

QUANTUM CHAIN PROCESSES IN ALL-TRANS-RETINAL AND ALL-TRANS-DIPHENYLBUTADIENE

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(Received 16 September 1996; accepted 25 November 1996)

Abstract - Quantum yield of photoisomerization of degassed *n*-hexane solution of all-*trans*-retinal (**1**) and all-*trans*-1, 4-diphenylbutadiene (**4**) at 25°C under direct irradiation conditions increases as the concentrations of **1** and **4** increase. Further, fluorescence lifetime of **4** at ambient temperature is also found to increase as the concentrations of **4** are increased. The results are discussed in terms of quantum chain process which occurs due to exchange of energy between various conformers of the compounds concerned.

INTRODUCTION

Light-induced geometrical isomerisation of conjugated linear polyenes particularly retinylidenes, has been known to be an important photobiological process taking place in the opsin family of proteins¹. Consequently, the nature of photoprocesses of retinylidene polyenes has been the subject matter of extensive multidisciplinary investigations in recent years^{2,7}. Absorption of photons by all-*trans*-retinal (**1**) in organic solvents predominantly results in geometrical photoisomerization process which has been investigated in great detail by many investigators^{2,4}. Both singlet and triplet state photochemistry has been observed. Recently, in the triplet photoisomerization, relation between rate of triplet sensitization with quantum yields of isomerization and photostationary state composition has been found to exist⁸. Further dependency of the quantum yield of photoisomerisation of retinal (**1**) on its concentration has recently been reported⁹. This dependence of quantum yield of isomerization on concentration of retinal (**1**) has been accounted for in terms of the quantum chain process arising from the triplet states. In our attempts to explore the nature of the excited states of retinylidene polyenes, we have taken advantage of the highly fluorescent characteristics of all-*trans*-1,4-diphenylbutadiene (**4**) at room temperature in solution and recently reported quantum-chain process of **4** in its singlet excited state manifold¹⁰.

In this paper we present the effect of concentration on the photoisomerisation process of all-*trans*-retinal (**1**) in addition to reporting the details of the quantum chain process in all-*trans*-1,4-diphenylbutadiene (**4**) under direct irradiation conditions where singlet excited states are produced.

EXPERIMENTAL

All-*trans*-retinal (**1**) was obtained from Sigma Chem. Co. U.S.A. Diphenylbutadiene (**4**) was synthesized as mentioned earlier¹⁰. All samples were handled under N₂ and in protective red light. *n*-Hexane of HPLC grade from Spectrochem (Bombay) was stored over 4 Å molecular sieves.

Quantum yield and photostationary measurements were carried out by irradiating degassed samples of **1** and **4** in *n*-hexane and potassium ferrioxalate was used for actinometry. Irradiations were done at 360 nm for **1** and 330 nm for **4** using a 150W Xe arc lamp coupled with monochromator having a slit width of 2 nm. For quantum yield measurements, conversion was kept to a minimum of 5% for samples of 1 × 10⁻⁵ M concentration. For each experiment, a control sample of equal concentration of **1** and **4** in *n*-hexane was kept in dark to ensure the absence of thermal isomerization during irradiation time. The photomixtures were analysed by HPLC^{11,12}. The conditions for HPLC analysis are: for retinal isomers: 250 mm × 10 mm, 5 μm Lichrosorb Si column, 5% diethylether-*n*-hexane, 1.5 mL/min flow rate, 365 nm detection; [*R*:9-*cis*:9 min, and 13-*cis*:7.4 min]; for diphenylbutadiene (**4**) isomers: 250 mm × 4.6 mm, 10 μm Altech Si-60 column, 1% ethyl acetate-*n*-hexane, 1 mL/min flow rate, 326 nm detection [*R*₁: 4:6 min, λ_{max}(*n*-hexane) 330 nm; *R*₂: 5:5.5 min, λ_{max}(*n*-hexane) 315 nm].

