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Liquid Crystals as Reaction Media. I. Photochemical Dimerization of Acenaphthylene in Cholesteric Liquid Crystal

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Synopsis. The photodimerization of acenaphthylene in liquid crystalline media exhibiting cholesteric or nematic phase was studied from the view point of the stereoselectivity of the products. In the cholesteric phase *trans*-isomer formation increased remarkably and the ratio of the *trans*-isomer to *cis*-isomer depended significantly upon the acenaphthylene concentration. These results suggest a steric effect of the cholesteric phase structure on stereoselectivity on photodimerization compared with the predominant *cis*-isomer formation in the nematic phase.

The photodimerization of acenaphthylene is known to yield both *trans*- and *cis*-stereoisomer.[1–2] Figure 1 and Table 1 show the results of the photodimerization in cholesteric, nematic liquid crystalline media and in an organic solvent. As reported recently by R. G. Weiss *et al.*[3] the quantum yield of photodimerization considerably increased in cholesteric phase media in comparison with that in nematic phase media or in benzene. The irradiation time required to attain the same degree of conversion was much shortened in the cholesteric phase media than in the nematic media or in benzene (Table 1). *cis*-Isomer formation was dominant in nematic media and in benzene, whereas in cholesteric media the *trans*-isomer formation increased significantly.

In cholesteric or nematic phase systems doped with acenaphthylene, the mesophase appears over a rather narrow concentration range of acenaphthylene, less than about 5%. More acenaphthylene destroys the mesophase structure and generates isotropic phase.

In Fig. 1-(a) it is shown that the dominant *trans*-isomer formation in the cholesteric phase media is restricted to a low concentration range of acenaphthylene. The ratio of *trans*-isomer (**1**) to *cis*-isomer (**2**) is remarkably depended upon the acenaphthylene concentration, increasing with decreasing acenaphthylene. In nematic phase media the ratio of **1** to **2** was rather constant over a wider concentration range, irrespective

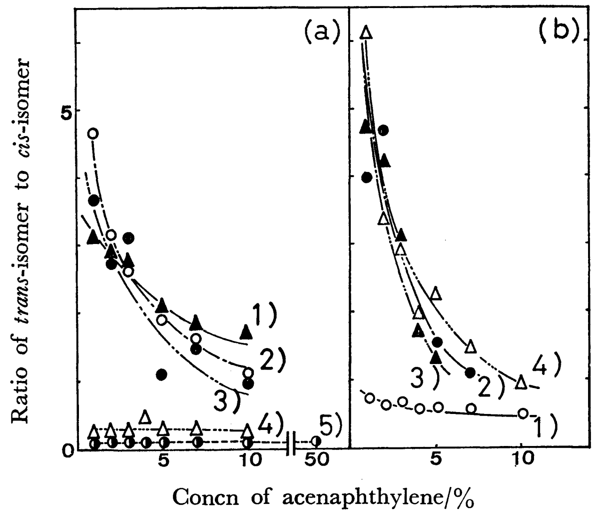

Fig. 1. The ratio of *trans*-isomer (**1**) to *cis*-isomer (**2**) *vs.* acenaphthylene concentration in photodimerization of acenaphthylene.
(a) In cholesteric, nematic liquid crystalline media and organic solvent. 1) In cholesteryl oleyl carbonate [▲], 2) in cholesteryl linolate [○], 3) in cholesteryl oleate [●], 4) In MBBA or EBBA [△], 5) in benzene [◑]. (b) in cholesteryl myristate at various temperatures. 1) at 60 °C (solid phase) [○], 2) at 70 °C (mesomorphic phase) [●], 3) at 75 °C (mesomorphic phase) [▲], 4) at 85 °C (mesomorphic phase) [△].

Table 1. The results in photodimerization of acenaphthylene in cholesteric, nematic liquid crystalline media and an organic solvent

Acenaphthylene(%) in 1 g solvent media	Not reacted Acenaphthylene (mg)	*trans*-Isomer (**1**) (mg)	*cis*-Isomer (**2**) (mg)	Ratio of (**1**)/(**2**)	Conversion of acenaphthylene %
1% in cholesteryl oleate[a)]	0.4	6.4	1.8	3.56	>96[a)]
7% in cholesteryl oleate[a)]	15.0	25.7	16.2	1.58	79[a)]
1% in cholesteryl oleyl carbonate[a)]	0.9	5.9	1.9	3.10	>90[a)]
7% in cholesteryl oleyl carbonate[a)]	30.4	23.0	12.2	1.88	57[a)]
1% in cholesteryl linolate[a)]	0.15	7.1	1.5	4.73	>98[a)]
7% in cholesteryl linolate[a)]	20.4	24.0	15.3	1.57	71[a)]
1% in EBBA[b)]	3.0	1.5	4.9	0.31	70[b)]
7% in EBBA[b)]	18.3	9.75	29.3	0.33	74[b)]
1% in benzene[c)]	7.1	0.13	0.91	0.14	29,[c)] 15,[d)] 40[e)]
7% in benzene[c)]	50.0	0.91	6.4	0.14	29[c)]

a) Irradiation was carried out in a Petri dish at 40 °C for 4 h. b) In a Petri dish at 40 °C for 24 h. c) In a Pyrex tube at room temperature for 6 h. d) For 4 h. e) For 24 h.

of the phase change of the medium.

