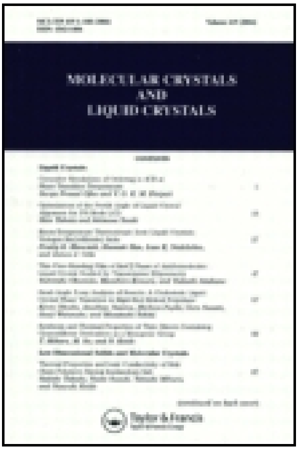

Molecular Crystals and Liquid Crystals

Photoreaction of Cholesteryl trans-Cinnamate in Mesomorphic States

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Photoreaction of Cholesteryl trans-Cinnamate in Mesomorphic States†

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The photoreaction of cholesteryl trans-cinnamate in KBr matrix was studied in the solid, mesomorphic and isotropic liquid states at 25–225° C, and compared with the solution reaction in *n*-hexane. Cholesteryl trans-cinnamate was converted into a dimer on irradiation at wave-length longer than 300 nm at these phases. The photoirradiation in the solution led to a cis-isomer at 25–30°C. The initial rate of the dimerization at the mesophase was found to be higher than that at the isotropic liquid phase. The photoreaction in the solid took place at a much slower rate than in the other states. These suggest that some kinds of ordering besides the mobility of the molecules of the cinnamate enhance the rate and affect the course of the reaction on irradiation in comparison with the reaction in the isotropic solution.

INTRODUCTION

Although the literature contains numerous references to the physical and chemical properties,[1] and the important role in the biological systems[2] of the liquid crystals, there is little information of the reaction in the mesophases.[3] This class of reaction in the mesomorphic states is currently receiving attention in both research and commercial application,[4] and the mesogens have two especially attractive features-preoriented state and mobility. The only source of such information, as far as the photoreaction is concerned, has been firstly reported by Sackmann[5] who has studied revercible color changes in

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cholesteric phases by photochemical trans-cis isomerization of dissolved molecules such as azobenzene and stilbene. Recently, Nerbonne and Weiss[6] have reported the effects of liquid crystal solvents on the reaction rate and the product distributions for the photodimerization of acenaphthylene.

In a previous paper,[7] we have reported a preliminary study on the photochemical reaction of cholesteryl trans-cinnamate in the mesomorphic state, and the present paper gives details of the reaction: The reaction of the cinnamate was studied at various states such as the solid, liquid crystalline and isotropic liquid phases at 22–225° C in KBr matrix. Isotropic solutions of this compound in *n*-hexane or diethyl ether were used as reference systems.

The photoreaction of some derivatives of cinnamic acids has been studied[8,9] in various solvents and at the solid state, but not in the mesomorphic state. The purpose of this work is to compare the influence of the helical ordered cholesteric state and the random order of the isotropic liquid on the photoreaction.

EXPERIMENTAL

Cholesteryl trans-cinnamate was reagent grade and recrystallized repeatedly with methyl ethyl ketone or benzene as the solvent and methanol as the precipitant. A purified sample showed a single spot in the thin layer chromatogram using a mixed solvent of cyclohexane/ethyl acetate (99.5/0.5) or petroleum ether/diethyl ether/acetic acid (90/10/1) for development at 25° C. The phase transition temperatures of this purified sample were obtained by using capillary method, light microscopy and calorimetry. A mesomorphic phase between 163–216° C (162.5–215.2° C[10]) was observed in heating curves of differential scanning calorimetry (DSC), using a Perkin Elmer differential scanning calorimeter DSC-1B. The temperature of transition was determined as peak temperature of a DSC curve.

The exciting light was furnished by an irradiator composed of a 500-W xenon lamp as the light source and filters. The irradiation for the measurement of the quantum yields was performed with a JASCO CRM-FM spectroirradiator composed of a 2000-W xenon lamp as the light source and a grating monochromator. The light intensity was measured by potassium ferrioxalate actinometry,[11] and the actinometric estimates were checked with an Eppley thermopile.

To examine the photoreaction of cholesteryl trans-cinnamate, ultraviolet and infra-red absorption spectra changes of the sample were measured during reaction upon irradiation with filtered light. For this purpose, KBr pellets containing the cinnamate were prepared by pressing in an evacuated die at 13–15 kbar for 5 min. KBr pellets made of carefully dried material prepared in this way were sufficiently transparent down to 220 nm; they exhibited a low degree of scattering and at low solute concentrations apparently they obeyed the Lambert-Beer law.