The fluorescence lifetime (τ_f) measurements of **4** were carried out using SP-70 nanosecond fluorescence spectrometer (Applied Photophysics, London) equipped with thyration gated discharge lamp with strong lines from 300 nm to 400 nm with amplitude output of < 1 ns and a photomultiplier tube type XP 2020 Q having working spectral range from 200 to 600 nm. The data were processed with DEC MINC computer using the software provided by the manufacturer. All the measurements were made on degassed samples at 25°C. For diphenylbutadiene's

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fluorescence measurements, the excitation was done at 330 nm.

Direct Irradiation of all-trans-Retinal (1). For direct irradiation, a solution of all-trans-retinal (**1**) was prepared in *n*-hexane ($3 \times 10^{-3} M$, 10 mL). From this solution, retinal samples of different concentration ($1.2 \times 10^{-5} M$ – $18 \times 10^{-5} M$) were prepared and used for direct irradiations. The respective solutions were taken in pyrex tubes, thoroughly degassed (dry N_2) and irradiated for about 5 minutes to achieve 3–5% conversion. The isomers were analysed using HPLC and percentage isomerisation was calculated from areas under the peak, after making corrections for the absorptivity of each isomer (all-trans, $\epsilon = 45,400$, 13-cis, $\epsilon = 57,500$, 9-cis, $\epsilon = 36,600$). Irradiation procedures for **4** were as described earlier¹⁰.

The photostationary states (PSS) in *n*-hexane for different concentrations of **1** and **4** were established by extended period of irradiations. The PSS composition was obtained by HPLC analysis of the photomixture which were characterized as reported earlier^{10,11}.

RESULTS AND DISCUSSION

Photolysis of all-trans-retinal (**1**) in *n*-hexane under direct irradiation conditions results in a photomixture which comprises of all-trans, 9-cis (**2**) and 13-cis (**3**) isomers of retinal (Fig.1). These isomers are easily separated by normal phase HPLC analysis.

The quantum yields (Φ_{iso}) and photostationary state (PSS) composition of photoisomerisation of **1** and **4** in *n*-hexane at various concentrations are given in Tables 1. and 2 respectively. Plots of concentrations vs. quantum yield of photoisomerisation for **1** and **4** are shown in Figures 2 and 3 respectively. A typical fluorescence decay profile of a $1 \times 10^{-3} M$ *n*-hexane solution of **4** is depicted in Figure 4. In Table 3 are given fluorescence lifetime for **4** at its different concentrations.

The quantum yield of photoisomerisation increases linearly with increase in concentration of **1** and **4**. Further, as the concentration of **4** increases, the

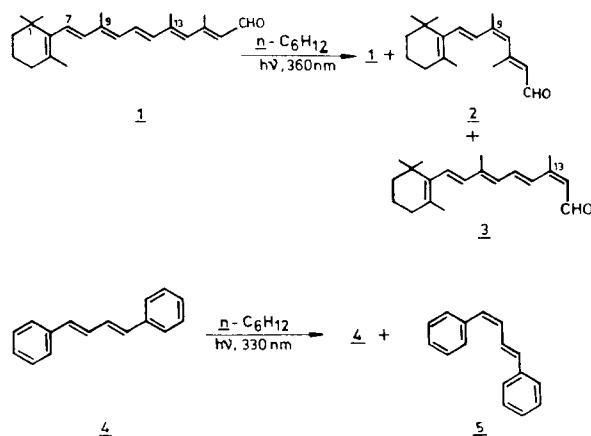


Figure 1. Singlet excited state photochemical reactions of all-trans-retinal (**1**) and all-trans-diphenyl butadiene (**4**) in *n*-hexane at 25°C.

fluorescence lifetime also increases. At relatively higher concentration of **4**, however, the fluorescence lifetime decreases.

These results indicate towards the involvement of quantum chain process which can be explained in terms of the exchange of energy between the excited state and the ground state molecules. The quantum chain process can be mediated by the presence of *s-cis* conformations of linear conjugated polyenes (e.g. as shown in Fig. 5). Existence of conformers in retinyl polyenes has been suggested earlier¹². It is further known that at room temperature approximately 25% of the emission of all-trans-**4** arises from its *s-cis* conformation (Fig.5).

