the cholesteric–isotropic transition point. This finding is consistent with the change in the spectral profiles discussed above.

Conclusions on the Exciplex Formation in 9Cz-2/CMT Systems. In the CLC mixtures of 9Cz-2/2N-2/CMT, the effect of liquid crystalline order on the efficiency and the geometry of exciplex formation is remarkable, especially at low temperatures. The experimental results obtained from CD, fluorescence, and CPF spectroscopy can be summarized as in Figure 10.

In the CLC phase, carbazolyl and terephthaloyl groups are oriented as shown in the figure. Exciplex formation at low temperatures may occur without a large change of the configuration, and the electronic structure of the exciplex is not very stable. Therefore, the emission peak is shifted to shorter wavelength than that of the stable exciplex which is formed in the isotropic media. At elevated temperatures, thermal motions become active enough for the two chromophores to take the most stable exciplex configuration during the excited lifetime of the carbazolyl group (12–13 ns). For the same reason, the polarization of the exciplex emission becomes randomized at high temperatures.

Registry No. **1**, 115246-52-1; **2**, 115246-53-2; **3**, 89922-24-7; **4**, 14914-99-9; **5**, 115288-61-4; **6**, 120-61-6.

Synthesis, Structure, and Excimer Formation of Cholesteric Liquid Crystals Containing Carbazolyl Groups Covalently Linked to a Cholesterol Group

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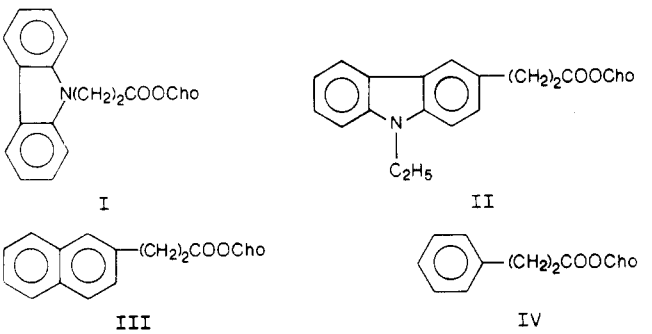
Cholesteryl 3-(9-carbazolyl)propanoate (9Cz-2) and cholesteryl 3-[3-(9-ethylcarbazolyl)]propanoate (3Cz-2) were synthesized. They did not show a cholesteric mesophase by themselves, but their 1:1 mixture with other cholesteryl arylpropanoates showed cholesteric mesophases near room temperature. The average orientations of the two types of carbazolyl groups in the quasinematic layer were determined by circular dichroism and circularly polarized fluorescence spectroscopy. Their fluorescence spectra showed a monomer fluorescence with a small contribution of excimer. The intensity ratio of the excimer to monomer fluorescence of 3Cz-2 was larger than that of 9Cz-2 and reached the minimum value at the cholesteric–isotropic transition temperature. Fluorescence decay analysis indicated that monomolecular decay processes of the carbazolyl excited state are not affected by the phase change. On the contrary, bimolecular decay processes, including excimer formation, were found to be sensitive to the phase change. Little photocurrent was observed by pulsed irradiation with a N_2 laser to the cholesteric liquid crystalline mixtures containing 9Cz-2.

Liquid crystals containing aromatic dyes have been used as electronic display devices. The basic principle of the devices is that the dye molecules are arranged along a particular direction, called a director, in the liquid crystalline mesophase, and the orientation of the director can be controlled by such external factors as electric field, magnetic field, temperature, and so on.[1] As compared with the technological development, our understanding on the elementary photochemical processes of chromophores in the liquid crystalline order is still very limited.[2-8] Weiss and co-workers[2,3] have been studying electronic interactions, such as excimer formation and exciplex formation, in cholesteric mesophases containing aromatic chromophores. In our previous report,[7] the synthesis and liquid crystalline structure of cholesteryl ω-arylalkanoates, $Ar(CH_2)_nCOOCho$ (Cho = cholesteryl group) were described. The advantages of using the covalently linked aromatic mesogens are as follows: (1) Not only the arrangement of the cholesteryl groups but also that of the aromatic groups will be highly ordered in the cholesteric liquid crystalline (CLC) mesophase. (2) The net concentration of chromophores can be increased much more than the case of a mixture of free aromatic molecules with mesogenic molecules. In this paper, the synthesis, structure, and photochemical properties of cholesteryl 3-(9-carbazolyl)propanoate (9Cz-2, I) and cholesteryl 3-[3-(9-ethylcarbazolyl)]propanoate (3Cz-2, II) will be described. Cholesteryl 2-naphthylpropanoate (2N-2, III) and phenylpropanoate (Ph-2, IV) were used as CLC solvents.



I II III IV

The carbazolyl group is a potential chromophore for photoconductivity. Chapoy, et al.[6b] observed an increase in photocurrent by mixing free carbazolyl molecules in a nematic liquid crystal up to 0.09 mol/L. In this study, static and dynamic photocurrent measurements were made on the cholesteric samples containing 9Cz-2 or 3Cz-2.

