence originates from highly polarized excited state. Such fluorescent excited state can be formed due to TICT process. Because of different electronegativities present in the dienes, intramolecular charge transfer can occur via the twisted nitro group, and the polar solvents can stabilize the TICT excited state resulting in much red-shifted fluorescence emission.

Fluorescence Studies of 1–7 in Methanol–Ethanol Matrix. Fluorescence data for **1**–**7** in 1:1 methanol–ethanol mixture at 298 and 77 K are shown in Table 3. There is considerable change in the fluorescence λ_{max} and in the Φ_f of these dienes at two temperatures in the methanol–ethanol matrix. In fluid environment, the dienes exhibit fluorescence at different wavelengths ranging from 418 to 600 nm depending on the substituents. However, in rigid glass matrix, the fluorescence occurs at lower wavelength in the range of 412–492 nm. The fluorescence maxima of nitro-substituted dienes **3** and **5**–**7** are most affected with maximum blue shift in the case of diene **3**. The Φ_f, however, increases in the rigid matrix at 77 K. The fluorescence spectra of these dienes at 77 K are characterized by well-defined structures. These observations indicate the absence of solvent effects, molecular motions, and related geometrical changes resulting in blue-shifted emission λ_{max}, and increased Φ_f. These results further indicate the involvement of TICT excited states in the photoprocesses of nitrodienes.

Thus, the nature of the lowest-lying singlet excited states of diphenylpolyenes has important consequences for their photophysics. The electronic nature of the substituent and solvent polarity can alter the relative positions of the lowest-lying excited states and change the shape of singlet excited state potential energy surface influencing fluorescence properties.

Electronic Spectroscopy of 1–7 in Dioxane–Water Mixture and in Micelles. Solvent polarity dependent fluorescence properties of substituted diphenylbutadienes prompted us to study the fluorescence properties of **1**–**7** in micelles of SDS, CTAB, and Triton-X-100. We have employed these fluorophores for characterizing the microenvironment of these micelles by calculating dielectric constant of the micelle–water interface, locating the probes in micelles, and calculating the cmc of the micelles. Since the solvatochromic fluorescence properties of these dienes were to be used to probe micellar environments, it was necessary to ensure that the fluorescence emission in surfactant solution is not due to any specific interaction between the diene and water molecules. The low solubility of dienes in water prohibits direct spectroscopic study in aqueous solution. Therefore, we examined electronic spectra of **1**–**7** in dioxane–water mixture. When the water content was varied between zero and 70% in dioxane, the absorption maximum did not shift for diene **4**, and shifted only by 3 and 5 nm, respectively, for dienes **2** and **3**. For dienes **5**, **6**, and **7**, the absorption maximum shift respectively was 15, 6, and 9 nm. The fluorescence shift was also not very significant in the case of dienes **2** and **4**. Thus, while no change in the fluorescence maximum of **4** was observed when the water content was increased to 70%, only a moderate red shift of 16 nm was registered in the case of diene **2**. However, dienes **3** and **5**–**7** exhibited dramatically red-shifted fluorescence in dioxane containing increasing amounts of water. Thus, 501 nm fluorescence of **3** in dioxane shifted to 630 nm when dioxane contained 70% water. Similarly, 463, 479, and 469 nm fluorescence of dienes **5**, **6**, and **7** in dioxane shifted, respectively, to 603, 613, and 605 in dioxane containing 70% water. Thus, fluorescence is highly red-shifted as the water content in the solvent mixture is increased. This observation is similar to that of the studies in organic solvents of different polarity. Since the dielectric constant of dioxane–water mixtures is known,[19] fluorescence λ_{max} of dienes **1**–**7** were plotted against the dielectric constant of the solvent to conclude that the λ_{max} of fluorescence of these dienes is governed by the bulk dielectric constant (ϵ) of the medium (Figure 5).