It has also been recently argued that *s-cis* rotamer of **4** is expected to absorb at longer wavelength than the *s-trans*-**4**. As a result selective excitation of one of the

Table 1. Quantum yield of photoisomerization (Φ_{iso}) and photostationary state composition (PSS) of all-trans-retinal (**1**) in *n*-hexane under direct and degassed irradiation (360 nm) conditions at 25°C.

Conc. of (1) $\times 10^{-5} M$	Φ_{iso}	% of isomers at PSS		PSS product ratio (2/3)
		9-cis (2)	13-cis (3)	
1.2	0.009	5.84	21.08	1/0.28
3.6	0.014	3.90	13.90	1/0.28
7.2	0.024	2.96	9.95	1/0.30
14.4	0.043	3.11	7.97	1/0.39
18.0	0.056	2.27	5.43	1/0.41

Table 2. Quantum yield of photoisomerization (Φ_{iso}) and photostationary state composition (PSS) of all-trans diphenylbutadiene (**4**) in *n*-hexane under direct and degassed irradiation (330 nm) conditions at 25°C.

Conc. of (4) $\times 10^{-5} M$	Φ_{iso}	% of isomers at PSS		PSS product ratio (4/5)
		9-cis (4)	13-cis (5)	
0.62	0.018	66.7	33.3	1/0.5
1.23	0.037	59.5	40.5	1/0.68
1.85	0.042	65.2	34.8	1/0.53
2.46	0.055	71.0	29.0	1/0.41
3.08	0.084	66.6	33.6	1/0.51

Table 3. Concentration dependent fluorescence lifetime of **4** in *n*-hexane at ambient temperature.

Conc. of DPB(4) $\times 10^{-1} M$	τ_f (ns)	Chi Square value
1.0	0.63	1.25
5.0	0.73	1.42
10.0	0.85	1.51
50.0	0.55	1.14

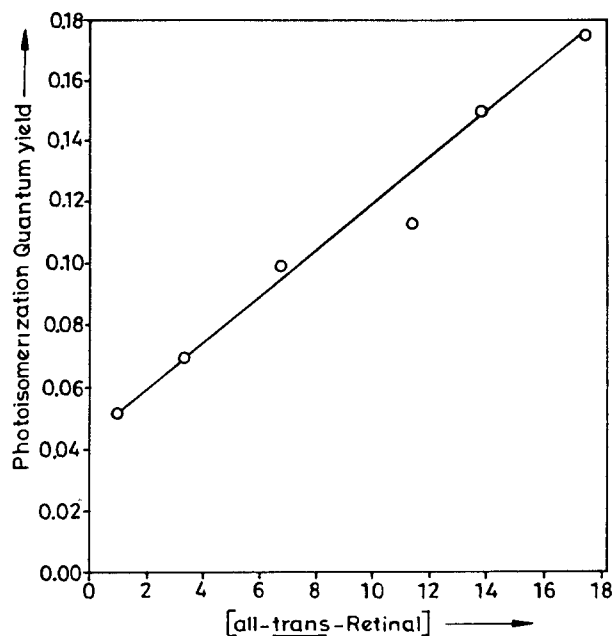


Figure 2. A plot of quantum yield of photoisomerisation (Φ_{iso}) vs. concentration for all-*trans*-retinal(1) under direct irradiation condition (360 nm, 25°C, *n*-hexane).

