PHOTOISOMERIZATION STUDIES OF SUBSTITUTED DIPHENYLBUTADIENES: ROLE OF POLARIZED EXCITED STATES IN THE PHOTOPROCESSES OF α, ω -DIPHENYLPOLYENES

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Abstract - Direct irradiation of 1Z, 3E-1-cyano-1,4-diphenylbutadiene (2) and 1Z, 3E-1-cyano-3-methyl-1,4-diphenylbutadiene (3) in organic solvents viz. n-hexane, methanol and acetonitrile results in preferential isomerization of the double bond substituted with cyano group via one-photon-one-bond isomerization process. The quantum efficiency of the isomerization of 3 is more than 2 in all the three solvents. Photoproducts of 2 and 3 (viz. 2a, 2b, 3a, 3b) also exhibited similar photoisomerization trends. The results are discussed in terms of the effects of substituents on the potential energy surface of the excited singlet states of α, ω -diphenylpolyenes, and the role of zwitterionic dipolar species in the photoisomerization process of linearly conjugated C=C polyenes is highlighted.

INTRODUCTION

Light-induced geometrical photoisomerization of linearly conjugated retinylidene polyenes has been known to be an important photobiological process taking place in the opsin family of proteins. Consequently, in recent years there has been a great deal of interest in the photoprocesses of such chromophores.²⁻⁵ Of particular interest have been the topics of electronic structure of polyenes in the excited state and their dynamic behaviour.

The α,ω -diphenylpolyenes⁶⁻¹¹ have extensively been studied as models of retinylidene polyenes as their fluorescent properties have made them easier to study than the nonemitting linear polyenes devoid of phenyl groups. Further, the presence of phenyl group makes it easier to study the effect of substituents on the polyene excited state. It is believed that all-trans-diphenylbutadiene (1) has two lowest singlet excited state viz. ¹A_g and ¹B_u and the energy gap in solution is small (approx. 200 cm⁻¹ with ¹B_u* lying below ¹A_g*); however, the actual ordering of the two states has not been resolved adequately.

Upon absorption of photons, diphenylpolyenes produce planar excited state which undergoes further twisting to yield the "perpendicular species" from where the isomerization products are obtained. It is also believed that planar ¹B_u states of linear C=C chromophores can have partial separations of charge and further considerable separation of charge may develop upon twisting to a perpendicular geometry. Based on theoretical studies it has been proposed that the development of charge as function of twist angle in olefins containing carbons of different electronegativities can cause a rapid increase in dipole

moment as the perpendicular geometry is reached and

1: R' = R'' = H; 1E, 3E

2: R' = CN; R" = H; 1Z, 3E

3: R' = CN; R" = CH₃; 1Z, 3E

Figure 1. Chemical structures of diphenylbutadiene compounds 1, 2, and 3.

zwitterionic intermediates can be involved in the photoisomerization of alkenes. 12.13 Some experimental studies have also been undertaken to examine the possibility of the zwittterionic species in the photoisomerization of linear C=C chromophores. 14,15 However, such studies are limited and additional experimental work is needed to establish whether the perpendicular excited singlet states of diphenylpolyenes are best described as nonionic or zwitterionic states.

In order to further characterize the nature of the polyene excited state we have studied the photoisomerization of model systems viz. 1Z, 3E-1-cyano-1,4diphenylbutadiene(2) and 1Z, 3E-1-cyano-3-methyl-1,4diphenylbutadiene (3) (Fig.1).

MATERIALS AND METHODS

All the synthetic materials and their solutions were kept and handled under protective red lamp. Solvents used were of UV/HPLC grade from Spectrochem., Mumbai. All the other

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chemicals were from Aldrich chemical company, USA. Quantum yields of photoisomerization were determined after effecting @ 5% photoconversion of the starting diene, and using potassium ferrioxalate actinometery. The UV-VIS spectra were recorded on Beckman DU6 or Hitachi U-2000 spectrophotometer. The IR spectra in nujol were obtained on a Perkin Elmer 681 spectrophotometer. The 300 MHz ^{1}H NMR spectra in C_6D_6 were recorded on a 300 MHz Varian NMR spectrometer.