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Experimental Section

Materials. 9-(2-Cyanoethyl)carbazole (V).[9] Carbazole (8.4 g, 0.05 mol) was dispersed in acrylonitrile (12.5 mL, 0.2 mol), and 40% methanol solution of benzyltrimethylammonium hydroxide (0.1 mL) was added under cooling with ice. The mixture was refluxed on a boiling water bath for 1 h. The precipitate appearing after cooling to room temperature was collected. It was recrystallized twice from acetone to yield white needles of V: yield 85%; mp 158–159 °C (lit.[9] mp 155–156 °C). Anal. Calcd for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.71. Found: C, 81.84; H, 5.36; N, 12.79.

3-(9-Carbazolyl)propanoic Acid (VI).[10] V (3.3 g, 15 mmol) was dispersed in a 10% methanol solution of KOH (100 mL) and refluxed for 12 h. After cooling to room temperature, the mixture was poured into a 10% methanol solution of KOH (250 mL), and the insoluble part was removed by filtration. The mixture was neutralized to pH 2 with hydrochloric acid, and the precipitate that appeared was collected. It was recrystallized from acetone and from benzene twice for each solvent; yield 39%; mp 175–177 °C (lit.[10] mp 171–173 °C). Anal. Calcd for $C_{15}H_{13}O_2N$: C, 75.29; H, 5.47; N, 5.85. Found: C, 75.44; H, 5.40; N, 5.75.

Cholesteryl 3-(9-Carbazolyl)propanoate (9Cz-2, I). VI (0.36 g, 1.5 mmol) was dispersed in benzene (5 mL). Oxalyl chloride (0.5 mL) was added to the mixture, and the mixture was stirred at room temperature for 2 h. The cycle of adding oxalyl chloride (0.5 mL) and stirring for 1 h was repeated two more times. Volatile components were removed by evaporation under vacuum, and the residual solid was redissolved in benzene and treated with charcoal. Cholesterol (0.58 g, 1.5 mmol) and pyridine (0.5 mL) were added to the solution, and the mixture was stirred for 3 h at room temperature. Benzene was removed, and the residue was extracted with an ether/water mixture. The ether layer was washed with 4% $NaHCO_3$ and water and dried with Na_2SO_4 overnight. The crude crystal obtained after evaporation of ether was recrystallized twice from 1-pentanol and twice from ether/methanol to yield white needles of VI: yield 53%; mp 145–148 °C. Anal. Calcd for $C_{42}H_{57}O_2N$: C, 82.96; H, 9.47; N, 2.55. Found: C, 83.04; H, 9.61; N, 2.30.

3-[3-(9-Ethylcarbazolyl)]propenoic Acid (VII).[11] 3-(*N*-Ethylcarbazole)carboxaldehyde (10.5 g, 47 mmol, Aldrich) and malonic acid (5.0 g, 48 mmol) were dispersed in 2-methylpyridine (4.5 g, 48 mmol) and refluxed on a boiling water bath for 10 h. After the mixture cooled to room temperature, dichloromethane (200 mL) was added, and the mixture was poured into 10% NaOH aqueous solution (200 mL) with vigorous stirring. The pH of the mixture was lowered with hydrochloric acid to 2–3, and the solid substance was collected and washed with dichloromethane. Repeated recrystallizations from dioxane/methanol mixture gave light yellow crystals of VII: yield 36%; mp 227–236 °C. (lit.[11] mp 254 °C).

3-[3-(9-Ethylcarbazolyl)]propanoic Acid (VIII).[12] V (500 mg, 1.9 mmol) was dissolved in dioxane (50 mL), and palladium on activated carbon (palladium content 10%, 250 mg) was added. Under hydrogen atmosphere, the mixture was stirred for 8 h at 50 °C and for a further 20 h at room temperature. After the catalyst and the solvent were removed, the crude solid was recrystallized twice from chloroform and once from benzene to yield white plates: yield 70%; mp 177–178 °C (lit.[12] mp 172 °C). Anal. Calcd for $C_{17}H_{17}O_2N$: C, 76.37; H, 6.42; N, 5.24. Found: C, 76.73; H, 6.39; N, 5.28.

Cholesteryl 3-[3-(9-Ethylcarbazolyl)]propanoate (3Cz-2, II). The esterification of VI with cholesterol was carried out by a similar method as described for I. The crude product obtained was fractionated with a silica gel column (LiChroprep Si 60, Merck) in benzene and recrystallized from ether/methanol; yield 30%; mp 102–105 °C. Anal. Calcd for $C_{44}H_{61}O_2N$: C, 83.08; H, 9.69; N, 2.20. Found: C, 83.02; H, 9.64; N, 2.21.