Determination of Dielectric Constant (ϵ) of the Micelle–Water Interface. Absorption and fluorescence data of **1**–**7** in SDS, CTAB, and Triton-X-100 micelles are summarized in Table 4. In a given micelle, absorption and fluorescence λ_{max} of **1**, **2**, and **4** do not change much. However for **3** and **5**–**7**, charge-dependent shift of absorption and fluorescence λ_{max} is observed. This indicates that the fluorophores occupy interfacial region, which may be due to the presence of polar nitro substituents. Using dienes **3** and **5**–**7**, the dielectric constants (Table 5) of the micelle–water interface in SDS, CTAB, and Triton-X-100 micelles was obtained by perusing Figure 5 and comparing it with the fluorescence λ_{max} of the dienes in micellar solutions. Table 5 also gives the dielectric constant of these micelles as determined by some other well-known probes like pyrene carboxaldehyde,[20] *p*-(*N*,*N*-dialkylamino)benzylidene malonitrile[21] and ANS.[22] The polarity of the interface is dependent on the nature of the headgroups and it is increasing from

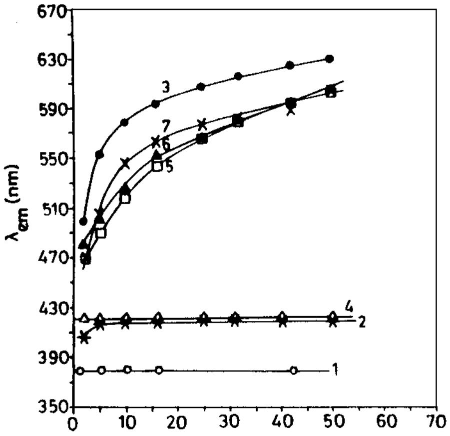

Figure 5. Plot of dielectric constants of dioxane−water mixtures vs fluorescence λ_{max} of **1**−**7** in dioxane−water mixtures: **1** (○), **2** (∗), **3** (●), **4** (△), **5** (□), **6** (▲), **7** (×).

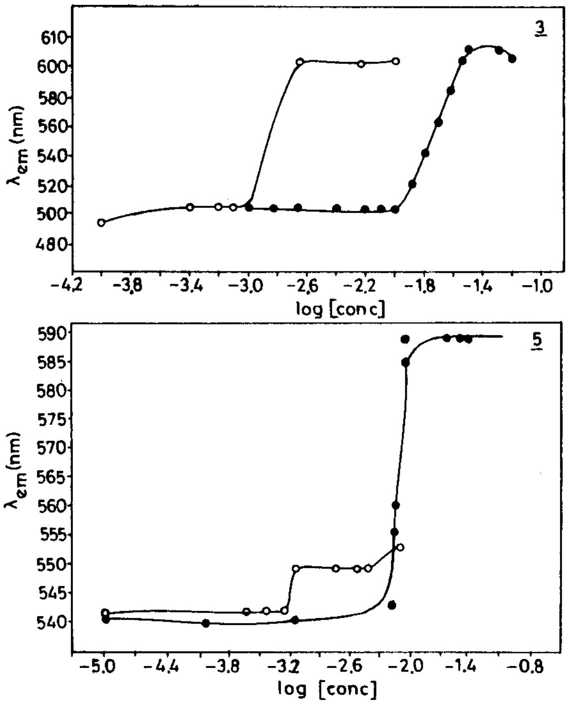

Figure 6. Plot of fluorescence λ_{max} of CTAB- and SDS-constituted **3** and **5** vs surfactant concentrations: CTAB (○), SDS (●).

nonionic to cationic to anionic micelles. The decrease in dielectric constant of the micelle−water interface compared to that of bulk water is due to the restrictive effect of the micellar surface charge on water molecules in the stern layer.[22]

Location of the Diene Probes in Micelles. The results in Table 4 show that the Φ_f of **3** and **5**−**7** in micelles of various surfactants are larger than those in nonpolar solvents. Since we already showed that there is an increase in Φ_f with increase in solvent polarity of the medium, the increase in Φ_f in micelles is attributable to the greater polarity of the media. The dielectric constant values calculated for **3** and **5**−**7** in different micelles are more than that of hydrocarbons ($\epsilon = {\sim}2$) and less than that of bulk water ($\epsilon = {\sim}80$). The intermediate range of dielectric constant values suggests that the diene fluorophores are located in the interfacial region of the micelles. Slight changes in the dielectric constant values compared to previously reported values can be attributed to the structural differences in various fluorophores which can locate differently in the micellar systems. For compounds **3** and **5**, which do not have any substituent on the diene moiety, the dielectric constants are observed to be low as compared to that of **6** and **7** in all the three micelles studied. This shows that **3** and **5** are most likely to be incorporated between hydrophobic alkyl chains with relatively more polar nitro group toward interfacial region. In **6** and **7**, the presence of cyano group on the diene moiety can cause changes in the geometry of the molecule and due to which the molecule will prefer location in the interfacial domain. On similar grounds, it is inferred that dienes **1**, **2**, and **4** occupy the hydrophobic regions of the micelles

