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Photochemistry of Oriented Molecules

The Photodimerization of Tetraphenylbutatriene Incorporated in Polyethylene and Nematic Matrices

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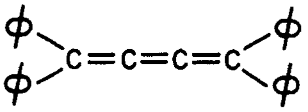
The photodimerization of tetraphenyl-butatriene (I), incorporated in a nematic phase, and in oriented polyethylene was studied.

Quantitative dimerization was achieved in a compensated cholesteric phase. Upon melting of the phase, the incorporated butatriene became unreactive. Dimerization took place also in polyethylene, however in stretched polyethylene there was three fold increase of the quantum yield.

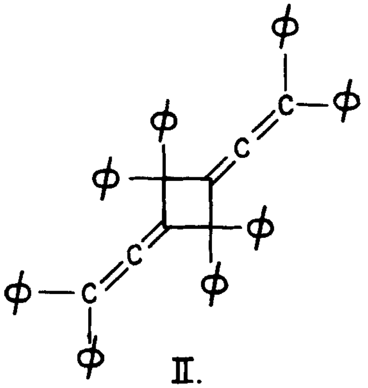
The study of photochemical behaviour of organized systems is of utmost importance for the understanding of basic molecular processes. While the role of molecular organization in affecting the paths of solid-state reactions has been thoroughly investigated,[1] much less attention has been paid to the study of ordered noncrystalline systems.

Tetraphenylbutatriene (I) dimerizes in the solid state, and its photodimer (II) is believed to be the product of a typical solid state controlled reaction.[1]



I.

In order to study the possible influence of other forms of molecular organization on the course of this reaction we decided to investigate the photochemical behaviour of tetraphenylbutatriene in isotropic and unidirectionally



II.

oriented, anisotropic solutions. Two types of oriented solutions were obtained by dissolving tetraphenylbutatriene in a nematic phase,* and in a stretched polyethylene film.

The orientation of the solute molecules in these anisotropic media was evaluated from uv linear dichroism (LD) measurements.[3] The LD spectra of tetraphenylbutatriene in stretched polyethylene and in a nematic solution aligned by means of an electric field (30–40 kv/cm)[2] are shown in Figure 1. Since the elongated tetraphenylbutatriene molecules are preferentially oriented with their longitudinal axes parallel to the optical axis of the anisotropic matrices† in which they are incorporated, a low limit value for the orientational parameter,[3] f, may be derived assuming the maximum value of the measured dichroic ratio‡ to represent a pure transition, polarized along the longitudinal molecular axis. Using $d_0(\max) = 2.0$ for the stretched film, and $d_0(\max) = 1.82$ for the nematic phase, both occuring at $\lambda \approx 280$ nm, we have calculated $f_{\min}(\text{polyethylene}) = 0.25$ and $f_{\min}(\text{nematic}) = 0.215$. It appears that the tetraphenylbutatriene molecules are oriented at a considerable extent¶ in both matrices, and that their degrees of orientation are similar.

Unstretched polyethylene films and compensated cholesteric mixtures at temperatures above T_{NI}§ were chosen as suitable reference isotropic solutions.

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* A 1.95/1 by weight mixture of cholesteryl chloride and cholesteryl laurate is nematic at $T_N = 30°\text{C}$.[3] This compensated cholesteric mixture is appropriate for photochemical studies, being transparent down to *ca.* 240 nm.

† The stretching direction of the polyethylene film and the direction of the applied electric field, in the case of a nematic oriented solution, coincide with the respective optical axes.

‡ The dichroic ratio is defined as $d_0 = OD_{\parallel}/OD_{\perp}$, where $OD_{\parallel}$ and $OD_{\perp}$ are the absorbances measured with light polarized parallel and perpendicular to the optical axis of an anisotropic, uniaxial medium, respectively.

¶ The orientational parameter f takes on values of zero and unity in unoriented and perfectly oriented media, respectively.[4]

§ T_{NI} is the temperature of the transition nematic–isotropic.