Cholesteryl 1- and 2-naphthylpropanoate (1N-2 and 2N-2) and cholesteryl phenylpropanoate (Ph-2) were prepared as described previously.[7]

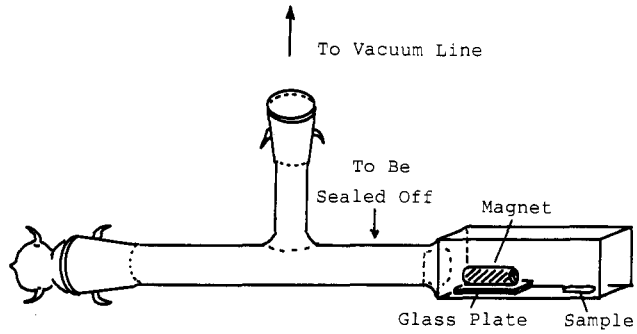

Figure 1. Optical cell for measuring fluorescence spectra and fluorescence decay curves of CLCs under vacuum.

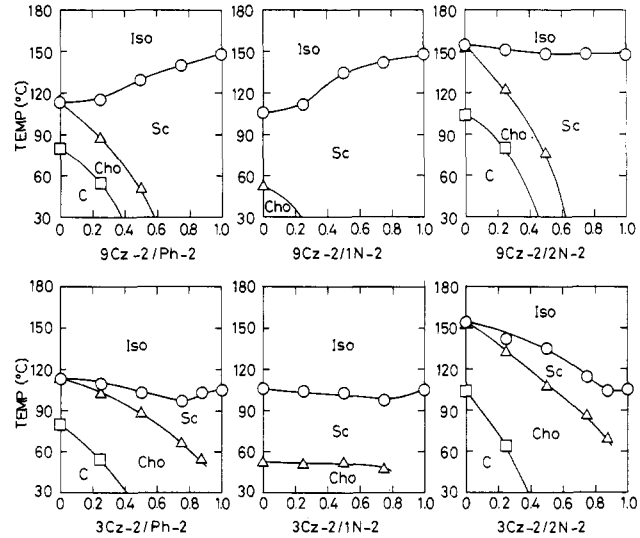

Figure 2. Phase diagrams for two-component mixtures of cholesteryl ω-arylalkanoates: Iso = isotropic liquid; Cho = cholesteric mesophase; Sc = supercooled liquid; C = crystal.

Measurements. Phase-transition points were measured on a hot plate equipped with a polarized microscope. Absorption, circular dichroic (CD), and fluorescence spectra were measured on a thin capillary film of CLCs placed between two quartz plates. The plates were rotated slightly after insertion of CLC substances to orient the helix axis of the CLCs perpendicularly to the quartz plates. The orientation of the helix axis can be confirmed by the appearance of a bright color of the selective reflection. Fluorescence decay was measured under vacuum by using an optical cell specially designed for this purpose (Figure 1). A CLC mixture and a small quartz plate on which a small magnet was fixed were inserted in the cell, the cell was connected to a vacuum line ($\sim 10^{-5}$ Torr), and the sample was outgassed by repeating a cooling–pumping–melting cycle five times. The cell was sealed off, and the small quartz plate was moved by using a magnet to hold the CLC mixture between the inner wall of the cell and the quartz plate. After the temperature was raised to a cholesteric temperature, the small plate was rotated slightly to align the helix axis of the CLC perpendicularly to the cell surface. Fluorescence decay curves were measured by irradiating the cell from a direction about 30° from the normal, and the fluorescence was detected from a direction perpendicular to the cell surface.

The following instruments were used for spectroscopic measurements: fluorescence, Hitachi MPF-4; circular dichroism, Jasco J-20; circularly polarized fluorescence, Jasco FCD-1;[8] fluorescence decay curves, a home-built time-correlated single-photon-counting apparatus (electronics, Ortec). An air discharge lamp was used as an exciting source. Several lines between 310 and 345 nm were passed through a combination of an aqueous solution of $NiSO_4$

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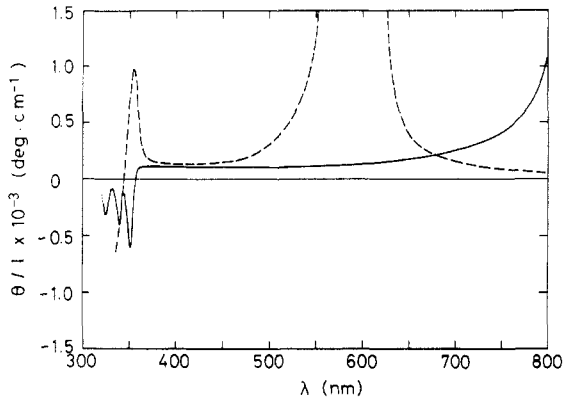

Figure 3. Circular dichroic spectra of CLC mixtures of 9Cz-2/2N-2 (50/50) at 40 °C (—) and of 3Cz-2/Ph-2 (50/50) at 60 °C (---); thickness = 12 μm.

and a band-pass filter. Monomer emission of the carbazolyl group was monitored by a combination of band-pass filters (360–390 nm). The decay curves were fitted to exponential functions by an iterative reconvolution technique.