Ultraviolet spectra measurements were performed with a Shimadzu UV-200 spectrophotometer equipped with a holder for KBr pellet. To attenuate the scattered light ultraviolet absorption spectra were measured by the method of an integrating sphere attached to a spectrophotometer. Infrared absorption spectra were obtained on a Hitachi EPI-G3 spectrophotometer equipped with NaCl prism.

To examine the photoreaction in solution, the cinnamate was dissolved in hexane and irradiated for four days. The solvent was evaporated on a rotary evaporator and the residue was collected as the reaction mixture for analysis. The reaction mixture was analyzed using a Shimadzu-DuPont LC-2 liquid chromatograph. The proton nuclear magnetic resonance spectra were obtained with a Hitachi Model JNM-C-60HL spectrometer at 30° C. Tetramethylsilane (1%) was used as an internal reference standard.

Cholesteryl cis-cinnamate, truxillic acid and dicholesteryl truxillate were obtained by the similar methods of Vaidya,[12] and Green and Rejtö.[13] The details of this experiment will be reported elsewhere.

RESULTS AND DISCUSSION

The ultraviolet absorption spectra of cholesteryl trans-cinnamate and representative results of photochemical experiments are shown in Figure 1. On the irradiation of the cinnamate (4.0×10^{-3}M) in *n*-hexane at a wave-length longer than 300 nm, the ultraviolet absorption maximum of the cinnamate at 275 nm decreased gradually, and finally the spectrum was changed into those similar to that of photodimers of cinnamic acids and cinnamates. Figure 1 also shows the spectral changes of the cinnamate in KBr pellets. Samples (1.45×10^{-5} mole/g) were irradiated at a wave length longer than 300 nm in the solid, mesomorphic and isotropic liquid states at the temperatures of 25, 165 and 225° C. The ultraviolet absorption spectra were changed gradually and similarly to that observed in *n*-hexane. No significant difference was found among these spectra.

Under these conditions, characteristic infrared absorption bands at 980 and 1630 cm^{-1}, which can be assigned to the out-of-plane hydrogen deformation mode of trans-alkene and to the stretching modes of the carbon-carbon double bond of olefinic hydrocarbons, respectively, decreased gradually, and then reached a constant level about one-fourth of the initial value. In Figure 2, are shown the infrared absorption spectra of cholesteryl trans-cinnamate in KBr matrix before and after irradiation for 2 hrs. The absorption band of the irradiated samples at 700 cm^{-1}, which may be assigned to the out-of-plane hydrogen deformation mode of cis-alkene, appeared gradually and reached a con-

