

PHOTOISOMERIZATION AND FLUORESCENCE STUDIES OF SOME 1,4-DIARYLBUTA-1E,3E-DIENE COMPOUNDS : ROLE OF POLARIZED EXCITED STATES IN THE PHOTOPROCESSES OF ALKENES AND RELATED LINEAR POLYENES

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Dipolar zwitterionic excited states have been suggested to be involved in the photoprocesses of alkenes and linear polyenes.¹ It has been argued that the development of charge as a function of twist angle in linear $>C=C<$ containing carbons of different electronegativities can cause a rapid increase in dipole moment as the perpendicular geometry is reached and zwitterionic intermediates can be involved in the photoisomerization reaction. However, experimental studies are limited and additional work is needed to establish whether the perpendicular excited states of such chromophores are best described as nonionic or zwitterionic state. α,ω -Diphenyl polyenes are considered to be a good model system for characterization of the excited state properties of linear polyenes.^{1c,e,f} We have prepared donor-acceptor / donor-donor and acceptor-acceptor substituted diaryl polyenes $[Ar-(CH=CH)_n-Ar]$ and investigated their fluorescence (steady state and time resolved, Stokes shifts, Φ_{flu} , τ_{flu} , P and r, red edge excitation shift studies) and photoisomerization (direct and triplet sensitized, initial and PSS compositions, Φ_{iso}) behaviour in organic solvents of varying polarity and in microheterogeneous media of micelles and vesicles. It is found that photoisomerization as well as fluorescence characteristics of these dienes are significantly influenced by both substituents as well as media. All the dienes exhibit one-photon-one-bond photoisomerization with solvent polarity-dependent quantum yields. The fluorescent emissions from these dienes are highly sensitive to solvent polarity, and to the position of the substituents. These dienes also exhibit good fluorescence probe properties. It has been concluded that dipolar, conformationally relaxed intramolecular charge transfer (CRICT) excited species play crucial role in both fluorescence as well as photoisomerization processes of these chromophores. The results are discussed in terms of the nature of excited states of linear polyenes in general and photobiologically important retinylidene chromophores in particular.²

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