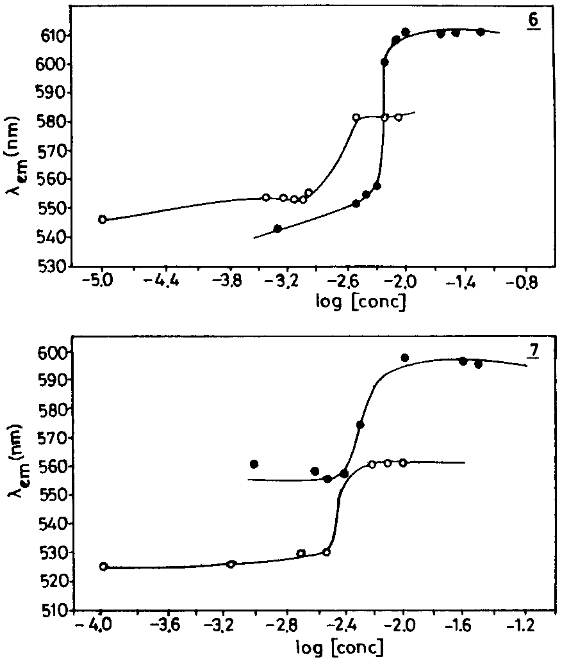

Figure 7. Plot of fluorescence λ_{max} of CTAB- and SDS-constituted **6** and **7** vs surfactant concentrations: CTAB (○), SDS (●).

TABLE 4: Absorption and Fluorescence Spectral Data of 1−7 in Micelles

		λ_{max} (nm)			Stokes' shift	
diene	media[a]	abs	em	ex	(cm^{-1})	Φ_f (±0.0001)
1	CTAB	323	400	329	5959	0.094
	SDS	332	402	331	5244	0.077
	Tri-X-100	331	400	332	5211	0.127
2	CTAB	347	428	364	5454	0.054
	SDS	350	426	360	5097	0.045
	Tri-X-100	348	423	350	5094	0.150
3	CTAB	395	603	399	8732	0.037
	SDS	389	612	394	9367	0.012
	Tri-X-100	397	538	402	6601	0.016
4	CTAB	350	421	364	4818	0.005
	SDS	347	434	360	5776	0.007
	Tri-X-100	348	424	360	5150	0.002
5	CTAB	363	548	375	9300	0.014
	SDS	382	585	381	9080	0.050
	Tri-X-100	372	544	377	8500	0.011
6	CTAB	399	581	362	7850	0.008
	SDS	389	610	385	9313	0.010
	Tri-X-100	394	535	380	6689	0.006
7	CTAB	362	557	381	9290	0.005
	SDS	378	596	385	9676	0.035
	Tri-X-100	378	500	392	6455	0.004

[a] 1.0×10^{-2} M. Tri-X-100 is Triton-X-100.

Determination of Critical Micellar Concentration (Cmc) of the Micelles. Long-chain amphiphilic molecules in aqueous solutions above a certain concentration, called critical micellar concentration (cmc), form micellar aggregates. Micelle aggregates formed by ionic and nonionic surfactants have often