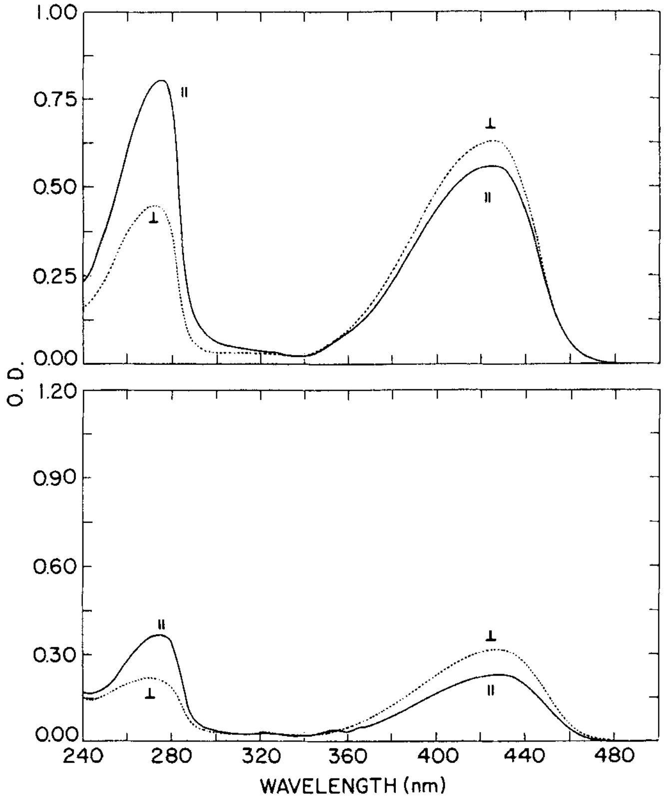

FIGURE 1 The LD spectra of tetraphenylbutatriene in stretched polyethylene (upper part) and in an oriented nematic solution (lower part): (————) the curve of optical density obtained with light polarized in the direction of the optical axis and (– – – – –) perpendicular to it.

Tetraphenylbutatriene dissolved in the anisotropic and isotropic solutions was irradiated under similar conditions regarding the concentrations and the absorbances of the starting material. The only photoproduct obtained in the nematic and polyethylene solutions was identified as dimer II, by comparing its characteristic UV, NMR and mass spectra with those of an authentic sample obtained in the solid state reaction.[1] No dimeric product could be detected when the temperature of the nematic phase was raised above its transition point to an isotropic phase ($t \approx 80°C$). The irradiations were repeated also with nematic phases containing in addition to the cholesteric mixture small amounts of diethyleneglycol-dibutylether, in order to lower their transition temperatures ($T_{NI} \approx 40°C$). In all these experiments dimer II was always identified as the single product of the photochemical reaction when the temperatures were within the range characteristic of an ordered phase, whereas no change in the spectrum of the starting material could be observed when the same solutions were irradiated at temperatures above T_{NI}.

Dimer II was formed in both stretched and unstretched polyethylene films, but the reaction of the former appeared to be much faster. The spectral changes recorded during the simultaneous irradiation† of a pair of stretched and unstretched polyethylene samples are illustrated in Figure 2.

We performed a comparative kinetic study of the dimerization in the isotropic and anisotropic polyethylene matrices, monitoring spectrally the formation of dimer II.‡ The photodimerization reaction may be represented schematically by the following sequence:

$$\mathrm{C} \underset{k_2}{\overset{h\nu}{\rightleftarrows}} \mathrm{C}^* + \mathrm{C} \xrightarrow{k_1} \mathrm{C}_2$$

where C represents the monomer concentration, C* is the concentration of the excited monomer molecules, and C_2 is the dimer concentration. k_1 is the rate constant for dimerization and k_2 represents the rate constant for the other deactivation processes of the excited molecules. If the absorbance of the matrix at the wavelength of irradiation is low ($\mathrm{OD} < 0.4$), uniform absorption of light at different points along the optical path is achieved. Under these conditions of irradiation, and assuming the steady state approximation for the concentration of the excited tetraphenylbutatriene molecules, the following kinetic equations may be derived:¶

