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Kinetic Study of an Esterification by Monitoring Pitch Changes in a Cholesteric Liquid Crystal Solvent†

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To evaluate critically the importance of cholesteric ordering on the kinetics of a bimolecular reaction, a high degree of orientation must be maintained, and chiral reactants and products should be chosen which show a high helical twisting power and stability in the liquid crystal solvent. In this study, the phase can be maintained in an ordered planar texture by utilizing wall effects on a thin film sample, and the kinetics can be monitored continuously by observing the changes in pitch of the cholesteric solvent. After screening fourteen compounds, including chiral acid anhydrides, phenols and esters, appropriate soluble reactants and products with high helical twisting power were found. Esterification of *p*-(*n*-heptyloxy)phenol by (+) *p*-(2-methylbutyl) benzoic anhydride was studied in detail. The reaction rate shows no discontinuity at the transition from cholesteric to isotropic phases and the activation parameters remain unchanged ($\Delta E_a = 15.8 \pm 0.7$ Kcal mole^{-1}, $\Delta H^{\neq} = 15.1 \pm 0.7$ Kcal mole^{-1}, and $\Delta S^{\neq} = -11.5 \pm 1.5$ cal mol^{-1} deg^{-1}).

INTRODUCTION

The possibility that the orientational ordering characteristic of solutes in a liquid crystal solvent will, in some way, alter the course of a reaction has been studied extensively in the last few years. In this paper, the emphasis will be placed on the study of a simple bimolecular reaction, and the considerable controversy dealing with the presence or absence of effects of liquid crystalline phases on polymerization reactions[1] will not be dealt with.

As to the literature on uni- or bimolecular reactions, approximately equal numbers of examples exist of enhancements, reductions, or no effect on rates

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or yields of reactions in a liquid crystalline matrix. Barnett and Sohn have reported enhanced yields of the pyrolysis of xanthates in nematic solvents.[2] Recently, Nerbonne and Weiss have claimed that the quantum yield of photodimerization of acenaphthylene was 74 times higher in a cholesteric solvent than in an isotropic solvent.[3] On the other hand, Mioskowski and co-workers have reported that the rate of photodecarbonylation of a chiral ketone was reduced by a factor of more than 10 in a nematic solvent as compared with the rate in the isotropic phase.[4] It has been reported that the rate of Claisen Rearrangement of *p*-substituted allylphenyl ethers and of cinnamyl phenyl ether was not affected by the phase transition from nematic to isotropic phases.[5,6] Aviv *et al.*,[7] have reported that the photo-dimerization of tetraphenylbutatriene can be achieved in a compensated cholesteric phase, but not in the isotropic phase of the same solvent.

In order to examine critically the effect of liquid crystal solvent on a reaction, it is very important to conduct a reaction in liquid crystal solvents with strong orientational ordering. Magnetic fields can be employed for this purpose.[1,6] Another method is to carry out a reaction in thin film form between two glass plates,[4,8] utilizing wall effects to control the solvent ordering.

Recently, Park and Labes developed a method of studying reactions in liquid crystal phases in thin film form and following the kinetics continuously.[9] In this report, this new kinetic method is applied to an esterification reaction between (+) *p*-(2-methylbutyl) benzoic anhydride and *p*-(*n*-heptyloxy) phenol in the cholesteric and isotropic phases of a solvent consisting of a mixture of cholesteryl nonanoate and *p*-pentyl-2-chloro-4-(*p*-pentylbenzoyloxy)-benzoate. The esterification is a second order reaction, where the effect of orientation is expected to be much larger than in a first order reaction. These reactants (and products) were chosen because of the large differences between their helical twisting powers.

KINETIC METHOD

A cholesteric liquid crystal reflects light for which the wavelength, $\lambda_{\max}$, is related to the pitch P of the cholesteric array by Eq. (1),

$$\lambda_{\max} = \bar{n}P \tag{1}$$

where $\bar{n}$ is the average refractive index.