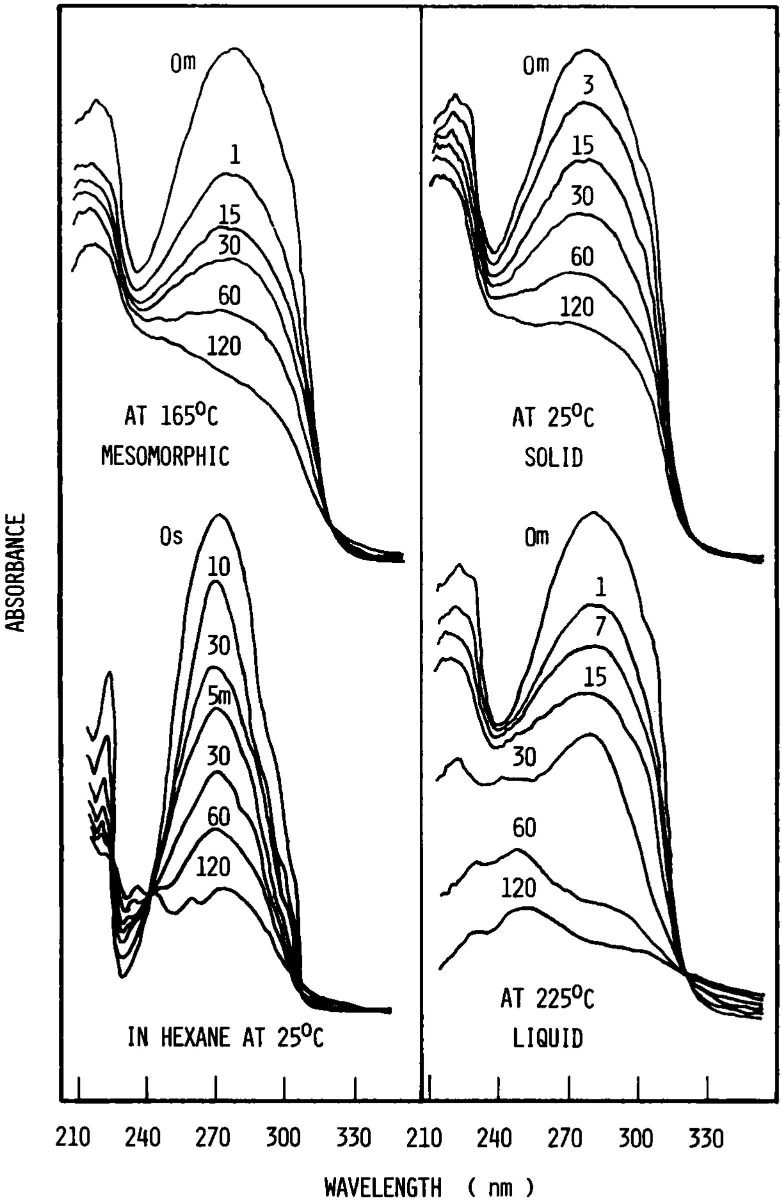

FIGURE 1 Changes in ultraviolet absorption spectra on irradiation of cholesteryl trans-cinnamate in KBr pellets at the solid, mesomorphic and liquid states, and in *n*-hexane solution. The exciting light is wavelength longer than 300 nm. The number shows the irradiation time in sec or min.

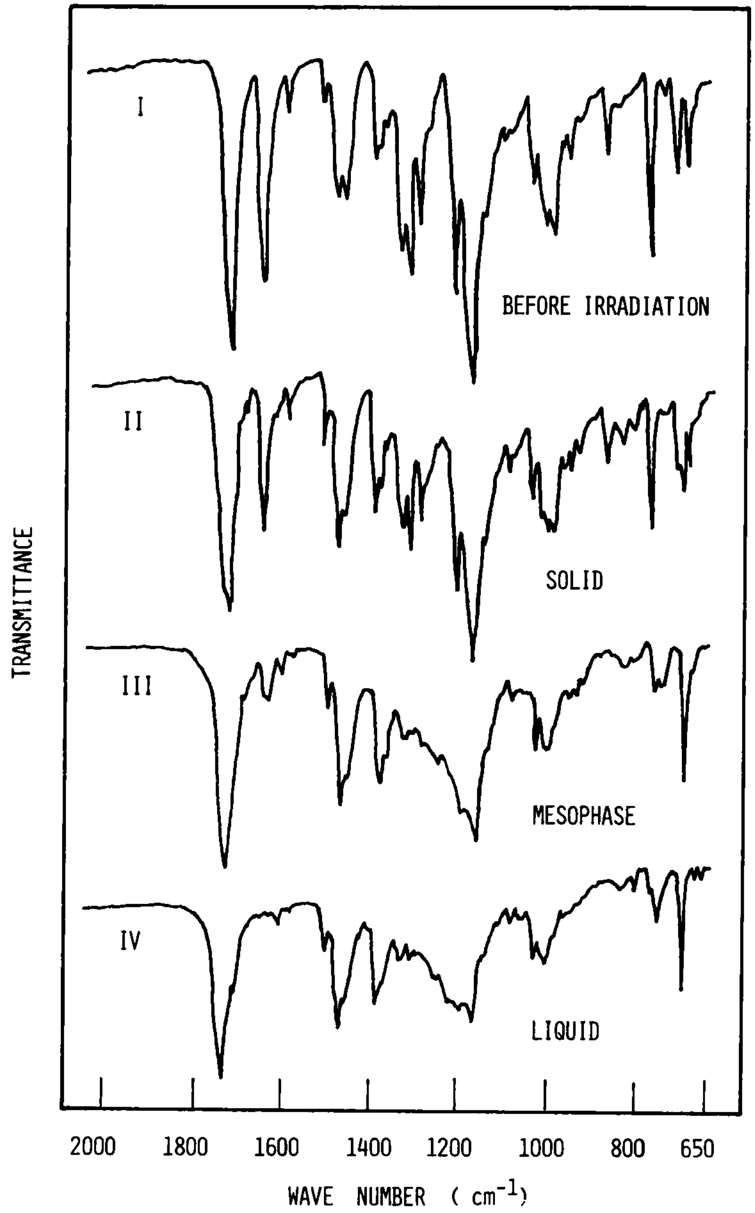

FIGURE 2 Changes in infrared absorption spectra of cholesteryl trans-cinnamate in KBr pellets on irradiation for 2 hrs at the solid, mesomorphic and liquid states. A 1.45×10^{-5} mole/g of sample was used and measured at 25°C.

stant level. These facts imply that cholesteryl trans-cinnamate in various states such as the solid, mesomorphic and isotropic liquid phases is converted mainly into a dimer on irradiation at wavelength longer than 300 nm. A small amount or a trace of cholesteryl cis-cinnamate was also found to be obtained in these states.

