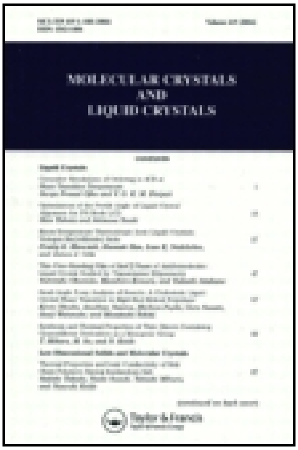

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Dependence of Helical Pitch on Composition in Mixtures of Nematic and cholesteric Liquid Crystals

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Dependence of Helical Pitch on Composition in Mixtures of Nematic and Cholesteric Liquid Crystals

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The dependence of helical pitch on composition and its phase diagram in many nematic-cholesteric mixtures was measured. It has been known about the nematic-cholesteric mixtures that the reciprocal pitch versus composition curve deviates considerably from a straight line. In this paper, the deviation is discussed in relation to the molecular structure of components and smectic thermal stability in the mixtures. It is concluded that a lateral intermolecular interaction plays an important role in the helical pitch of nematic-cholesteric mixtures.

1 INTRODUCTION

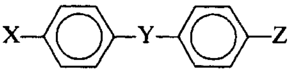
It has been known that nematic-cholesteric liquid crystal mixtures show various electro-optical effects, such as the optical storage effect,[1] which are not observable in nematic liquid crystals. Such characteristics of the mixtures depend greatly on the helical pitch, so that it is necessary to clarify the relation between the helical pitch and composition ratio.

It has been already reported that the helical pitch in the nematic-cholesteric mixtures is inversely proportional to cholesteric concentration at the low concentration,[2] and reciprocal pitch versus composition curves show a maximum value or saturation at the high concentration.[3–5] Furthermore, it has been observed that the helical pitch becomes infinite and the mixture changes into a nematic state at a particular composition in a mixture of right-handed cholesteric and nematic compounds.[6] These phenomena are physically interesting because the nematic molecules are optically inactive and do not form helical structure by themselves. But the investigation seems to have been inadequate to clarify the phenomena. Recently it has been suggested through theoretical consideration that the phenomena can be explained by considering the intermolecular interaction between nematic and cholesteric compounds.[4,7,8] However, the physical basis of the intermolecular interaction has never been explained clearly. In order to understand the physical basis, the relationship between helical pitch dependence on composition and the molecular structure of components in many mixtures should be adequately investigated.

The authors previously reported the dependence of helical pitch on composition in some mixtures and indicated that such characteristics were related to the molecular structure of components.[5] In this paper, the characteristics in many other nematic-cholesteric mixtures are shown and discussed in connection with the molecular structure of components. The relationship between the helical pitch dependence on composition and phase diagrams of the mixtures is also described.

2 EXPERIMENTS

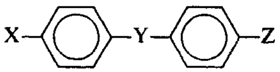
The majority of nematic compounds have general formula as follows:



In the experiments, these compounds with various terminal groups (X, Z) and central group (Y) shown in Table I were used. The cholesteric compounds used are shown in Table II. All cholesteric compounds were commercially available, some of which were purified further by recrystallization from appropriate solvents.

TABLE I

Nematic liquid crystal substance used in the experiments



Abbreviation	X	Y	Z
I. *p*-*n*-alkoxybenzylidene-*p*′-*n*-butylaniline			
[a]MBBA	CH_3O	CH=N	C_4H_9
[a]EBBA	C_2H_5O	CH=N	C_4H_9
[a]PBBA	C_3H_7O	CH=N	C_4H_9
[a]BBBA	C_4H_9O	CH=N	C_4H_9
II. *p*-*n*-alkoxybenzylidene-*p*′-aminobenzonitrile			
[a]EBAB	C_2H_5O	CH=N	C≡N
[a]BBAB	C_4H_9O	CH=N	C≡N
[a]HBAB	$C_6H_{13}O$	CH=N	C≡N
[a]DBAB	$C_{10}H_{21}O$	CH=N	C≡N

TABLE I (*continued*)