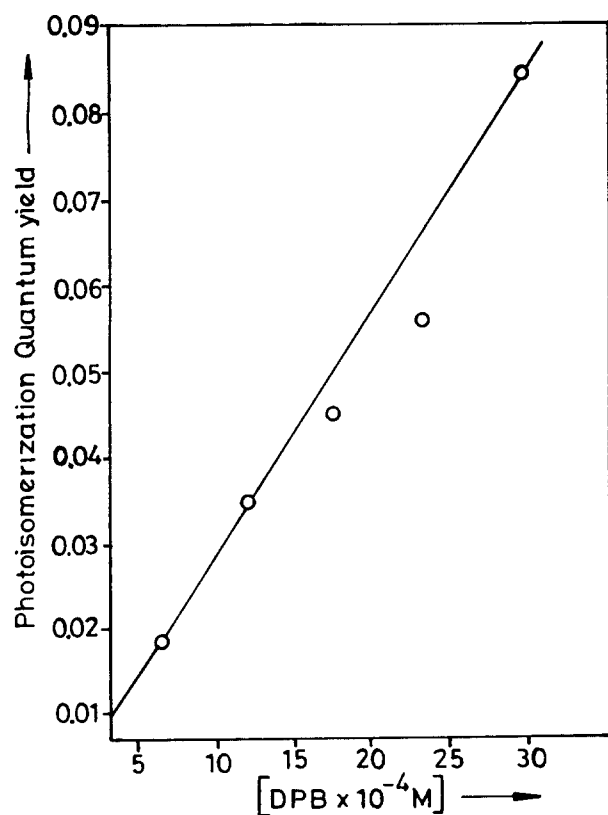


Figure 3. A plot of quantum yield of photoisomerisation (Φ_{iso}) vs. concentration for all-*trans*-diphenylbutadiene(4) under direct irradiation condition (330 nm, 25°C, *n*-hexane).

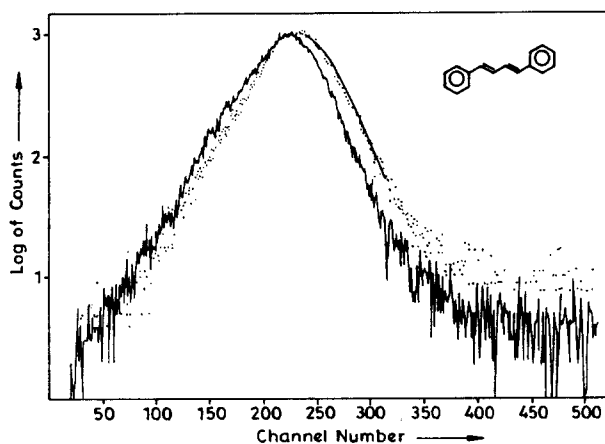


Figure 4. A typical fluorescence decay profile of a 1.0×10^{-3} M *n*-hexane solution of 4 at 25°C.

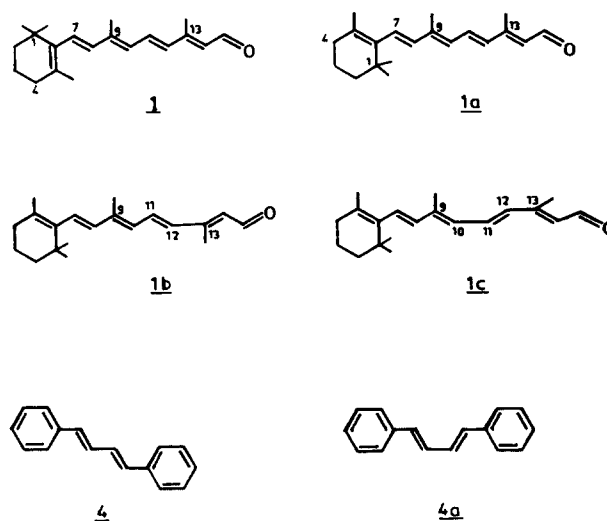


Figure 5. Different ground state conformational structures of all-*trans*-retinal(1) and all-*trans*-diphenyl butadiene(4) in solution.

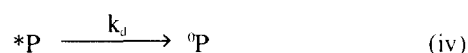
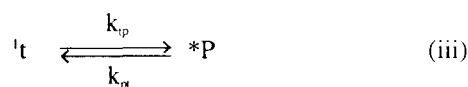
rotamer is possible.