Results and Discussion

Phase Diagram. The two carbazolyl compounds did not show a cholesteric phase by themselves. Figure 2 shows phase diagrams of mixtures of 9Cz-2 and 3Cz-2, respectively, with other cholesteryl ω-arylpropanoates. Some of the mixtures show a cholesteric mesophase near room temperature. All mixtures examined showed a monotropic phase change; that is, a cholesteric mesophase was seen only when the mixture was cooled from a molten state. In most of the following studies, equimolar mixtures of 9Cz-2 and 2N-2 and of 3Cz-2 and Ph-2 were used, because of their tractable transition temperatures. The cholesteric–isotropic temperatures of the two mixtures are 76 (9Cz-2/2N-2) and 88 °C (3Cz-2/Ph-2).

Orientation of Carbazolyl Chromophores in the Ground State. A CLC structure reflects a light whose wavelength is equal to its helical pitch multiplied by the average refractive index ($\lambda = p\bar{n}$).[13] Furthermore, a right-handed CLC reflects selectively a right circularly polarized light, and a left-handed one reflects left circularly polarized light. Figure 3 shows CD spectra of CLC mixtures of 9Cz-2/2N-2 (50/50) and 3Cz-2/Ph-2 (50/50). A very intense positive CD of the latter mixture around 560–620 nm indicates that a left circularly polarized light is selectively reflected at this wavelength. The 9Cz-2/2N-2 mixture also shows a positive shoulder at the longest wavelength limit of the spectrometer. It is concluded that the two CLC mixtures have a left-handed helix sense.

According to the optical theory of CLC, chromophores incorporated in a left-handed CLC will show a negative CD when their transition moments are oriented parallel to a molecular axis (director) of the quasinematic layer.[14] A positive CD is predicted when the moments are perpendicular to the director. It is also known that the longest absorption peak of a carbazolyl group (0–0 peak of the ^1L_b band) is parallel to the short axis of the carbazolyl group.[15] Figure 3 shows a negative peak at 352 nm for the 9Cz-2 case and a positive peak at 351 nm for the 3Cz-2 case. The same CD signs were observed in dilute CLC mixtures containing less than 3% of 9Cz-2 or 3Cz-2. The signs of the CD peaks indicate that the average orientation of the short axis of the carbazolyl group of 9Cz-2 is parallel to the molecular axis, whereas that of 3Cz-2 is perpendicular. The orientations are consistent with the molecular structures of the two compounds as shown in Figure 4. In these structures the methylene chains are assumed to take an extended structure. In our previous study, other cholesteryl ω-arylalkanoates containing 1- and 2-naphthyl, 1-pyrenyl, and 9-anthryl groups have been shown to take the same configuration

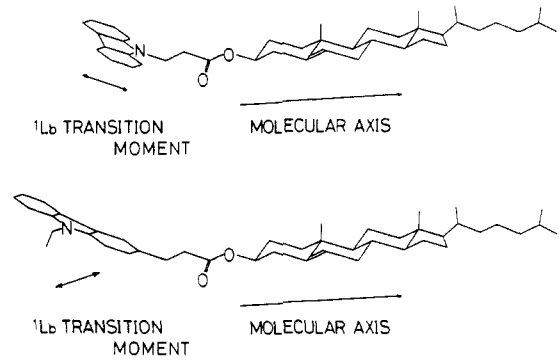

Figure 4. Probable molecular structures of 9Cz-2 and 3Cz-2 in a CLC mesophase.

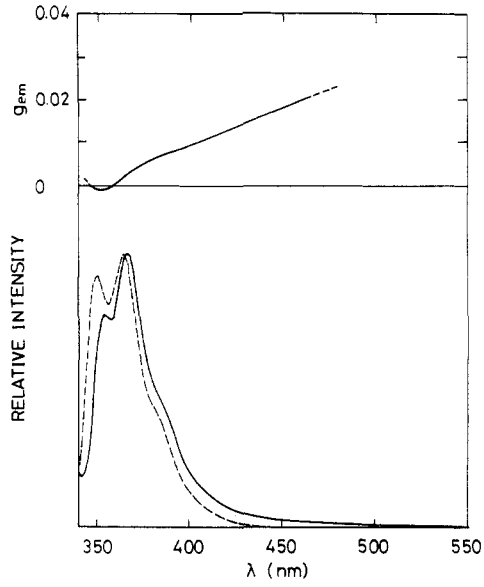

Figure 5. Fluorescence (lower curves) and CPF spectra of a 9Cz-2/2N-2 (50/50) mixture in a CLC mesophase at 40 °C (—). λ_{ex} = 338 nm for fluorescence spectrum and 330 nm for CPF spectrum. The fluorescence spectrum of a CLC mixture of 9Cz-2/Ph-4/Ph-2 (1/33/66) at 60 °C is also shown (---).

in the CLC mesophase.[7] Ceaser and Cray[16] reported that 9-ethylcarbazole dispersed in a CLC mesophase orients its long axis parallel to the molecular axis. In contrast, in the case of the carbazolyl groups covalently linked to a cholesteryl group the chromophore orientations are determined by the link positions.