The crystals of the trans-cinnamate were deposited on a quartz plate in the form of a thin layer by slow evaporation from a concentrated solution in benzene and then irradiated at a wave-length longer than 300 nm with a 500-W xenon lamp. The ultraviolet absorption spectra of the irradiated sample were changed in similar manner to those of the KBr pellet at the solid phase. The reaction mixture in the thin layer after 2 hrs had also similar infrared absorption spectra to those in the KBr pellet, as shown in Figure 3.

To compare with this, the photoreaction in the isotropic solution was performed in *n*-hexane or benzene at 25–30° C using $3\text{-}4 \times 10^{-3}$ M of the trans-cinnamate, and the characteristics of the reaction mixture were examined. In the infrared absorption spectrum, shown in Figure 3, the characteristic band at 980 cm^{-1} corresponding to the out-of-plane hydrogen deformation mode of trans-alkene decreased but the bands attributable to the stretching modes of the carbon-carbon double bond of olefinic hydrocarbons were observed at 1660–1640 cm^{-1}. This suggests that the product obtained on irradiation in solutions is the cis-isomer of the cinnamate, different from those obtained in the solid, mesomorphic and liquid states. Figure 3 also shows the infrared absorption spectrum of dicholesteryl truxillate as a reference.

In Figure 4, are shown the proton nuclear magnetic resonance spectra of cholesteryl trans-cinnamate, dicholesteryl truxillate and the reaction mixtures obtained in the solid and the solution on irradiation. The spectra of the reaction mixtures show the peaks of protons attached to the trans- and cis-alkenes near 6.5–6.9, and 5.9–6.2 ppm, respectively. The peaks of protons attached to the cyclobutane ring were also found to appear near 4.2–4.4 ppm. Comparison with the spectrum of dicholesteryl truxillate suggests that the photodimers obtained in the solid and the solution are different from the truxillate, which has the peaks of protons attached to the cyclobutane ring near 3.8–4.0 ppm. The detailed study on the structure of the dimers is now in progress and will be published elsewhere.

A small amount (ca. 1 mg) of a sample was dissolved in 1–2 ml of tetrahydrofuran and 1 μl of its solution was put on the Shimadzu PCH-05 column, developing and eluting with methanol/tetrahydrofuran/water (1.5×10^{-3}M, K_2HPO_4) (76.5/8.5/15) under pressure of 110–120 kg/cm^2 at room temperature. Chromatograms were monitored at 254 nm with a flow-rate of 0.8 ml/min.cm^2 and shown in Figure 5, which shows good resolution of trans- and cis-isomers of the cinnamates, truxillic acid and dicholesteryl truxillate was