$$-\frac{dOD_1(t)}{dt} \approx -\frac{\Delta OD_1(t)}{\Delta t} = \frac{2k_1}{k_2} \cdot C(t) \cdot \varepsilon_1 \cdot I_o[1 - 10^{-OD_2(t)}] \tag{1}$$

where $OD_1(t)$ is the instantaneous absorbance of the reacting compound at time t and at the wavelength λ_1 at which the reaction is monitored, and ε_1 is the corresponding extinction coefficient; $OD_2(t)$ is the instantaneous absorbance of the reacting compound at the wavelength of irradiation, λ_2, and I_o is the intensity of the incident light at λ_2. It can be easily shown that:

$$-\frac{\Delta OD_1(t)}{\Delta t} = \phi(c) \cdot \varepsilon_1 \cdot I_{\mathrm{abs}}(t) \tag{2}$$

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† The irradiations were performed with a high pressure HBO 200 W lamp equipped with a cut-off filter at 430 nm, in an oxygen-free atmosphere.

‡ The formation of dimer II may be followed either by the appearance of its characteristic absorption band at $\lambda \simeq 310$ nm, or by the equivalent disappearance of the monomer peak at $\lambda \simeq 425$ nm (see Figure 2).

¶ Equation (1) is applicable to a dichroic medium, like the stretched polyethylene film, only if the irradiation is performed in a spectral region where $d_o \approx 1$. As shown in Figure 1, this condition is fulfilled at $\lambda \approx 435$ nm in the tetraphenylbutatriene spectrum. In cases of compounds having highly dichroic bands a more elaborate equation, taking into account the dichroism effect, should be employed.