The pitch is perturbed by the presence of a chiral (or nonchiral) solute. The induced change of the reciprocal pitch, $\Delta(1/P)$, is given by Eq. (2),

$$\Delta\left(\frac{1}{P}\right) = \alpha \cdot \Delta C \tag{2}$$

where α is the helical twisting power[10] (or induced helical twisting power for non-chiral compounds) and ΔC is a small change of the chiral solute concentration. If these changes are produced by the following second order reaction,

$$A + B \underset{k_r}{\overset{k_f}{\rightleftarrows}} C + D$$

the overall pitch change at time t is given by Eq. (3),

$$\Delta\left(\frac{1}{P}\right)_t = \alpha^\circ \Delta C_A \tag{3}$$

where α° is the change of the helical twisting power caused by the reaction,

$$\alpha^\circ = \alpha_C + \alpha_D - \alpha_A - \alpha_B. \tag{4}$$

When $k_f \gg k_r$ and $C_{A,t=0} = C_{B,t=0} = a$, the following rate equation is obtained by assuming a negligible change of $\bar{n}$ during reaction

$$\frac{a^2}{\Delta(1/\lambda_{\max})_t} = \frac{\bar{n}}{\alpha^\circ \cdot k_f \cdot t} + \frac{a\bar{n}}{\alpha^\circ} \tag{5}$$

A successful application of this kinetic method requires the following three conditions: (1) the reaction system should have a large value of α°; (2) both reactants and products should be soluble in a cholesteric solvent; and (3) the cholesteric solvent should be stable under reaction conditions and should have a relatively sharp reflection band.

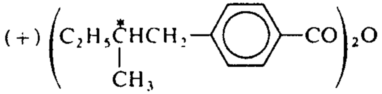
HELICAL TWISTING POWER

The values of the helical twisting power of 14 compounds shown in Table I were determined in cholesteric solvents, in order to find the most suitable reaction system for the kinetic study. Several *p*-alkoxybenzoic acids and *p*-methoxycinnamic acids were also investigated, but those compounds did not have enough solubility in the cholesteric solvents used, which were binary to quaternary mixtures of cholesteryl nonanoate (CN), cholesteryl chloride (CC), cholesteryl oleyl carbonate (COC), "Nematic-V" (a commercial eutectic mixture of *p*-methoxy-azoxybenzenes which are *p*′-substituted with ethyl and *n*-butyl groups (E. Merck and Co.)), and *p*-pentylphenyl-2-chloro-4-(*p*-pentylbenzoyloxy)-benzoate (PCPB).

Plots of $1/\lambda_{\max}$ vs. C for all compounds were linear, from the slope of which the values of $\alpha/\bar{n}$ were determined with an experimental error less than ±150 l/cm · mol. Typical results are given in Table II. The helical twisting power was sensitive to the molecular structure of both the solute molecule

TABLE I

Materials for which Helical twisting power was determined.



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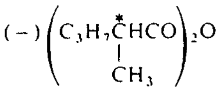
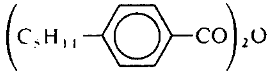


$$(-)\left(\mathrm{C_3H_7}\underset{\mathrm{CH_3}}{\overset{*}{\mathrm{C}}}\mathrm{HCO}\right)_2\mathrm{O}$$

2



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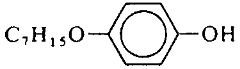

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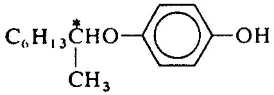
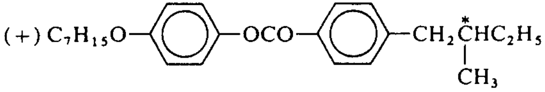


(+) **5a**
(−) **5b**



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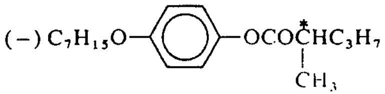

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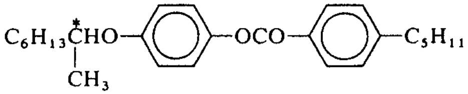
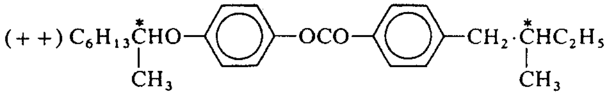


(+) **8a**
(−) **8b**



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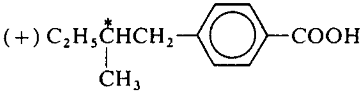

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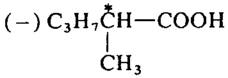

$$(-)\,\mathrm{C_3H_7}\underset{\mathrm{CH_3}}{\overset{*}{\mathrm{C}}}\mathrm{H{-}COOH}$$

11

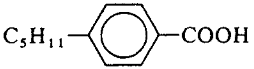

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TABLE II

$\alpha/\bar{n}$ and $\alpha^{\circ}/\bar{n}$ values of Esterification reaction systems at 50°C.

