

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

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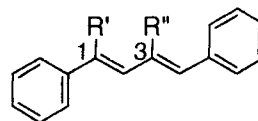
Abstract – Direct irradiation of 1Z, 3E-1-cyano-1,4-diphenylbutadiene (**2**) and 1Z, 3E-1-cyano-3-methyl-1,4-diphenylbutadiene (**3**) in organic solvents viz. *n*-hexane, methanol and acetonitrile results in preferential isomerization of the double bond substituted with cyano group via one-photon-one-bond 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.¹ 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 zwitterionic 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-1,4-diphenylbutadiene(**2**) and 1Z, 3E-1-cyano-3-methyl-1,4-diphenylbutadiene (**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 actinometry. 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 ^1H 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 N_2 . The reaction mixture was stirred for additional 30 min and left undisturbed for overnight under N_2 . 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 (CH_3OH) λ_{max} 339 nm; ^1H NMR (C_6D_6) 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 (CH_3OH) λ_{max} 329 nm; ^1H NMR (C_6D_6) 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 ether-petroleum ether, 60-80 °C fraction) when 1E, 3E-1-cyano-1,4-diphenylbutadiene (**2a**), 1Z, 3Z-1-cyano-1,4-diphenylbutadiene (**2b**), and 1E,3E-1-cyano-3-methyl-1,4-diphenylbutadiene (**3a**) and 1Z, 3Z-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 (C_6D_6) 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 (C_6H_6) δ 1.38 (3 H, d, J=1.14 Hz, -C₃-CH₃), 6.30 (1 H, s, Ph-C(CN)=C₂H-), 6.66 (1 H, d, J=1.14 Hz, -CH₃ - C=C₄H-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, 10 μ , 250 \times 4.6 mm, 1% ethyl acetate-*n*-hexane, 1 ml/min, 340 nm; R_t: **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 (μL) 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 red-shifted 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

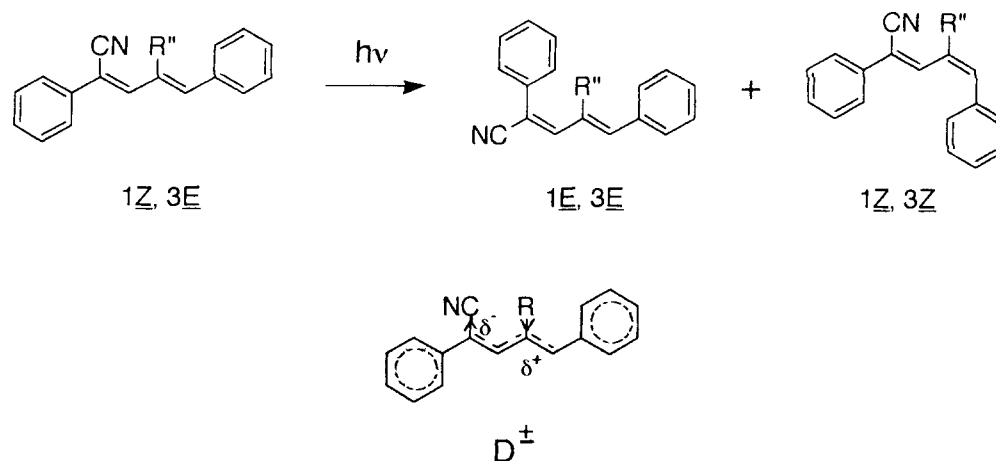


Figure 2. Photoisomerization reactions of diphenylbutadiene compounds substituted with electron-withdrawing (*viz.* -CN) and electron-supplying (*viz.* -Me) groups. Zwitterionic species (D^{\pm}) mediates the photoisomerization process.