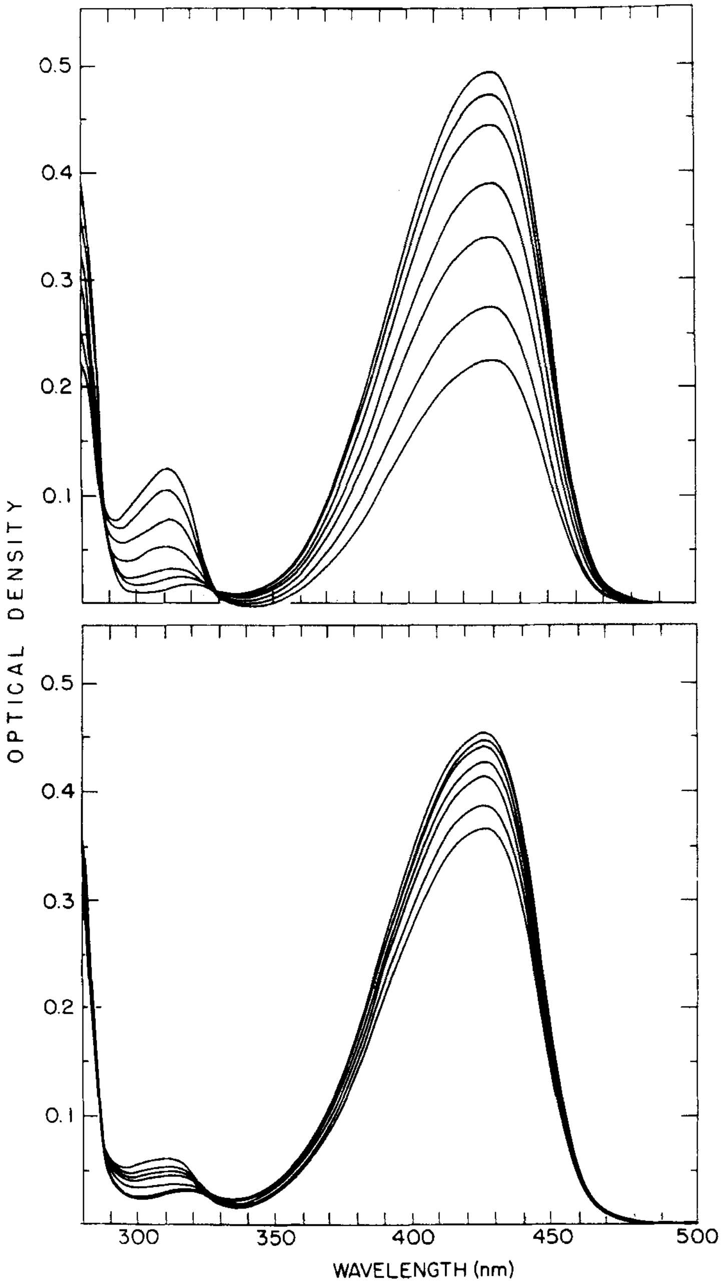

FIGURE 2 Simultaneous irradiation of tetraphenylbutatriene in a stretched polyethylene film (upper part), and in an unstretched one (lower part). Dimer II absorbs at $\lambda \approx 310$ nm.

and combining with Eq. (1):

$$\phi(c) \equiv \frac{2k_1 C(t)}{k_2}; \; I_{\mathrm{abs}}(t) \equiv I_o[1 - 10^{-OD_2(t)}] \tag{3}$$

where $I_{abs}(t)$ is the light absorbed at time t and $\phi(c)$ is the concentration-dependent quantum yield of dimerization.†

Eq. (1) may be rewritten in a more convenient form as

$$P(t) = \frac{-\Delta OD_1(t)/\Delta t}{1 - 10^{-OD_2(t)}} = \frac{2k_1 \cdot I_o}{k_2} \frac{OD_1(t)}{l} \tag{4}$$

where l is the thickness of the polyethylene film in centimeters.

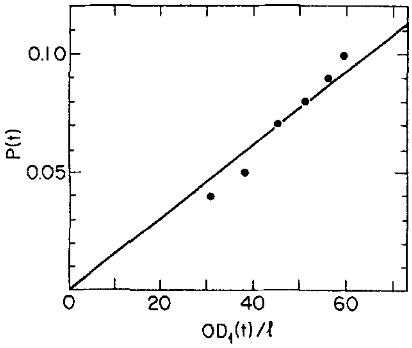

FIGURE 3 The plot of $P(t)$ versus $OD_1(t)/l$ for $OD_1(t)$ measured at $\lambda_1 = 425$ nm in a stretched polyethylene film.

A plot of function $P(t)$ versus $OD_1(t)/l$ measured at $\lambda_1 = 425$ nm in a stretched polyethylene film ($l \approx 0.008$ cm) is shown in Figure 3. The points fall approximately on a straight line, thus confirming the assumptions leading to Eq. (4). The slight deviation from linearity is probably due to a small decrease of I_o with time, which was neglected in these calculations.

Comparing the relative quantum yields of the reaction in stretched and unstretched films, I_o may be eliminated if both films are placed in the same cell and irradiated simultaneously.

Using Eqs. (1)–(4), the following expressions are derived:

$$\phi_{\mathrm{corr}} = \frac{\phi(c)}{C} = \frac{2k_1}{k_2} = \frac{P(t) \cdot l}{I_o \cdot OD_1(t)} \tag{5}$$

$$R = \frac{\phi_{\mathrm{corr}}^{\mathrm{stretched}}}{\phi_{\mathrm{corr}}^{\mathrm{unstretched}}} = \frac{[P(t) \cdot l/OD_1(t)]^{\mathrm{stretched}}}{[P(t) \cdot l/OD_1(t)]^{\mathrm{unstretched}}} \tag{6}$$

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† $\Delta OD_1(t)/\Delta t$ is a good approximation for $dOD_1(t)/dt$ if Δt is small on the time scale characteristic of the reaction.

The concentration-corrected quantum yields, ϕ_{corr}, are defined in Eq. (5) as true constants of the reaction, their ratio, R, being therefore a time independent factor which depends only on the characteristic rate constants of the reaction in the two media.

Results obtained in two typical irradiations are summarized in Table I. It appears that $R = 3.5 \pm 0.5$, or $\phi_{\text{corr}}^{\text{stretched}} = (3.5 \pm 0.5) \cdot \phi_{\text{corr}}^{\text{unstretched}}$. As suggested by Eq. (5), this difference may be attributed either to the rate constant of the dimerization step itself, k_1, or to the rate constant of the other deactivation processes, k_2, or to both of them.