Upon absorption of photons carbon-carbon double bonds of linear olefins and conjugated polyenes produce planar singlet-excited state which decays into a perpendicular geometry⁵. This perpendicular species further decays to an energy maximum on the ground state potential energy surface from where an exothermic 90° rotation produces either the *cis* or the *trans* isomer. At relatively higher concentration, the distance between the excited state and the ground state molecule is decreased leading to exchange of energy due to close interaction. At infinite concentration, the distance between the excited state molecule and ground state molecule is further decreased and self quenching occurs. Recently it has been shown that the first excited singlet state of *trans*-

stilbene can be quenched by ground state *trans*-stilbene at high diffusion limit and upon quenching a new intermediate with charge transfer characteristics is formed. This new intermediate subsequently collapses to cycloadduct⁴. Though non-emittive all-*trans*-retinal(**1**) is difficult to study by fluorescence techniques, the concentration dependent photochemistry observed in retinal(**1**) can be explained by invoking secondary triplet-triplet energy transfer from retinal triplet to its *cisoid* conformers. It is known that in *n*-hexane, retinal(**1**) has high intersystem crossing efficiency¹. Further, all-*trans*-retinol acetate and related polyenes undergo Diels-Alder reaction or form stable organometallic complexes involving the dienic moiety between C11-C14 of the retinyl chain, implying that 12-(*s*)-*cis* conformers(*viz.* **1b** and **1c**) are readily available at room temperature. Therefore, *cisoid* conformers of retinal(**1b** and **1c**) might act as selective acceptors in secondary energy transfer processes and hence the observed photochemistry.

Compound **4** exhibits quantum chain processes as the quantum yield of photoisomerization is linearly increasing with increase in substrate concentration. Unlike retinal(**1**), the involvement of triplet state in photoisomerization of **4** is not likely as reported quantum yield of intersystem crossing is very low(0.02)⁵. Compound **4** can exist in *s-cis* and *s-trans* conformations. It has been shown that at room temperature, 25% of compound **4** exist in *s-cis* conformation. It has recently also been shown that the *s-cis*-**4** has maximum absorption at 350 nm. In the present experiment, the solutions of **4** are irradiated at 330 nm, where *s-trans*-**4** absorbs maximum light. Further, fluorescence lifetime of **4** in *n*-hexane increases with increase in substrate concentration.

The following mechanism is forwarded to explain the observed results.



where ${}^0\text{t}$ is ground state of compound **4**, ${}^0\text{c}$ is ground state of one bond-isomerized product, ${}^1\text{t}$ is singlet excited state **4**, *P is twisted perpendicular state of carbon-carbon double bonds, and 0P is dissociated state from where the isomerization takes place. The respective K 's are rate constants of each process. On excitation the ${}^0\text{t}$ state goes

to the ${}^1\text{t}$ state and an energy barrier of 4-5 kcal/mol can exist between the ${}^1\text{t}$ state and *P state. Due to the low activation energy between the two states it is expected that the two states are in equilibrium at room temperature. It is observed that the fluorescence rate constant ($k_f = 1/\tau_f$) decreases with the increase in concentration of compound **4**. This may happen if the backward reaction rate in step(iii), k_{pt} decreases and the equilibrium shifts towards the formation of *P , which will subsequently leads to the formation of photoisomerized products from the very fast decaying 0P . From Table 2, it can be seen that the PSS ratio is not affected by the concentration and it implies that the quantum chain process is only at the primary stage of photoisomerization and not at the later stage. It can also be argued that *s-cis* conformer absorbs at longer wavelength than *s-trans* conformer and as a result selective excitation of one of the conformer is possible. Upon excitation *s-trans* conformer exchanges energy with *s-cis* conformer. In the excited state, the carbon-carbon double bond is twisting perpendicularly out of plane. At relatively higher concentration, the distance between the excited state and the ground state molecules is decreased leading to the exchange of energy due to close interaction. At infinite concentration, the distance between the excited state molecule and the ground state molecule is further decreased and self quenching occurs.

The observed increase in quantum yield of photoisomerization with increase in substrate concentration for compound **4** in singlet excited state is similar to the quantum chain process in retinal isomers. Further studies are needed to understand the mechanisms of energy exchange between the *s-cis* and *s-trans* conformers using transient spectroscopy and ultrafast techniques.

Thus in the present study it has been demonstrated that the quantum chain process can also occur in the singlet excited state of linearly conjugated polyenes. Further, the results of this study show the relevance of conformational structures of the chromophores in the photoprocesses of retinal binding photoreceptors.

Acknowledgement -- Research grants from the Board of Research in Nuclear Science, Department of Atomic Energy, Government of India are gratefully acknowledged.

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