The effect of a triplet quencher (ferrocene) on the photodimerization in cholesteric phase media was examined. In the presence of 1 w/w% ferrocene, the *trans*-isomer was scarcely detected at acenaphthylene concentrations ranging from 1 to 10 w/w %. The amount of the *cis*-isomer formed was, however, nearly the same as in the absence of ferrocene (*cis*-Isomer was formed to the extent of more than 98%.). These results indicate that the preferable *trans*-isomer formation in the cholesteric phase is to be attributed to the increase of dimerization *via* the triplet state compared to *via* the singlet state.1) The preferable formation of the *trans*-isomer with high quantum yield in the cholesteric phase implies that photodimerization *via* the triplet state is more enhanced in the cholesteric phase than that *via* the singlet state.

Generally photodimerization *via* the triplet state is more probable in dilute and highly viscous media, such as liquid crystalline media, owing to the difference of the life times of the triplet and singlet states.3,4) In nematic phase media as highly viscous as cholesteric, dependence of the ratio of **1** to **2** upon the acenaphthylene concentration was scarcely observed, *cis*-isomer formation being dominant and the enhancement of the quantum yield not being observed. Accordingly the preferance for *trans*-isomer formation and the dependence of the ratio of **1** to **2** upon acenaphthylene concentration in the cholesteric phase might scarcely be attributed to the high viscosity of the solvent media, but these results might be characteristic of photodimerization in cholesteric phase media.

The effect of tetralin, which disturbs solvent order but does not interfere electronically with the photodimerization, is shown in Table 2. The ratio of **1** to **2** diminished with increasing tetralin concentration. This effect suggests that the ordered structure of the cholesteric phase definitely affects the *trans*-isomer formation advantageously.

Table 2. The effect of tetralin addition on stereoisomeric product distribution (**1**)/(**2**) in the photodimerization of acenaphthylene in cholesteric phase media

Acenaphthylene (%) in solvent media	Tetralin (%)a)			
	No addition	5%	10%	20%
1% in cholesteryl myristate (70 °C)	5.40	3.55	2.70	3.02
1% in cholesteryl oleate (40 °C)	3.74	3.01	2.85	2.78

a) Tetralin (%) stands for percentage to the weight of solvent media. The mesophase appears at 5% concentration, whereas it raises the isotropic phase above 10% concentration of tetralin.

In cholesteryl myristate a remarkable change in the ratio of **1** to **2** was recognized between cholesteric phase regions ($T > 70$ °C) and the solid phase region (60 °C) (Fig. 1-(b)). The influence of the ordered structure of the cholesteric phase on stereoselectivity is also supported by this result.

Experimental

Materials. Commercially available acenaphthylene was recrystallized several times from methanol. The *trans*-isomer and the *cis*-isomer were isolated from the reaction mixture obtained by irradiation of acenaphthylene in benzene, by silica-gel column chromatography using cyclohexane as eluent. The mp, NMR, and UV spectra of these compounds were identical with those reported by R. Livingston.1) The mesomorphous reaction media were recrystallized before use.

Photochemical Reaction Procedures. Irradiation was carried out using a 1000 W-high pressure mercury arc lamp (TOSHIBA H 1000 L) filtered through a Toshiba cut-off glass filter UV-34. The sample solutions were irradiated in Pyrex tubes or Petri dishes without de-aeration and the reaction temperature was controlled in a thermostated oil bath with an accuracy of ±2 °C.

LC Measurement. After removal of the reaction media, high performance liquid chromatography(LC) was carried out using a WATERS ASSOCIATES ALC/GPC 204 using a 3.9 mm × 30 cm column packed with μ-Bondapack C_{18}. The mobile phase solvent was acetonitrile–water (85:15) at a flow rate of 1.0 ml/min. The detector wavelength was 254 nm. Retention times were 3.86 min for acenaphthylene, 4.90 min for the *cis*-isomer, and 7.24 min for the *trans*-isomer respectively. The ratio of **1** to **2** was determined from the ratio of the peak areas by an external standard method.

DSC Measurements. The transition temperatures for liquid crystals doped with acenaphthylene were measured by differential scanning calorimetry (Rigaku Denki DSC) and polarization microscope observation. It was confirmed that the properties of liquid crystalline reaction media underwent no change under these irradiation conditions.

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