Fluorescence and CPF Spectra of the 9Cz-2/2N-2 System. Figure 5 (lower curves) shows fluorescence spectra of CLC mixtures of 9Cz-2/2N-2 (50/50) and 9Cz-2/Ph-4/Ph-2 (1/33/66). The intensity of the shortest wavelength peak of the concentrated system is distorted by the self-absorption of the carbazolyl groups. Although monomer emission dominates the spectra of both the dilute and the concentrated systems, the spectrum of the concentrated system at $\lambda > 400$ nm shows a small amount of excimer emission. The second peak of the monomer emission of the concentrated system is shifted to longer wavelength (367 nm) than that of the dilute system (364 nm). However the change of the spectrum profile is not large enough to assert the presence of the second excimer, which has been found around 380 nm in polymeric systems carrying carbazole groups on their side chains.[17] The upper curve of Figure 5 shows a circularly polarized fluorescence (CPF) spectrum[18] of the concentrated mixture. The spectrum is shown with a Kuhn's emission dissymmetry factor g_{em} as an ordinate, which is defined as

$$g_{em} = 2(I_L - I_R)/(I_L + I_L) \quad (1)$$

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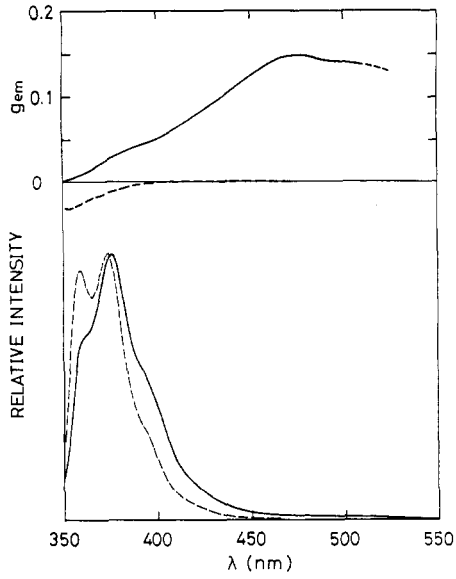

Figure 6. Fluorescence (lower) and CPF (upper) spectra of a 3Cz-2/Ph-2 (50/50) mixture in a CLC mesophase at 60 °C (—), λ_{ex} = 340 nm; fluorescence spectrum of a CLC mixture of 3Cz-2/Ph-4/Ph-2 (1/33/66) at 60 °C (---, lower); CPF spectrum of a 3Cz-2/Ph-2 (1/99) mixture in a CLC mesophase at 76 °C (---, upper).

where I_L and I_R are the intensities of left and right circularly polarized fluorescence, respectively. A very small negative CPF signal is observed around 350 nm. The absence of CPF signal for the monomer emission in a highly concentrated system has been reported also in CLC mixtures containing other aromatic chromophores and interpreted by interchromophoric interactions that mix up differently polarized vibronic states.[7,19]

The presence of an excimer emission in the concentrated system is unambiguously seen in the CPF spectrum as a strong positive signal at longer wavelengths. According to the optical theory for CPF of CLC, a left-handed CLC shows a positive CPF signal when the fluorescence is polarized perpendicular to the molecular axis.[20] The observed positive CPF signal indicates that the excimer fluorescence is polarized perpendicular to the molecular axis in a quasinematic layer. No CPF signal was detected when the mixture was in an isotropic phase.

Fluorescence and CPF Spectra of the 3Cz-2/Ph-2 System. Figure 6 shows fluorescence (lower curves) and CPF (upper curve) spectra of CLC mixtures containing 3Cz-2. A contribution of excimer emission is evident in the concentrated CLC mixture containing 3Cz-2. The upper curve of Figure 6 shows the CPF spectrum of a 3Cz-2/Ph-2 (50/50) mixture in a CLC phase. Similar to the case of 9Cz-2, little CPF signal is observed in the monomer fluorescence region, whereas a strong positive signal is seen at the excimer fluorescence region. The positive sign indicates that the excimer fluorescence is polarized perpendicularly to the molecular axis in the quasinematic layer of the CLC. Contrary to the highly concentrated system, a CLC mixture containing 1 mol % of 3Cz-2 shows no CPF signal at wavelengths longer than 400 nm. The absence of the CPF signal supports the assignment of the excimer CPF signal observed in the highly concentrated system. The negative CPF signal of the dilute system comes from the monomer fluorescence of isolated chromophores, in which no mixing of the polarization is occurring.[8]