Reaction System No.	Compounds	$\alpha/\bar{n}$ or $\alpha^{\circ}/\bar{n}$[l/cm · mol]	
		Solvent A[a]	Solvent B[b]
I	1	8800	12100
	4	4300	6400
	6	12300	17000
	10	10200	16100
	($\alpha^{\circ}/\bar{n}$)	9400	14600
II	2	—	-2400
	4	—	6400
	7	—	2750
	11	—	-500
	($\alpha^{\circ}/\bar{n}$)	—	-1750
III	3	~0	550
	5a	2290	6140
	8a	5500	7580
	12	750	2200
	($\alpha^{\circ}/\bar{n}$)	3960	3090
IV	3	—	550
	5b	—	-590
	8b	—	800
	12	—	2200
	($\alpha^{\circ}/\bar{n}$)	—	3040
V	1	8800	12100
	5a	2290	6140
	9	15100	20000
	10	10200	16100
	($\alpha^{\circ}/\bar{n}$)	14200	17900

[a] CN:CC:Nematic V = 75:25:150 (weight ratio). The width of the reflection band ($\Delta\lambda$) is ~50 nm, and the temperature dependence of λ_{max} ($d\lambda_{max}/dT$) is 1.5 nm/°C.

[b] CN:PCPB = 40:60 (weight ratio); $\Delta\lambda$ = 30 nm; $d\lambda_{max}/dT$ = 1.2 nm/°C.

and the cholesteric solvent. All compounds investigated showed larger values of $\alpha/\bar{n}$ in the cholesteric solvents composed mainly of PCPB than in the solvents composed mainly of Nematic-V. All non-chiral compounds showed positive values of $\alpha/\bar{n}$. The $\alpha/\bar{n}$ values of the phenols are especially large; that is, 6400 for 4, and 2640 for the racemic mixture of 5a and 5b in solvent B (see Table II). The (+) chiral esters 6, 8a and 9 have large positive values of $\alpha/\bar{n}$, and the (−) esters 7 and 8b still have positive values. This fact suggests that $\alpha/\bar{n}$ of the non-chiral or racemic esters would also have large values. In the case of 9, two positive chiral centers in a molecule seem to act cooperatively, judging from the larger value of $\alpha/\bar{n}$ as compared to 6 and 8a. On the other hand, the (+) acid anhydride 1 has a much smaller value of $\alpha/\bar{n}$ than the (+) corresponding acid 10. From these data, the reaction systems I and V in solvent B, having large values of $\alpha^{\circ}/\bar{n}$, are possible candidates for use in kinetic studies.

KINETIC STUDY

The esterification reaction between 1 and 4 in solvent B[11] was studied over the temperature range 45–90°C by monitoring the change in pitch with time. The cholesteric-isotropic transition temperature of the solutions used (a = 0.2 mol/l) was 68°C before reaction and became higher than 80°C after reaction. Typical plots of $a^2/\Delta(1/\lambda_{max})_t$ vs. $1/t$ are shown in Figure 1 for the cholesteric phase and in Figure 2 for the isotropic phase. Linear plots were obtained up to conversions of more than 70%. From intercepts and slopes of the straight lines, the values of k and $\alpha^{\circ}/\bar{n}$ were determined with the experimental errors less than ±10%. The value of $\alpha^{\circ}/\bar{n}$ determined in this way at