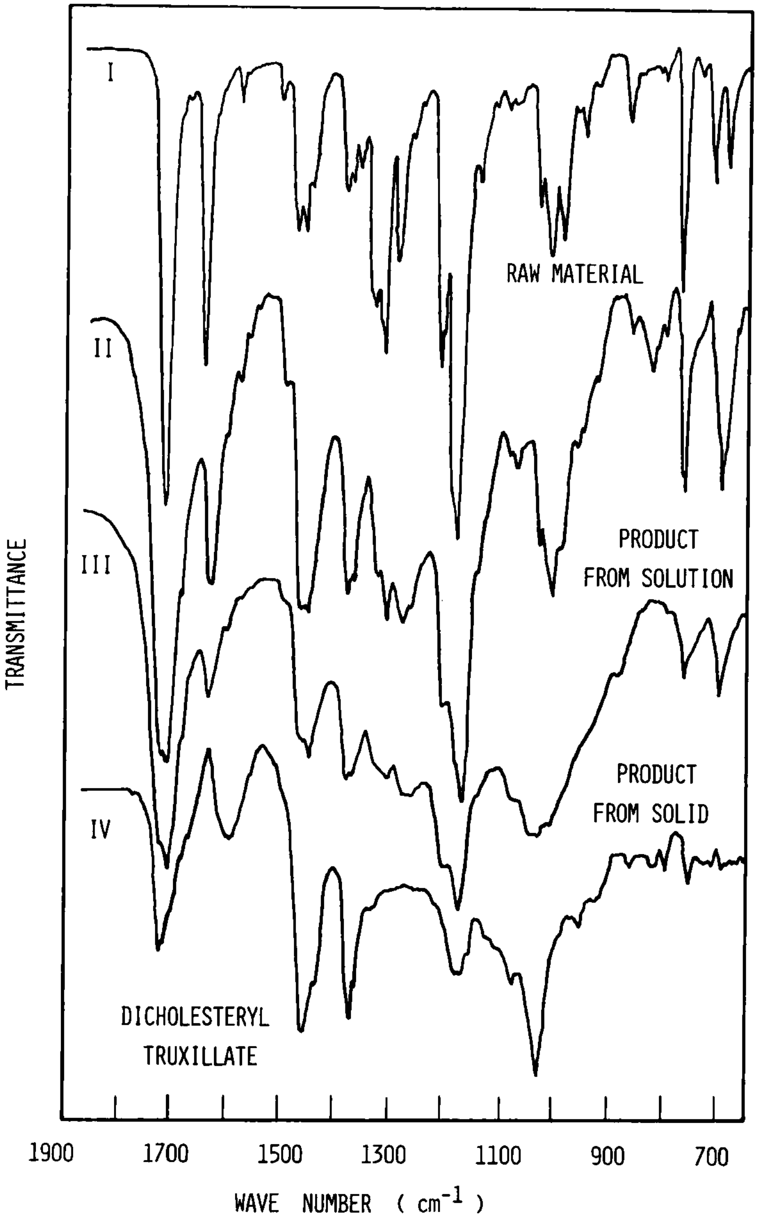

FIGURE 3 The infrared absorption spectra of cholesteryl trans-cinnamate, dicholesteryl truxillate and the reaction mixtures obtained in the solid and the solution after irradiation for four days.