TABLE I

A			*B*		
t (minutes)	*R*	⟨*R*⟩	*t* (minutes)	*R*	⟨*R*⟩
5.5	3.5	3.3 ± 0.5	1.0	3.7	3.7 ± 0.4
14	2.9		27.5	3.9	
18.5	4.0		50.5	4.0	
50	2.8		81	3.3	
80	3.5		113	3.5	

The experiments described above indicate that noncrystalline modes of orientation, in this case unidirectional alignment, may also affect the reactivity of the oriented molecules. In general it is rather difficult to isolate the effect of orientation from other changing physical or chemical parameters, which may be responsible for the observed phenomena.

The experiments with the polyethylene films are particularly useful in this respect, as no temperature or chemical composition changes are involved in the orientational process of this system.† It should be emphasized that, although the photodimerization of tetraphenylbutatriene is slower in unstretched polyethylene, this apparently unoriented material seems to be completely different from the other isotropic solutions in which no dimerization reaction could be detected. It is very likely that unstretched polyethylene also contains oriented domains which are aligned by stretching, in addition to the alignment of individual polymeric chains.[4] On a microscopic scale the unstretched polyethylene is thus a partially oriented system, too.

The fact that dimerization takes place only in anisotropic solution cannot be explained on the basis of preferred orientation alone, since at least a

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† The possibility that the reacting molecules are dispersed in the polyethylene film as microcrystals, or other form of aggregates was rejected, as no concentration effect on the LD spectrum was observed, and no change of the tetraphenylbutatriene dichroism during the irradiation could be detected. The kinetics of the dimerization also indicate that the reacting molecules are dispersed in polyethylene in the form of a true, homogeneous solution.

fraction of the molecules in the isotropic solution may collide at the proper orientation. It was recently proposed by V. Yakhot[5] that the probability of radiationless transitions be high in the cases in which the transition is accompanied by deformation of the molecule. It is possible that in the non-isotropic media which were used in our experiments the deformation in the oriented molecule is restricted by the matrix. The restriction of deformation deactivates the radiationless process and the overall lifetime of the excited state increases.[†] Extention of the lifetime of the excited state enables collisions of excited molecules over a long distance, and dimerization becomes possible, whereas in isotropic media the excited state is deactivated to the ground state by radiationless transitions prior to collision.

The "Stokes shift" serves as a measure of the value of deformation during excitation, it is expected that a compound will be photochemically more reactive in a matrix where it shows a smaller "Stokes shift."

The absorption and emission spectra of butatriene (I) in the various phases are summarized in Table II. It is seen from the table that by melting the nematic phase the Stokes shift increases from 70 nm to 92 nm and dimerization was quenched completely. Similarly, by stretching the incorporated polyethylene there was a three-fold increase in the reactivity, accompanied by a small decrease in the Stokes shift.

TABLE II

Media	Emission nm	Absorption nm	Stokes shift nm
Solid	440	414	26
Stretched polyethylene film	489	427	62
Unstretched polyethylene film	492	424	68
Nematic liquid crystal	502	430	70
Melted nematic	514	422	92
Heavy paraffin solution	475	422	53
Cyclohexan solution	590	423	167

In the solid state the restriction of deformation is accompanied by freezing of the rotation and translation of the molecule and reactions occur only over a distance of 4 Å. In our experiments in liquid crystals the average distance exceeded 100 Å. Thus, diffusion of excited molecules and collisions were possible under condition of restriction of deformation because of relatively long lifetimes. Isotropic viscous solution like heavy paraffin oil[‡] where diffusion is also inhibited, photo dimerization did not take place.

[†] Increase of excited state's life time of oriented molecules in liquid crystal mesophase, have been previously observed by R. Dreher and H. Schomburg, *Chem. Phys. Lett.*, **25**(4), 527 (1974).

[‡] The heavy paraffin contains 10% diethylene glycol dibutylether to improve missicibility.

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