It is noteworthy that positive CPF signals were observed for the excimer fluorescence from both 9Cz-2 and 3Cz-2 systems, although the CD signs of the two CLC mixtures were opposite to each other. These apparently opposing results fit the excimer structures shown in Figure 7. In the figures, excimers are formed within the quasinematic layer of the CLC by the rotations of the carbazolyl groups by 90°. A similar excimer structure has been

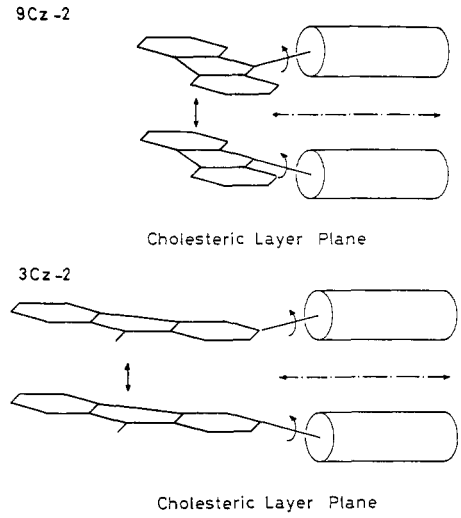

Figure 7. Probable configuration of excimers in CLC mixtures of 9Cz-2/2N-2 (50/50, top) and of 3Cz-2/Ph-2 (50/50, bottom). Note: a head-to-tail configuration is also possible.

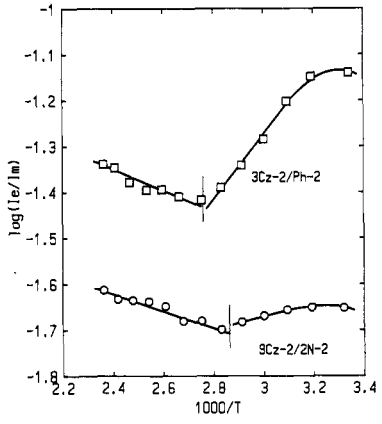

Figure 8. Arrhenius-type plot of excimer (480 nm) to monomer (367 nm for 9Cz-2 and 377 nm for 3Cz-2) intensity ratios for CLC mixtures of 9Cz-2/2N-2 (50/50) and 3Cz-2/Ph-2 (50/50).

suggested for CLCs containing cholesteryl 1- and 2-naphthylpropanoate.[7]

Figure 8 shows excimer (480 nm) to monomer (367 nm for 9Cz-2, 377 nm for 3Cz-2) intensity ratios plotted against temperature. The ratio reached the minimum value at the cholesteric–isotropic transition point. The temperature dependence of Figure 8 is opposite to those commonly observed in other excimer systems, where a maximum point has been observed.[21] The unusual profile may be interpreted by considering different situations for the isotropic and the cholesteric phases. In the cholesteric phase a maximum point of the I_e/I_m ratio seems to exist around 20–30 °C ($1/T = (3.3\text{–}3.4) \times 10^{-3}$). (Unfortunately, the fluorescence spectrum below 30 °C could not be measured, because of the start of crystallization.) Incidentally, a maximum I_e/I_m ratio has been observed at 40 °C for *meso*-dicarbazolylpentane.[22] The negative temperature dependence observed in the CLC phase is, therefore, explained by the predominance of excimer dissociation over the radiative and nonradiative decay of the excimer.

The increase of the I_e/I_m ratio with temperature in the isotropic phase may be explained in a different way. Since the arrangement of carbazolyl chromophores becomes more disordered at higher temperatures in the isotropic phase, the number of excimer-forming site (EFS) increases with temperature. The increase of the I_e/I_m ratio in the isotropic phase is explainable by the predominance of the effect of the increasing number of EFS over

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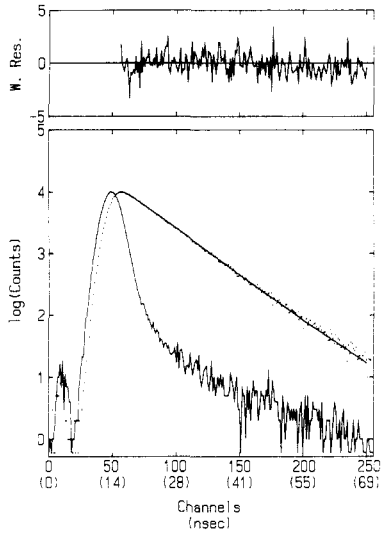

Figure 9. Fluorescence decay curve of a CLC mixture of 3Cz-2/Ph-2 (50/50) at 80 °C. The decay curve was fitted to a single-exponential function with a light scattering of the excitation pulse: $I(t) = 0.89 \exp(-t/7.79) + 1.37E(t)$; $\chi^2 = 1.14$.

the effect of the increasing rates of the excimer dissociation.

A similar discussion appears to hold for the case of 9Cz-2. However, the temperature dependence observed in the cholesteric phase is less marked. The smaller temperature dependence indicates a smaller stabilization energy of the excimer.[21] The small stabilization energy is suggested also from a smaller I_e/I_m ratio than that of the 3Cz-2/Ph-2 mixtures.