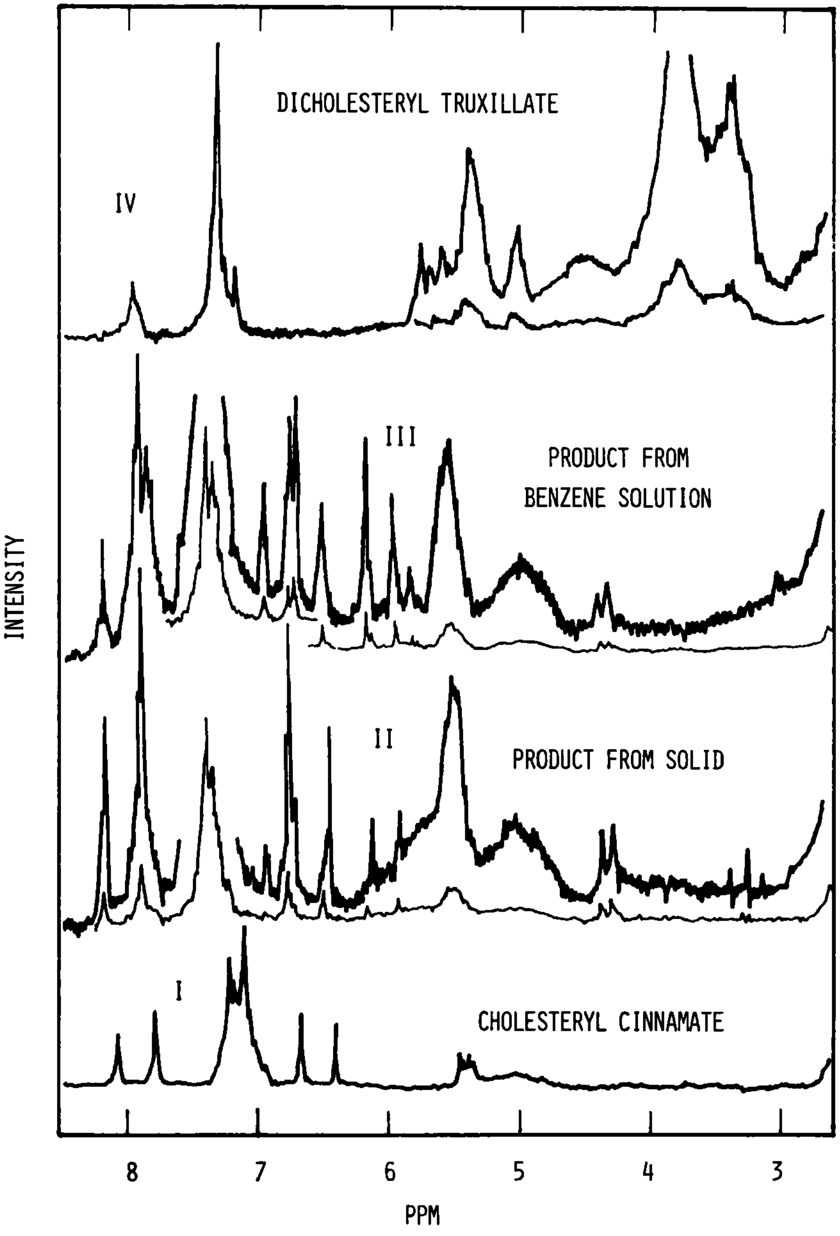

FIGURE 4 The proton nuclear magnetic resonance spectra in C_6D_6 of cholesteryl trans-cinnamate, dicholesteryl truxillate and the reaction mixtures obtained from the solid and solution in benzene after irradiation.

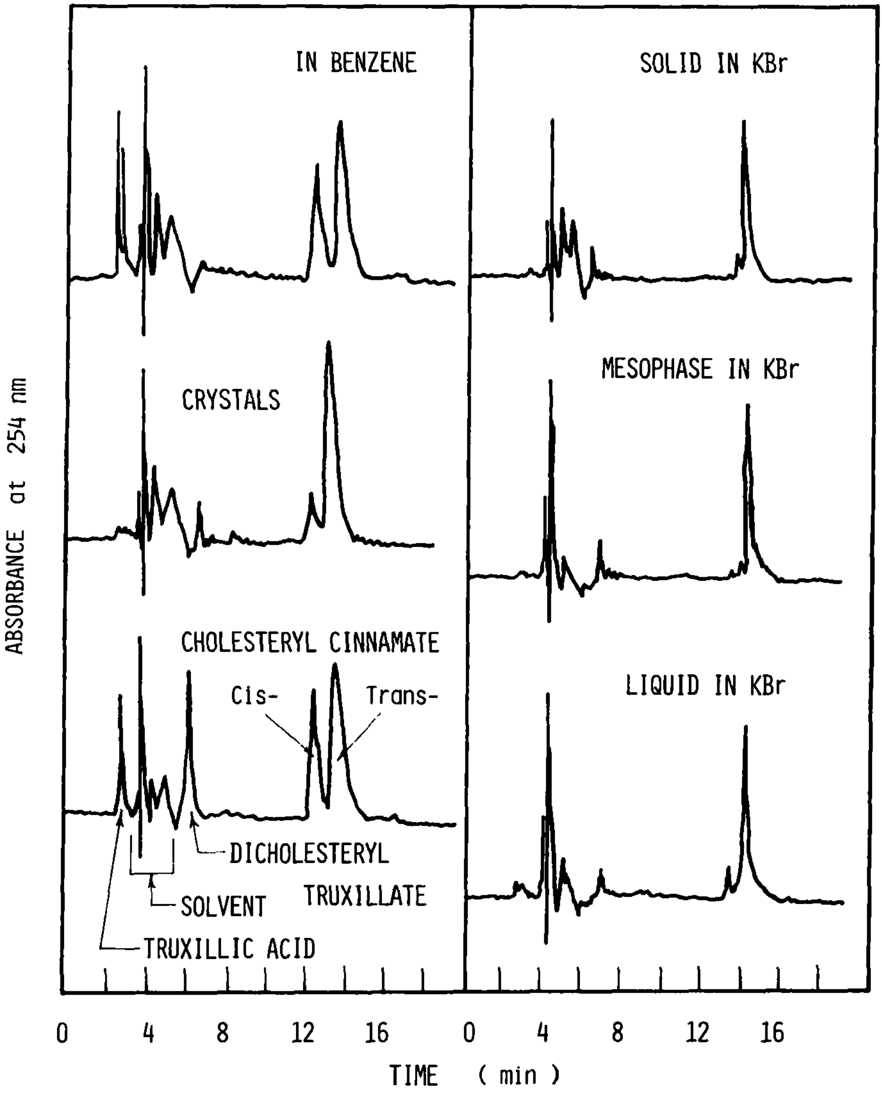

FIGURE 5 The chromatograms of cholesteryl trans- and cis-cinnamates, truxillic acid, dicholesteryl truxillate, and the irradiated samples in various phases on a Shimadzu PCH-05 column monitored at 254 nm with a flow rate of 0.8 ml/min.cm^2 under 110–120 kg/cm^2 at room temperature.

obtained. The spectra of the reaction mixtures obtained from KBr matrix have small peaks corresponding to truxillic acid, dicholesteryl truxillate, and cholesteryl cis-cinnamate besides the trans-cinnamate. Thus, cholesteryl trans-cinnamate in various states seems to be converted partly into the cis-cinnamate and mainly to a dimer or dimers on irradiation at a wavelength longer than 300 nm.