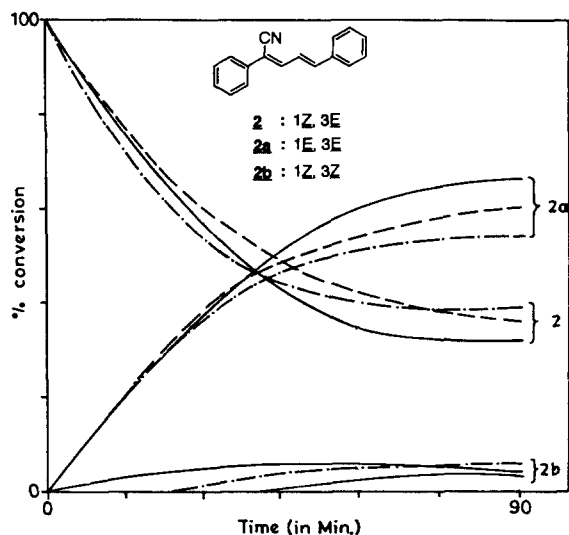


Figure 3. Action plot for photoisomerization of **2** in *n*-hexane (—), methanol (----), and acetonitrile (— · —). Photoproduct plots are : **2a** (1*E*, 3*E*) and **2b** (1*Z*, 3*Z*) in *n*-heptane (—); in methanol (----); and in acetonitrile (— · —).

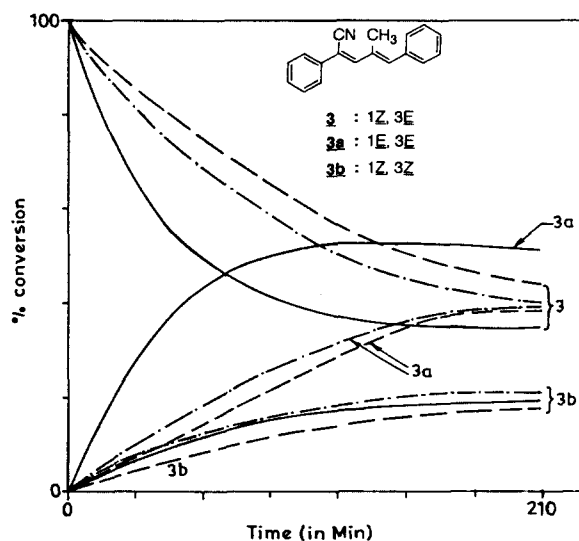


Figure 4. Action plot for photoisomerization of **3** in *n*-hexane (—), methanol (----) and acetonitrile (— · —). Photoproduct plots are : **3a** (1*E*, 3*E*) and **3b** (1*Z*, 3*Z*) in *n*-hexane (—); in methanol (----); and in acetonitrile (— · —).

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 1*Z*, 3*E* isomer of dienes **2** and **3** primarily resulted in one-photon-one-bond isomerization yielding the corresponding 1*E*, 3*E* and 1*Z*, 3*Z*-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 electron-withdrawing 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

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

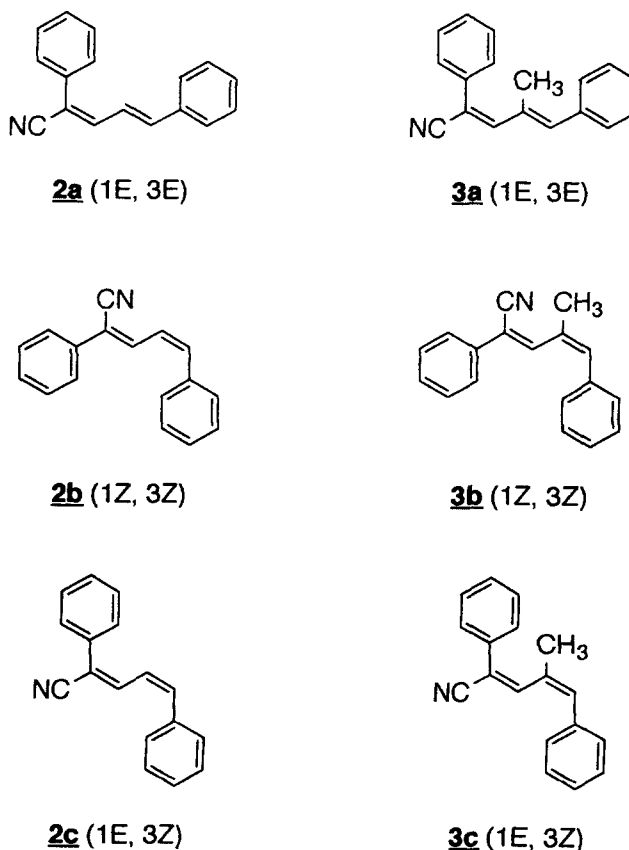


Figure 5. Chemical structures of the photoproducts of **2** and **3** (**2a**, **2b**, **3a** and **3b**).