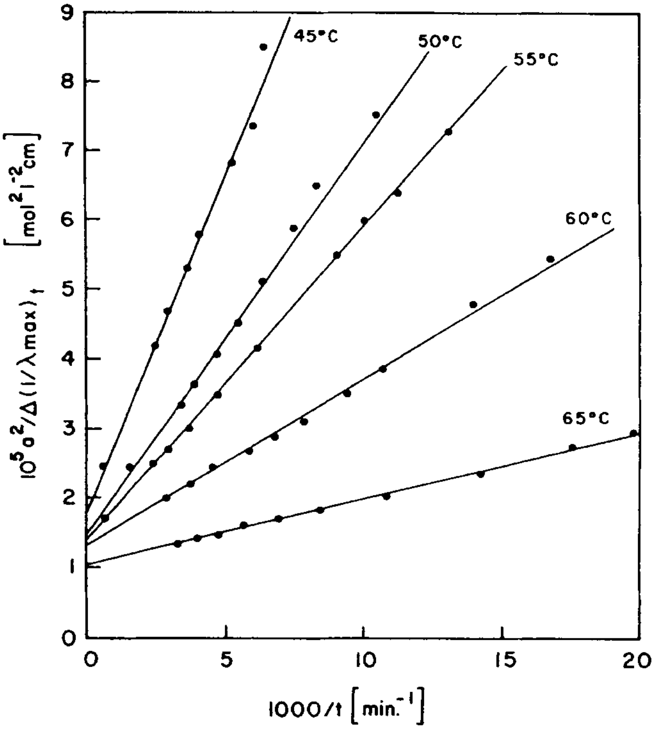

FIGURE 1 Kinetic data plotted according to Eq. (5) for the esterification reaction between 1 and 4 in the cholesteric phase. a = 0.20 mol/l.

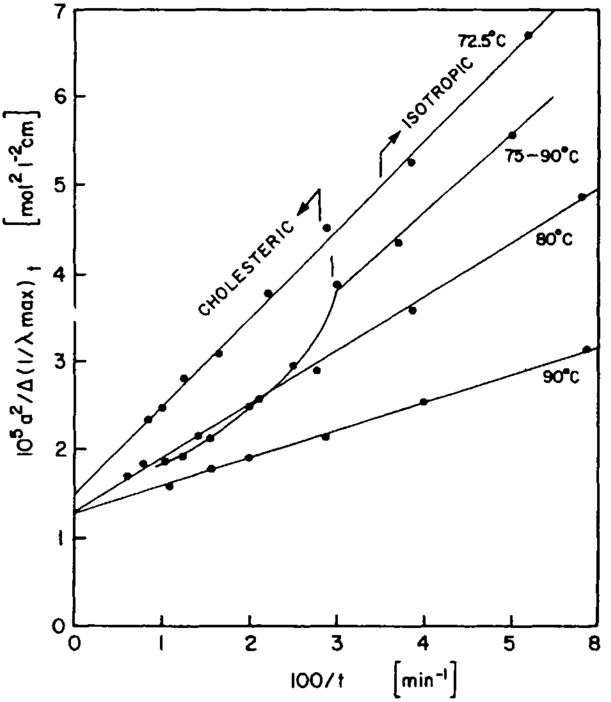

FIGURE 2 Kinetic data plotted according to Eq. (5) for the esterification reaction between 1 and 4 in the isotropic phase. a = 0.20 mol/l. See the text for descriptions of the first and second lines from the top in the figure.

50°C (13900 + 1400 l/cm · mol) was in good agreement with the value determined directly (14400 ± 100 l/cm · mol). Furthermore, the values of k and α°/n determined from these plots were constant over the initial concentration range 0.15 to 0.25 mol/l. These results indicate the validity of Eq. (5) for the esterification reaction.

Figure 2 shows that this method is also useful for kinetic study of the reaction in the isotropic phase. When the reaction was carried out at 72.5°C, the solution was isotropic during the initial reaction period, and then became cholesteric. Even in this case, a good single straight line was, however, observed in a plot of $a^2/\Delta(1/\lambda_{max})_t$ vs. 1/t, as is shown by the uppermost line in Figure 2. When the temperature was suddenly changed from 75°C to 90°C during reaction, a clear deviation from the straight line was observed, as is shown by the second line from the top in Figure 2. This deviation, of course, corresponds to an increase in the reaction rate caused by an increase in temperature. These facts indicate that there is no difference in the reaction rate between cholesteric and isotropic phases at the same temperature.