The intensities of infrared absorption spectrum of the sample in KBr matrix at 980 and 680 cm^{-1} were found to decrease in proportion to the decrease of the olefinic double bond and to the increase of the cyclobutane-ring, respectively, in the reaction system.[14] Under the same condition, the intensity of ultraviolet absorption spectrum of the sample (4.37×10^{-6} and 1.45×10^{-5} mole/g) was also found to decrease as shown in Figure 1. The results of typical kinetics of photoreaction in KBr are plotted in Figure 6, in which the relative intensity changes of 280 nm are plotted against the irradiation time. The intensity decreased gradually and then reached a constant level in all phases. The relative rate of photodimerization of the trans-cinnamate at the mesomorphic state was found to be higher than that at the isotropic liquid phase at the initial state. The photoreaction in the solid phase takes place at a much slower rate than in the other phases. This suggests that some kinds of ordering or arrangement besides the mobility of the molecules of cholesteryl trans-cinnamate enhance the rate and affect the course of the reaction in condensed states on irradiation.

The quantum yields for the dimerization of the trans-cinnamate were measured. The quantum yield, ψ, is defined by the equation:

$$\psi = -[d(\text{double bonds})/dt]/I_{\text{abs}} \tag{1}$$

where $-[d(\text{double bonds})/dt]$ is the disappearing rate of the olefinic double bond per unit of volume, and I_{abs} is the rate at which the incident light is absorbed per unit of volume of a pellet containing the sample. There are two infrared absorption bands, at 980 and 1630 cm^{-1}, attributable to the olefinic double bond. The former was used for the measurement in this work.

An infrared absorption coefficient of the trans-cinnamate was exactly determined from the calibration curve of the intensity vs the reactant concentration in a pellet. I_{abs} could not be precisely evaluated because of the ambiguity in the amount of scattered light, and should be equal to the intermediate value between two extreme ones calculated on the assumption that the scattered light is either all lost or not lost at all.[15] The extreme values are calculated as the difference between the intensity of the radiation transmitted through a pure KBr pellet (I_{KBr}) and a pellet containing the sample (I_{samp}) in the former case, and between the incident light intensity (I_0) and I_{samp} in the latter case. I_{KBr} was about 70–80% of I_0 at 280 nm under these conditions. The substitution of