Synthesis of 1Z, 3E-1-cyano-1,4-diphenylbutadiene (2). trans-Cinnamaldehyde (1.32 g, 0.01 mole) and benzyl cyanide (1.17 g, 0.01 mole) were taken in methanol (10 ml) and to this mixture was added 10% of sodium methoxide (0.015 mole) at ambient temperature with constant stirring under N₂. The reaction mixture was stirred for additional 30 min and left undisturbed for overnight under N₂. The reaction mixture was subjected to the usual work-up procedure and the solid obtained after evaporation of ether was recrystallized from benzene when, 2 was obtained in 14% yield: m.p. 118-19°C (lit. 14 m.p. 118°C); IR ν_{max} 3000 - 2900, 2240, 1640 cm⁻¹; UV-Vis (CH₃OH) λ_{max} 339 nm; ¹H NMR (C₆D₆) δ 6.45 (1 H, d, J = 15 Hz), 6.83 (1 H, d, J = 10 Hz), 7.9-7.1 and 7.38-7.5 (11 H, m).

Synthesis of 1Z, 3E-1-cyano-3-methyl-1,4-diphenylbutadiene (3). Compound 3 was synthesised by a procedure analogous to the one adopted for the synthesis of 2. Reaction of α-methyl-trans-cinnamaldehyde with benzyl cyanide gave 3 in 12% yield: m.p. 120-21° (lit.¹³ 118-19°C); IR ν_{max} 3000-2850, 2220, 1620 cm⁻¹; UV-Vis (CH₃OH) λ_{max} 329 nm; ¹H NMR (C₆D₆) δ 2.29 (3 H, d, J = 1.14 Hz, - C₃ -CH₃), 6.46 (1 H, s, Ph-C₄H=C₃-), 6.76 (1 H, d, J = 1.4 Hz, Ph-C₁-(CN) = C₂H), 7.0-7.2 and 7.44 (10 H, m, Ar).

Irradiation of 2 and 3. n-Hexane solutions of compounds 2 and 3 (0.075 M) taken in quartz tubes were degassed by passing N_2 and the quartz containers were sealed. The solutions were irradiated in a merry-go-round photoreactor (Applied Photophysics, London) using 450W Hg vapor lamp for 20 min. The photomixtures obtained were subjected to

silica gel column chromatography (10% diethyl etherpetroleum ether, 60-80 °C fraction) when 1*E*, 3*E*-1-cyano-1,4-diphenylbutadiene (**2a**), 1*Z*, 3*Z*-1-cyano-1,4-diphenylbutadiene (**3a**) and 1*E*,3*E*-1-cyano-3-methyl-1,4-diphenylbutadiene (**3b**) were separated from their respective photomixture: **2a**, UV-Vis (*n*-hexane) λ_{max} 337nm; **2b**, UV-Vis (*n*-hexane) λ_{max} 327nm; ¹H NMR (C₆D₆) δ 6.33 (1 H,d, J = 15 Hz, C₄-H), 6.64 (1 H, d, J = 10 Hz, C₂H), 6.90 (1 H, d.d, J_{3,4} = 16 Hz, J_{2,3} = 10 Hz, C₃-H), 7.0-7.30 (10 H, m, Ar). **3a**, UV-Vis (*n*-hexane) λ_{max} 314 nm; ¹H NMR (C₆H₆) δ 1.38 (3 H, d, J=1.14 Hz, -C₃-<u>CH₃</u>), 6.30 (1 H, s, Ph-C(CN)=<u>C₂H</u>-), 6.66 (1 H, d, J=1.14 Hz, -CH₃ -C=<u>C₄H</u>-Ph), 6.90-7.20 (10 H, m, Ar). **3b**, UV-Vis (*n*-hexane) λ_{max} 321 nm.

Analysis of the photomixture. The photomixtures were analyzed by HPLC for determination of photoisomerization quantum yields and photostationary state compositions under the following conditions: Altech Si column, 10μ , 250×4.6 mm, 1% ethyl acetate-n-hexane, 1 ml/min, 340 nm; R_i : 2, 12.4 min.; 2a, 5.6 min; 2b, 14.6 min.; 3, 9.4 min; 3a, 14 min; 3b, 8.6 min. Action plots (Figs. 3 and 4 vide infra) were constructed by plotting % conversion of the 1Z, 3E isomers and % formation of the photoproducts viz. 1E, 3E and 1Z, 3Z isomers vs. time of irradiation. After certain interval of time an aliquot (μ L) of the photomixture was analyzed by HPLC to obtain the isomer percentage.