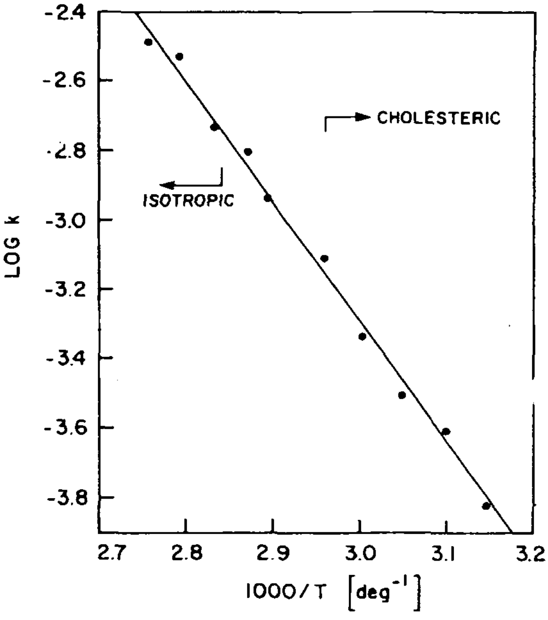

FIGURE 3 Arrhenius plot for the esterification reaction. k is expressed in units of $\text{mol}^{-1}\text{l sec}^{-1}$.

Figure 3 shows an Arrhenius plot of k for the esterification over the range 45–90°C. Each rate constant represents three to seven experimental determinations. All points are on a single straight line within the experimental error, and there is no discontinuity at the transition temperature. From the straight line, the activation energy ΔE_a, the enthalpy of activation $\Delta H^{\neq}$, and the entropy of activation $\Delta S^{\neq}$ were determined to be 15.8 ± 0.7 Kcal mol^{-1}, 15.1 ± 0.7 Kcal mol^{-1}, and -11.5 ± 1.5 cal $\text{deg}^{-1}\text{mol}^{-1}$ (at 70°C), respectively, for both phases. The orientation of both reactants and products in the cholesteric solvent was thus found to have a negligible effect on the rate and the activation parameters for the esterification reaction.

Because of the high viscosity of these solutions, one must consider the possibility that the rates are diffusion-controlled. This possibility can be eliminated because of the following facts. The k values did not depend on the initial concentration of both reactants. Further, if the reaction studied was a case of a diffusion-controlled reaction, the k value should increase as one goes through the cholesteric-isotropic transition because of a decrease in the viscosity. Lastly, the observed value of ΔE_a (15.8 ± 0.7 Kcal mol^{-1}) is too high to be attributed to a diffusion-controlled reaction, for which ΔE_a is usually less than 10 Kcal mol^{-1}.

In the thin film form in which the esterification reaction was conducted, the cholesteric phase adopts the so-called planar texture, with the helical axes perpendicular to the glass plates, and the solute molecules are well oriented with their long axes parallel to the glass wall. Let us consider the entropy changes in a bimolecular reaction between two anisotropic reactants. The hindered rotation of solute molecules in such an oriented cholesteric solution should lead to a smaller loss of entropy when they combine to form a transition complex. The entropy of activation and likewise the reaction rate would be expected to be larger in a cholesteric phase than in a corresponding isotropic phase. However, the results obtained for the esterification reaction, being a very favorable system to check this speculation, showed that the effects of orientation of this kind are negligible.

CONCLUSIONS

The rate of esterification of *p*-(*n*-heptyloxy)phenol by (+) *p*-(2-methylbutylbenzoic anhydride) shows no discontinuity at the transition from cholesteric to isotropic phase, and the activation parameters remain unchanged. Despite the reported examples of dramatic effects of liquid crystalline phases on reaction kinetics and yields, it seems to us unlikely, in light of these results on the esterification reaction, that one should expect liquid crystalline solvents to effect significantly reaction pathways. In studies where a bulk liquid crystalline solvent is used, without magnetic field or wall ordering, the effective orientational ordering is certainly reduced appreciably. Many studies have neglected careful determination of mutual solubility, and since liquid crystalline phases often reject solute molecules, concentration effects at the interface of liquid crystalline zones might explain rate enhancements or reductions. In photochemical reactions, one characteristic of the focal conic texture of cholesterics is their strong light scattering as opposed to a planar texture, and indeed absorption (and emission) of cholesteric phases can be different depending on their orientational ordering. One cannot be certain, without eliminating factors such as those just discussed, if a purported effect on a reaction rate in liquid crystals is truly due to orientational ordering. Further work on these interesting questions is underway.