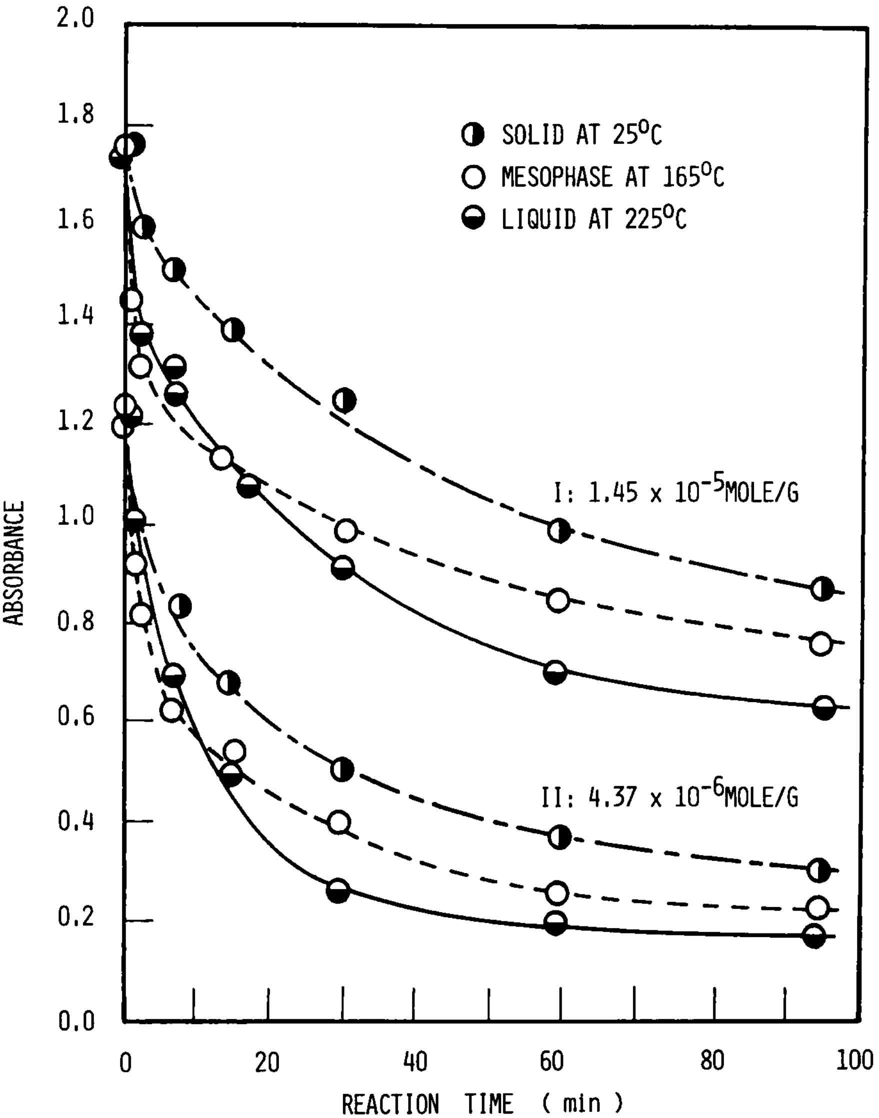

FIGURE 6 Kinetics of the photoreaction of cholesteryl trans-cinnamate in KBr irradiated at a wavelength longer than 300 nm in the solid (◑, at 25°C), mesomorphic (○, at 165°C) and liquid (◒, at 225°C). I: 1.45 × 10^{-5} mole/g, II: 4.37 × 10^{-6} mole/g. The average of the three or four measurements was used for plot.

the upper limit of I_{abs}, I_0-I_{samp}, in the denominator of Eq. 1 gives the quantum yield at the low limit, and vice versa.

The initial quantum yields for the dimerization at the lower limit are 0.2, 0.3 and 0.2 in the solid, mesomorphic and isotropic liquid states, respectively, at 280 nm. This indicates that these photoreactions all belong to one and the same type of reaction and that they do not proceed as efficiently compared with the model compounds photodimerized in the crystalline state, such as trans-cinnamic acid.[2] The true value of the quantum yield may be expected to be larger than those mentioned above. The reason for the difference between the quantum yields in cholesteryl trans-cinnamate and trans-cinnamic acid[2] could not be explained until more detailed studies on the photochemical behavior and the crystal structure of the trans-cinnamate are made.

The photoreaction of trans-cinnamic acid or trans-cinnamates is known[8,9] to yield various dimers and cis-isomer. The product distribution has been described to be state and solvent dependent.[8,9] Cholesteryl trans-cinnamate was mainly converted into a dimer in the solid, mesomorphic and liquid phases, whereas the cis-isomer in the solution. This difference in the product distribution among these phases may be described partly by concentration effects of the compound, and suggests that some kinds of ordering are enhancing the collision fraction that results in dimerization.

If association species such as ground-state complexes were suggested to be involved in the dimerization mechanism for the cinnamate, the rate and the product distribution data would require that association be much more favored in the mesomorphic than in the liquid, which may be more favorable for the aggregation than the isotropic solution. The formation of aggregates should have some effects on the dimerization: At a given concentration, the dimerization should more rapidly in the mesophase than in the liquid or in the isotropic solution; as the concentration of the cinnamate is increased, the rate of dimerization should increase more rapidly than that estimated from diffusion.

The larger initial rate in mesophase than in the liquid, and the larger amounts of the dimer obtained in the liquid than in the isotropic solution reveal that the first effect is realized. However, the data of reaction at the concentrations between 2.7×10^{-6} to 1.45×10^{-5} mole/g in KBr matrix, as shown partly in Figure 6, indicate that the second effect is not. The fraction of collisions leading to dimerization is greater than in the isotropic solution phase, but the number of collisions per unit time is lower due to the greater viscosity of the compound. The net effect may be that the distribution is similar to that in the isotropic solution. The observation, however, that the distribution of the dimer to the cis-isomer in the mesophase is greater than in the liquid, and that one in the latter is much greater than in the isotropic liquid phase indicate that the order effect is more important than the kinetic effect.

The rate data and the product distribution indicate conclusively that the order in the mesophase exerts a dramatic influence on the efficiency of dimerization, but play little or no role in determining the stereochemical course of the reaction of cholesteryl trans-cinnamate in KBr matrix. The significant effects of matrix phase described here demonstrate the tremendous potential of mesomorphic phases in elucidating reaction mechanisms and governing reaction rates.

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