TABLE 5: Dielectric Constants (ϵ) and Critical Micelle Concentration (Cmc) of Micelles As Determined Using Probe Dienes 3 and 5−7 and Some Other Known Probes

diene	media	calculated ϵ	cmc (M)
3	CTAB	22	4×10^{-3}
	SDS	28	3×10^{-2}
	Triton-X-100	4	
5	CTAB	9	9×10^{-4}
	SDS	27	9.5×10^{-3}
	Triton-X-100	8	
6	CTAB	7	4×10^{-3}
	SDS	45	7×10^{-3}
	Triton-X-100	5	
7	CTAB	16	4×10^{-3}
	SDS	45	7×10^{-3}
	Triton-X-100	10	
Py-CHO	CTAB	36	9×10^{-4}
	SDS	40	8×10^{-3}
	Triton-X-100	28	3×10^{-4}
DABMN	CTAB	36	7×10^{-4}
	SDS	40	8×10^{-3}
	Triton-X-100	28	3×10^{-4}
ANS	CTAB	36	9×10^{-4}
	SDS	25	9×10^{-3}
	Triton-X-100	35	3×10^{-4}

[a] Py-CHO: pyridinecarboxaldehyde. DABMN: (dimethylamino)-benzylidene malonitrile. ANS: anilinonaphthalenesulfonic acid.

been used as model systems for studying more complex bioaggregates.[23] Despite numerous efforts in this area, the solvent properties of the micellar environment are still poorly understood. Among various physical methods employed, fluorescence probes have been widely used because of their simplicity, wide scope, and extreme sensitivity at very low probe concentration[24.] Comparison of the spectral data in micelles with those in homogeneous solvent systems provides information on the micellar environment.

Herein, fluorescent dienes **3** and **5−7** have been employed to determine the cmc values for SDS and CTAB. In Triton-X-100, since no change in fluorescence $\lambda_{\max}$ of the four probe dienes with increasing concentration of the surfactant was observed, studies were done only in SDS and CTAB micelles. The dependence of fluorescence $\lambda_{\max}$ of **3** and **5−7** on surfactant (SDS and CTAB) concentrations is shown in Figures 6 and 7. The calculated cmc values are given in Table 5. The fluorescence $\lambda_{\max}$ of the probe dienes in CTAB and SDS is constant over a narrow range of concentrations, which is the critical micellar concentration. These cmc values are in fair agreement with the cmc values obtained by using other known probes.[19−21] Below the cmc of SDS and CTAB, there is blue shift in fluorescence $\lambda_{\max}$ for all the four probe dienes (**3**, **5−7**). However, above the cmc of SDS and CTAB, dienes **5−7** exhibited blue-shifted fluorescence, while for diene **3**, no shift in fluorescence $\lambda_{\max}$ was observed above cmc in the two micelles. This can be attributed to the interaction between monomeric surfactant with probe molecules and to the presence of premicellar aggregates. Previous reports with *p*-(*N*,*N*-dialkylamino)benzylidine malonitrile as a fluorescence probe showed that there is formation of premicellar aggregates below the cmc.[21] Slightly above the cmc range, there is change in fluorescence wavelength and it is observed to be constant for very high concentrations of the surfactants used. Thus, this change in the fluorescence wavelength can be attributed to the change in shape of the micelle with increase in surfactant concentration. It is well established that in the vicinity of the cmc anionic, cationic, and nonionic surfactant micelles are mostly approximate to spheres but with increase in total concentration micelles become asymmetric.[24] In Triton-X-100, the fluorescence $\lambda_{\max}$ is smaller as compared to that in ionic SDS and CTAB. For example, diene **3** in SDS shows fluorescence at 612 nm and in Triton-X-100 at 538 nm. Further, no change in fluorescence $\lambda_{\max}$ with increasing concentration of Triton-X-100 was observed for probe dienes **3** and **5−7**. These observations suggest that the excited states of probe dienes are affected by ionic micelles much more than the neutral micelles like Triton-X-100. Thus, donor−acceptor dienes **3** and **5−7** can serve as good fluorescence probes. for microenvironment of charged micelles.

In conclusion, it can be said that 1,4-diarylbuta-1*E*,3*E*-diene compounds with *p*-nitro substituent on the aromatic ring are capable of exhibiting TICT fluorescence. Further, the fluorescence properties of nitro-substituted dienes can be used to probe the microenvironment of ionic micelles and related organized assemblies. This study has brought out interesting features of the excited state structure and potential energy surface of linear polyenes. It further provides new directions for the development of fluorescence probes as sensors and reporters of microenvironments of organized assemblies.

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Supporting Information Available: IR, UV−vis absorption, and fluoresence data for **2**, **3**, and **5−7** in dioxane water mixtures at 298 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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