EXPERIMENTAL SECTION

Acids

(+) *p*-(2-methylbutyl) benzoic acid (**10**) was prepared from (+) *p*-(2-methylbutyl) benzene (Eastman Kodak Company) by means of a reaction with oxalyl chloride and aluminum chloride,[12,13] and purified by recrystallization from *n*-hexane solution. m.p. 133.5–134.3°C. Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39; O, 16.64. Found: C, 75.03; H, 8.31; O, 16.94.

(–) 2-methylpentanoic acid (**11**) (optical purity 99%) was obtained from Norse Laboratories, Inc.

p-pentylbenzoic acid (**12**) was a commercial sample recrystallized from *n*-hexane, m.p. 87.5–88.5°C (lit. m.p. 88°C).[12]

Phenols

p-heptyloxyphenol (**4**) was a commercial sample recrystallized from *n*-hexane, m.p. 59.8–60.7°C (lit. m.p. 60°C).[14]

(+) *p*-(1-methylheptyloxy)phenol (**5a**) was prepared by means of a reaction of (–) 2-octylbromide[15] ($[\alpha]_D^{25} = -33.3°$) with hydroquinone in the presence of sodium ethoxide[16] and separated from the reaction mixture by chromatography (alumina-benzene containing 5% ethanol); yield, 35%, b.p. 143–145°C (1.5 mm Hg); $[\alpha]_D^{25} = +13°$ (benzene); ir 3350 (OH), 1220 (ether), 824 (para substitution) cm^{-1}; Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97; O, 14.39. Found: C, 75.40; H, 9.90; O, 14.43.

(–) *p*-(1-methylheptyloxy)phenol (**5b**) was prepared from (+) 2-octylbromide[13] $[\alpha]_D^{25} = -15°$ (benzene); ir the same as above; Anal. Found: C, 75.67; H, 9.74; O, 14.61.

Acid anhydrides

(+) *p*-(2-methylbutyl)benzoic anhydride (**1**) was prepared from (+) *p*-(2-methylbutyl)benzoyl chloride, which was obtained from its acid by using thionyl chloride, by the method similar to the preparation of *p*-chlorobenzoic anhydride,[17] and purified by vacuum distillation; yield, 50%; b.p. 237–239°C (1.5 mm Hg); $[\alpha]_D^{25} = +17.5°$ (benzene); ir 1780 and 1725 cm^{-1} (carbonyl); Anal. Calcd. for $C_{24}H_{30}O_3$; C, 78.65; H, 8.25; O, 13.10. Found: C, 78.62; H, 8.17; O, 13.01.

p-pentylbenzoic anhydride (**3**) was prepared by the method just described above; yield, 65%; b.p. 225–228°C (1.5 mm Hg); m.p. 33.9°C; ir 1780 and 1720 cm^{-1} (carbonyl); Anal. Calcd. for $C_{24}H_{30}O_3$: C, 78.65; H, 8.25; O, 13.10. Found: C, 78.67; H, 8.20; O, 13.03.

(–) 2-methylpentanoic anhydride (**2**) was prepared by means of a reaction between the (–) acid chloride and the sodium salt of the (–) acid; yield, 40%; b.p. 84–85°C (1.5 mm Hg); $[\alpha]_D^{25} = -18°$ (neat). ir 1802 and 1735 (carbonyl) cm^{-1}; Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.26; H, 10.35; O, 22.40. Found: C, 67.07; H, 10.38; O, 22.56.

Esters

The following esters were prepared by means of a reaction between the phenol and either the acid chloride or the acid anhydride, and purified by chromatography (silica gel-benzene).