RESULTS AND DISCUSSION

In comparison to parent diphenylbutadiene 1 (λ_{max} 326 nm in *n*-hexane), diene 2 substituted with an electron withdrawing and conjugating cyano group showed redshifted absorption at 339 nm in *n*-hexane and methanol. Similar shifts were observed in polar acetonitrile (λ_{max} 343 nm for 2). In contrast, 3 showed a blue shifted absorption (325 nm in *n*-hexane, 329 nm in methanol and 327 nm in acetonitrile) because of the presence of

Figure 2. Photoisomerization reactions of diphenylbutadiene compounds substituted with electron-withdrawing (viz. -CN) and electron-supplying (viz. -Me) groups. Zwitterionic species (D⁺) mediates the photoisomerization process.

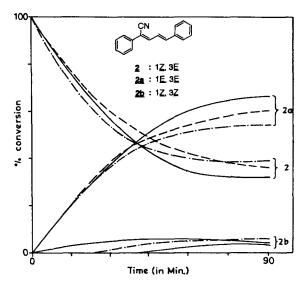


Figure 3. Action plot for photoisomerization of 2 in n-hexane (——), methanol (——), and acetonitrile (——). Photoproduct plots are : 2a (1E, 3E) and 2b (1E, 3E) in n-heptane (——); in methanol (——); and in acetonitrile (——).

methyl group at C-3. The methyl group is a relatively bulkier group than the hydrogen and hence causes steric hindrance leading to a certain degree of non-planarity in the polyene chain.

Direct irradiation of 1Z, 3E isomer of dienes 2 and 3 primarily resulted in one-photon-one-bond isomerization yielding the corresponding 1E, 3E and 1Z, 3Z-isomers (viz. 2a, 2b, 3a, and 3b; Fig. 2). The quantum yields of photoisomerization (ϕ_{iso}) and photostationary state compositions (PSS) in three different solvents for 2 and 3 are presented in Table 1. The action plots for photoisomerization of 2 and 3 in n-hexane, methanol and acetonitrile are shown in Figs. 3 and 4, respectively. It is observed that the ϕ_{iso} for 2 is lower than 3 in all the solvents. The PSS mixture of 2 is found to contain predominantly 2a which results due to isomerization across the double bond substituted with the electronwithdrawing cyano group. However, its percentage is decreased as the polarity of solvent is increased (viz. 61.5% in MeOH and 51% in CH₃CN). Similarly, at PSS of 3, isomerization of cyano substituted double bond dominates resulting in higher percentage of 3a in the three solvents studied. It may however be noted that the photoisomerization process in compound 3 is expected

Table 1. Photoisomerization quantum yield (ϕ_{iso}) and photostationary state (PSS) composition for 2 and 3.

PSS composition					PSS composition			
Solvent	ϕ_{iso}	2	2a	2b	ϕ_{iso}	3	3a	3b
$n-C_6H_{12}$	0.03	33.5	63.2	3.3	0.06	36.2	49.6	14.7
CH ₃ OH	0.03	33.1	61.5	2.1	0.09	43.3	40.5	16.2
CH ₃ CN	0.03	38.7	51.0	6.3	0.08	39.5	43.6	16.9

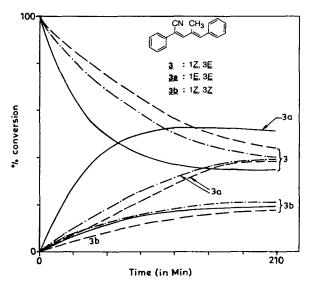


Figure 4. Action plot for photoisomerization of $\bf 3$ in n-hexane (_____), methanol (_____) and acetonitrile (____). Photoproducts plots are : $\bf 3a$ (1E, 3E) and $\bf 3b$ (1Z, 3Z) in n-hexane (_____); in methanol (_____); and in acetonitrile (____).

to be influenced by both the substituents. While methyl group presents steric hindrance (kinetic), the cyano group manifests itself by its electron-withdrawing

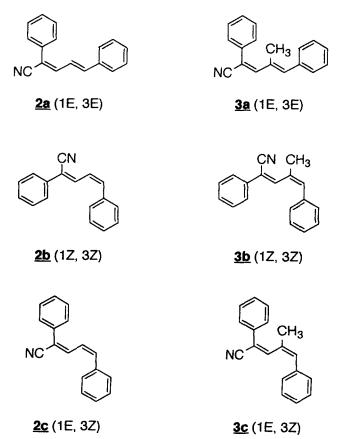


Figure 5. Chemical structures of the photoproducts of 2 and 3 (2a, 2b, 3a and 3b).