Fluorescence Decay Analysis of the 3Cz-2/Ph-2 System. Fluorescence decay curves of the monomer fluorescence of 3Cz-2/Ph-2 mixtures at different temperatures were measured. The decay curves were fitted to a single-exponential decay function with a small contribution from the light scattering of the exciting pulse, $E(t)$ (eq 2). The curve fitting was fairly reasonable in all

$$I(t) = G_1 \exp(-t/T) + G_2E(t) \qquad (2)$$

cases analyzed ($\chi^2 < 1.5$), indicating that the contribution of excimer emission is not large in the decay curve. A typical decay curve and the fitted curve are shown in Figure 9. Since the rise and decay curves for excimer emission could not be measured with sufficient accuracy, no detailed kinetic analysis will be attempted in this study.

Figure 10 shows the decay times, T, of CLC mixtures containing 50 and 1 mol % of 3Cz-2 plotted against temperature. As shown in Figure 6, the 50 mol % mixture shows an excimer fluorescence, but virtually no excimer emission is detected in the 1 mol % mixture. The decay time for the 1 mol % mixture is around 13 ns over the temperature range examined and continuous before and after the cholesteric–isotropic transition temperature, which is indicated by a vertical line. The insensitiveness of the decay time indicates that the monomolecular processes of radiative and nonradiative deactivations of the carbazolyl excited state are not affected by the phase change. Presumably, the local environments of the carbazolyl groups are not much affected by the phase change, as has been suggested by other studies on CLCs.

The decay times of the 50 mol % mixture are considerably smaller than those of the 1 mol % mixture, due to interchromophore interactions including excimer formation. The decay times are 7.7–7.9 ns in the cholesteric phase and 6.3–7.6 ns in the isotropic phase. The decay time shows a discontinuous change at the cholesteric–isotropic transition point, indicating that in contrast to the monomolecular processes, the bimolecular decay processes are considerably affected by the phase change. The temperature and the phase dependence of the decay time of the 50% mixture are consistent with the temperature dependence of the excimer/monomer intensity ratios shown in Figure 8. The increase of the I_e/I_m ratios with temperature in the isotropic phase was accounted for by a rapid increase of the number of EFS. The sharp decrease of the decay time in the isotropic phase reflects

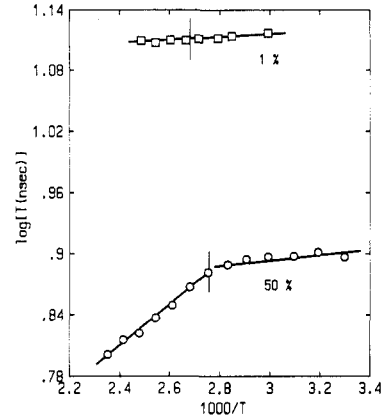

Figure 10. Arrhenius-type plot of decay times of monomer fluorescence of CLC mixtures of 3Cz-2/Ph-2 (50/50, ○) and 3Cz-2/Ph-4/Ph-2 (1/33/66, □).

the increase of bimolecular collisional processes, including excimer formation.

Decay curves of monomer fluorescence of CLC mixtures containing 9Cz-2 were also measured. The decay curves for a mixture containing 1 mol % of 9Cz-2 were fitted to single-exponential functions, and the Arrhenius plot of the decay time was straight and continuous before and after the transition point [12.5 (75 °C)–11.5 ns (148 °C)]. The decay curves for the CLC mixture containing 50 mol % of 9Cz-2 fitted neither to single exponential functions nor to two-component exponentials. The average lifetimes calculated from the decay curves were a little smaller than those of 3Cz-2 [6.5 (30 °C)–4.7 ns (111 °C)]. Although the Arrhenius plot of the average lifetime scattered considerably, no discontinuous change was seen at the cholesteric–isotropic transition point. The absence of the discontinuous change is consistent with the result of the I_e/I_m ratio shown in Figure 8, where only a small change was observed at the transition point.

Attempts to Observe Photocurrents through the CLC Cell. One of the primary purposes of this study was to develop a CLC cell that has some photoelectric properties. Chapoy et al.[6b] observed a photocurrent in a nematic liquid crystal containing 0.09 mol/L of carbazole. A sandwich cell, in which a 9Cz-2/2N-2 (50/50) mixture (carbazolyl group concentration is about 0.85 mol/L) was placed between a pair of ITO electrodes, was prepared, and a dc voltage up to 100 V was applied to the electrode. An N_2 laser pulse was irradiated on the cell, and the photocurrent was detected by an oscilloscope. A very little photocurrent was observed during the irradiation by the laser pulse (about 13 ns). However, the decay of the photocurrent after the irradiation was so fast that no quantitative discussion could be made by using the time-of-flight method. Cholesteryl methyl terephthalate and other acceptors were mixed with the 1:1 mixture to increase the carrier concentration, but again no photocurrent was observed. No photocurrent was detected by a static measurement using a xenon lamp as a light source. Impurities may not be responsible for the absence of the photocurrent in our systems, since fluorescence decay curves showed reasonable lifetimes. At present, no definite interpretation is possible for the results.