(+) *p*-heptyloxyphenyl-*p*-(2-methylbutyl)benzoate (**6**): m.p. 25.2–26.0°C; this shows a monotropic cholesteric phase ($T_{\text{iso-cholesteric}} = +18.4$°C). $[\alpha]_D{}^{25} = +11.5°$ (benzene); ir 1742 (carbonyl) cm^{-1}. Anal. Calcd. for $C_{25}H_{34}O_3$: C, 78.49; H, 8.96; O, 12.55. Found: C, 78.65; H, 8.84; O, 12.39.

(−) *p*-heptyloxyphenyl-2-methylpentanoate (**7**): $[\alpha]_D{}^{25} = -12°$ (neat); ir 1750 (carbonyl) cm^{-1}. Anal. Calcd. for $C_{19}H_{30}O_3$: C, 74.47; H, 9.87; O, 15.66. Found: C, 74.59; H, 9.73; O, 15.84.

(+) *p*-(1-methylheptyloxy)phenyl-*p*-pentylbenzoate (**8a**): m.p. −6.6°C; $[\alpha]_D{}^{25} = +10°$ (benzene); ir 1740 (carbonyl) cm^{-1}. Anal. Calcd. for $C_{26}H_{36}O_3$: C, 78.75; H, 9.15; O, 12.10. Found: C, 78.83; H, 9.12; O, 12.13.

(−) *p*-(1-methylheptyloxy)phenyl-*p*-pentylbenzoate (**8b**): m.p. −8.5°C; $[\alpha]_D{}^{25} = -10.5°$ (benzene). Anal. Found: C, 78.91; H, 9.08; O, 12.29.

(1+, 2′+)-*p*(1-methylheptyloxy)phenyl-*p*(2′-methylbutyl) benzoate (**9**): $[\alpha]_D{}^{25} = +12.0°$ (benzene). ir 1738 (carbonyl) cm^{-1}. Anal. Calcd. for $C_{26}H_{36}O_3$: C, 78.75; H, 9.15; O, 12.10. Found: C, 78.91; H, 9.18; O, 12.05.

Liquid crystalline solvents

CN, CC, COC, and PCPB were obtained from Eastman Kodak Co. Nematic-V was obtained from EM Lab., Inc.

Kinetic measurements

The reactants were separately dissolved in a cholesteric solvent and mixed on a glass slide just before starting the reaction. A thin film of the mixture was placed between two glass plates previously rubbed with cheese cloth and the cover slide was slightly dragged over the surface of the liquid crystal, in order to achieve a planar texture of molecules.[18] The uniformity of the sample texture was checked with a polarizing microscope. A sample cell obtained in this manner was placed in a temperature-controlled brass cell holder which was mounted in a Cary 14 Spectrophotometer to measure the wavelength of minimum transmission (maximum reflection). At an appropriate time interval, the cover slide was slightly dragged as before, and the spectrum was measured.

The reaction was also carried out in the isotropic phase. In this case, we used two thermostated cell holders. One was kept at a reaction temperature and the other at 50°C to measure the spectra. After being kept at a reaction temperature for an appropriate time period, the cell was quenched quickly to the cholesteric phase in the other cell holder to measure the spectrum, and then put back in the original cell holder to continue the reaction. It took about 3 minutes to perform this operation. This quenching time was not counted in the reaction time. The same equipment was used for the measurement of the helical twisting power.

Acknowledgments

We would like to thank Dr. L. J. Yu for helpful discussions.

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11. The cholesteric solvent B was not the "best" solvent in terms of its $\alpha°/n$ value and its cholesteric temperature range. The largest value ($\alpha°/n = 16600$) of $\alpha°/n$ for reaction system I was observed for the mixture of CN, CC, COC and PCPB (90:10:40:150 weight ratio), which also showed the widest cholesteric temperature range (room temperature—95.6°C). However, in this solvent, the acid anhydride was not stable chemically at the reaction temperatures, judging from the gradual red shift of λ_{max} with time. We therefore chose cholesteric solvent B as a reaction solvent primarily because of its chemical stability with both reactants and products. In this solvent, the reaction had to be carried out at temperatures above 45°C, because of the gradual crystallization of the solution at temperatures below 40°C. Reaction system I was then selected for further study, since the kinetics could be studied over a wider temperature range (45–65°C) than system V (45–58°C).
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