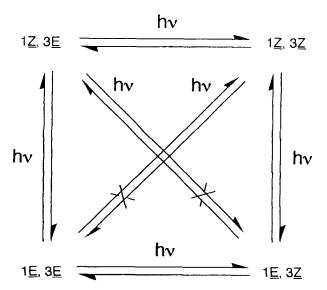


Figure 6. A general scheme showing photoisomerization pathways of **2** and **3**.

(thermodynamic) nature. Because of the steric hindrance of methyl group and resulting non-planarity, both double bonds are expected to undergo independent twisting in the excited state. It is interesting to note the enhanced PSS percentage of 2a and 3a in contrast to rather low amount of 2b and 3b. Thus, it is quite clear that the substituents (polar as well as steric) affect the photoisomerization process of the singlet excited state of diphenylpolyenes by influencing the potential energy surface leading to the formation of perpendicular species. The photoisomerization of these dienes can be mediated by zwitterionic polar species (D) as shown in Fig. 2 (vide supra). The polar substituents can cause the potential energy surface of dienes to yield the zwitterionic species from where the photoisomerization products will arise.

To further characterize the nature of photoisomerization of double bonds in 2 and 3, the photoproducts 2a, 2b and **3a**, **3b** (Fig. 5) were isolated and their photoisomerization was studied. The isolated isomers 2a and 2b were irradiated at 330 nm and the progress of the photoreaction was monitored by absorption spectroscopy. Compound 2a $(\lambda_{\text{max}} 337 \text{ nm})$ on direct irradiation in *n*-hexane showed a gradual blue shift to 331 nm. In contrast, irradiation of 2b $(\lambda_{\text{max}} 327 \text{ nm})$ in *n*-hexane showed a gradual red shift to 331 nm. From these absorption behaviour, it can be concluded that 2a and 2b give the photoproduct other than 2. The new product obtained could be 1E, 3Z-1cyano-1,4-diphenylbutadiene 2c which is obtained by one-photon-one-bond rotation of 2a and 2b. Direct conversion of 2a to 2c (i.e. one-photon-two-bond photoisomerization) is highly unlikely, as only onephoton-one-bond photo-isomerization is observed in diphenylpolyenes. Similarly, 3a and 3b isomers were also isolated from the photomixture of 3 and further

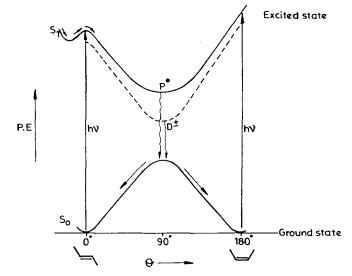


Figure 7. Schematic potential energy surface for photoisomerization of linear C=C chromophores. P* represents the perpendicular geometry and D^+ represents the zwitterionic species of the excited singlet state. D^+ is stabilized by polar solvent and appropriate electron withdrawing and donating substituents on C=C.

irradiated at 315 nm in *n*-hexane. The progress of the photoreaction was monitored by absorption spectroscopy. On photolysis, the λ_{max} of **3b** at 321 nm gets blue shifted gradually to 318 nm while the λ_{max} of **3a** at 314 nm gets red shifted gradually to 318 nm. Apparently, the photoproduct formed from **3a** and **3b** is different from **3** and it is most likely to be the 1*E*, 3*Z*-1-cyano-3-methyl-1,4-diphenylbutadiene (**3c**) isomer. However, it has not been possible in the present studies to isolate the 1*E*, 3*Z* isomers **2c** and **3c** due to small quantities (μ g) of the dienes handled in these photochemical experiments. The isolation of these dienes is important for their unambiguous assignment. Fig. 6 presents a general cyclic scheme that can explain the photoisomerization process in **2** and **3**.

The excited singlet state behaviour of alkenes (e.g. stilbene) and linearly conjugated C=C polyenes is believed to be governed by two processes. Fluorescence, from S₁ competes effectively with the activated twisting of double bond into a perpendicular geometry. This state decays within picoseconds to an energy maximum on the ground state potential surface. From there, an exothermic 90° rotation produces either the cis or the trans isomer. From the present results it is apparent that the potential energy surface from planar to perpendicular state is influenced by the presence of substituents. As shown in Fig. 7, the perpendicular species can have lower energy if charge separation occurs and zwitterionic state (D₁) is formed.

Thus, the present studies indicate towards the involvement of dipolar, zwitterionic species in the photochemical isomerization of diphenylpolyenes from their singlet manifold. It is believed that photophysical studies (e.g. fluorescence studies) of these and other related dienes will provide further information on the nature of the excited states of these chromophores.

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