Conclusions

Cholesteryl 3-arylpropanoates carrying 9- and 3-carbazolyl groups as the aromatic group were synthesized. They showed a CLC phase when mixed with an equimolar amount of cholesteryl naphthyl- or phenylpropanoate. The orientation of carbazolyl groups in the quasinematic layer were determined as shown in Figure 4. The two carbazolyl compounds showed small excimer emissions in their CLC mesophases. CPF spectra indicated that the structures of the excimers are as shown in Figure 7. The I_e/I_m ratio was larger for the CLC mixtures containing 3Cz-2 than for those containing 9Cz-2. The stability of the excimer was higher for 3Cz-2 than for 9Cz-2. The temperature dependence of I_e/I_m ratio suggested that the number of EFS increases rapidly with

temperature above the transition point. The analysis of fluorescence decay curves of monomer emission supported the conclusions from the static spectroscopy.

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Reorientation of Tryptophan and Simple Peptides: Onset of Internal Flexibility and Comparison with Molecular Dynamics Simulation

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Absorption anisotropy decays were recorded for tryptophan and a series of dipeptides with a time resolution of less than 1 ps. Fluorescence anisotropies for tryptophan and several of its derivatives were also recorded. The data show that polar interactions retard the reorientational motion significantly. Molecular dynamics simulations of the reorientation, using SPC (single point charge) model water, give reorientation times about 4 times shorter than the experimental values. By studying fragments of the hormone ACTH, we find that internal flexibility of the peptide becomes detectable at a length of six residues, implying that the motion of longer peptides can be modeled by considering the motion of units larger than single residues.

Introduction

L-Tryptophan is an important intrinsic probe of protein and polypeptide structure and dynamics.[1-3] In particular the decay of the fluorescence anisotropy, $r(t)$, provides direct information on the internal mobility of the macromolecule. For example, we have recently used tryptophan anisotropies to investigate the flexibility of polypeptide hormones[4] and the difference in mobility of surface and buried tryptophans in the blue-copper protein azurin.[5] In the hormone study the data were discussed in terms of an analytical theory due to Perico and Guenza,[6] while the azurin results have been compared with molecular dynamics simulations.[7] In interpretation of the experimental data in terms of theory or simulation, the well-known fact[8] that the limiting anisotropy of tryptophan never reaches the value of 0.4 expected for parallel absorption and emission transition dipoles complicates the comparison at short times. In other words, with finite time resolution, if the measured value of $r(0)$ is less than 0.4, it is difficult to be certain that a rapid component in the anisotropy decay has not been missed.

There are a number of possible origins of the low initial fluorescence anisotropy of tryptophan. Perhaps the most likely possibility is the involvement of rapid interconversion between the two low-lying excited states L_a and L_b, whose transition moments make a large angle with each other.[9,10] A previous theoretical study by Cross et al.[11] showed that for incoherent coupling of the levels, the initial fluorescence anisotropy will be 0.4 regardless of the proportions of L_a and L_b excited, but the anisotropy will decay as the memory of the initial excitation distribution is lost, without the involvement of any molecular motion. In a study of solvation dynamics, using coumarin 153 as the probe, Maroncelli and Fleming[12] observed a component in the fluorescence anisotropy that decayed too rapidly to be attributed to overall motion. This fast component correlated with the Stokes shift time scale and was suggested to arise from rotation of the transition dipole in the molecular frame as solvation proceeded. The solvation time scale in water is expected to be ~0.5 ps, and thus a similar effect in tryptophan would not be resolvable in, for example, a time-correlated single-photon counting study. By contrast, a ground-state anisotropy measurement—provided the relevant motions are short compared to the excited-state lifetime—is uninfluenced by the excited-state level kinetics or by changes in the transition moment direction during solvation. Thus an absorption anisotropy measurement, carried out with a high time resolution pump–probe technique, should provide an unambiguous measure of tryptophan mobility in peptides and proteins.

In this paper we describe our first efforts in this direction: absorption anisotropy studies of tryptophan, some of its derivatives, and some dipeptides. The data were obtained by the technique of anisotropic absorption or polarization spectroscopy[13,14] with a time resolution of ~1 ps. Complementary fluorescence anisotropy measurements were carried out by using the single-photon counting technique. The presence of the charged groups $-NH_3^+$ and CO_2^- on tryptophan provides an opportunity to assess the importance of interactions between such groups and water molecules in retarding motion. We compare our data with predictions from both standard hydrodynamic models and from molecular dynamics simulations. Our new data on small peptides, when combined with a previous study of the hormone fragments, enable an estimate to be made of the onset of internal mobility, i.e., the onset of motions on a time scale shorter than the overall reorientation time, as the number of residues in the peptide increases.

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