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

Solvent	ϕ_{iso}	PSS composition			ϕ_{iso}	PSS composition		
		2	2a	2b		3	3a	3b
<i>n</i> -C ₆ H 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

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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REFERENCES

1. Findlay, J. B. C and D. J. C. Pappin (1986) The opsin family of proteins. *Biochem. J.* **238**, 625-642.
2. Ottolenghi, M. (1980) The photochemistry of rhodopsins. *Adv. Photochem.* **12**, 97-200.
3. Liu, R. S. H. and A. E. Asato (1984) Photochemistry and synthesis of stereoisomers of vitamin A. *Tetrahedron*, **40**, 1931-1969.
4. Becker, R. S. (1988) The visual process: photophysics and photoisomerization of model visual pigments and the primary reaction. *Photochem. Photobiol.* **48**, 369-399.
5. Birge, R. R. (1990) Nature of primary photochemical events in rhodopsin and bacteriorhodopsin. *Biochim. Biophys. Acta*, **1016**, 93-327.
6. Saltiel J. and J. L. Charleton (1980) In *Rearrangements in Ground and Excited States*. (Edited by de P. Mayo), Academic Press, New York.
7. Hudson, B. S., B. E. Kohler and K. Schulten (1982) *Excited States* Vol. 6 (Edited by P. Lim), Academic Press, New York.
8. Goldbeck, R. A., A. J. Twarowski, E. L. Russel, J. K. Rick, R. R. Birge, E. Switkes and D. S. Kliger (1982), Excited state absorption spectroscopy and state ordering in polyenes.II. α,ω -Diphenylpolyenes. *J. Chem. Phys.*, **77**, 3319-3328.
9. Allen, M. T. and D. G. Whitten (1989) The photophysics and photochemistry of α,ω -diphenylpolyene singlet states. *Chem. Rev.*, **89**, 1691-1702.
10. Saltiel, J. and Y. -P. Sun (1990) *cis-trans* Isomerization of C=C double bonds. In *Photochromism : Molecules and Systems* (Edited by Heinz, Durr and Henri Bouas-Laurent), pp. 64-163, Elsevier, New York.
11. Whitten, D. G. (1993) Photochemistry and photophysics of *trans*-stilbene and related alkenes in surface assemblies. *Acc. Chem. Res.* **26**, 502-509.
12. Salem, L. (1979) The sudden polarization effect and its possible role in vision. *Acc. Chem. Res.*, **12**, 87-92.
13. Vlasta, B. K., P. Brukman, P. Hiberty, J. Koutecky, C. Leforestier and L. Salem (1975) Sudden polarization in the zwitterionic Z_1 excited states of organic intermediates. Photochemical implications. *Angew. Chem. Internat. Edn.* **14**, 575-576.
14. Bartz, B. H., A. K. Singh and R. S. H. Liu (1981) Photochemical *cis-trans* isomerization of three cyano substituted diphenyl-1,3-butadienes and a diphenyl-1,3-hexatriene. The dipolar character and S^1 State. *Nouv. J. Chim.* **5**, 297-303.
15. Liu, R. S. H., M. Denny, M. Grodowsky and A. Asato (1979) Photoisomerization of 10-fluoro-, 14-fluoro-, and 3-dehydroretinal. The polar character of the excited state intermediates. *Nouv. J. Chim.* **3**, 503-505.
16. Reddy, M. A. and V. J. Rao (1992) Ionic photodissociation of polyenes *via* a highly polarized singlet excited state. *J. Org. Chem.* **57**, 6727-6731.