Abbreviation	X	Y	Z
III. *p*, *p*′-di(*n*-alkoxy) azoxybenzene			
[a]PAA	CH_3O	$\overset{\overset{O}{\uparrow}}{N{=}N}$	OCH_3
[b]POAB	$C_5H_{11}O$	$\overset{\overset{O}{\uparrow}}{N{=}N}$	OC_5H_{11}
VI. *p*, *p*′-di(*n*-alkyl) azoxybenzene			
[b]BAB	C_4H_9	$\overset{\overset{O}{\uparrow}}{N{=}N}$	C_4H_9
[b]HAB	C_6H_{13}	$\overset{\overset{O}{\uparrow}}{N{=}N}$	C_6H_{13}
V. *p*-*n*-alkyl-*p*′-cyanobiphenyl			
[b]PCB	C_5H_{11}	—	$C{\equiv}N$
[b]HCB	C_7H_{15}	—	$C{\equiv}N$
VI. *p*-*n*-hexyloxybenzylidene-*p*′-ethylaniline			
[a]HBEA	$C_6H_{13}O$	$CH{=}N$	C_2H_5
VII. *p*-*n*-hexyloxybenzylidene-*p*′-ethoxyaniline			
[a]HBEOA	$C_6H_{13}O$	$CH{=}N$	OC_2H_5
VIII. *p*-cyanobenzylidene-*p*′-*n*-alkylaniline			
[a]CBEA	$N{\equiv}C$	$CH{=}N$	C_2H_5
[a]CBBA	$N{\equiv}C$	$CH{=}N$	C_4H_9
IX. *p*-cyanobenzylidene-*p*′-*n*-alkoxyaniline			
[a]CBMOA	$N{\equiv}C$	$CH{=}N$	OCH_3
[a]CBEOA	$N{\equiv}C$	$CH{=}N$	OC_2H_5
X. *p*-methoxybenzylidene-*p*′-methoxyaniline			
[a]MBMOA	CH_3O	$CH{=}N$	OCH_3
XI. *p*-*n*-pentylbenzylidene-*p*′-aminobenzonitrile			
[b]PBAB	C_5H_{11}	$CH{=}N$	$C{\equiv}N$
XII. *p*-methoxy-*p*′-*n*-alkylazobenzene			
[b]MBAZB	CH_3O	$N{=}N$	C_4H_9
[b]MHAZB	CH_3O	$N{=}N$	C_6H_{13}

[a] Synthesized in our laboratory.

[b] Commercially available.

TABLE II

Cholesteric liquid crystal substance used in the experiments

$C_{27}H_{45}$—R

R	Name	Abbreviation
a) Left-handed helix type		
OCOH	Cholesteryl formate	CF
$OCOCH_3$	Cholesteryl acetate	CA
$OCOC_2H_5$	Cholesteryl propionate	CP
$OCOC_4H_9$	Cholesteryl valerate	CV
$OCOC_6H_{13}$	Cholesteryl heptanoate	CH
$OCOC_8H_{17}$	Cholesteryl nonanoate	CN
$OCOC_{11}H_{23}$	Cholesteryl laurate	CL
$OCOC_{13}H_{27}$	Cholesteryl myristate	CMy
$OCOC_{15}H_{31}$	Cholesteryl palmitate	CPa
$OCOC_{17}H_{35}$	Cholesteryl stearate	CS
b) Right-hand helix type		
Cl	Cholesteryl chloride	CC

The mixtures of these liquid crystals were sandwiched between two glass plates separated by a Mylar spacer, and the cell was placed in a sample holder in which temperature could be controlled. The helical pitch p of cholesteric phase was determined by measuring the wavelength of selective reflection $\lambda_0(= np$: n is the mean refractive index).[5] Since the mean refractive index of liquid crystals has been known to scarcely vary with the molecular structure and temperature,[9,10] the variation of λ_0 with composition and the molecular structure is due to that of the helical pitch.[3]

The phase transition temperature was determined by observing a change of the texture of liquid crystal phase by using a polarizing microscope. At the temperature of smectic-cholesteric phase transition which is discussed mainly in this paper, the change from focal conic texture (smectic phase) to Grandjean plane texture (cholesteric phase) was clearly observed.

3 EXPERIMENTAL RESULTS

3.1 Relationship of nematic compounds with the helical pitch dependence on composition

First, the effects of terminal groups of nematic molecules on the helical pitch of mixtures are described. Figures 1, 2 and 3 show the dependence of the reciprocal wavelength of selective reflection on composition (hereinafter abbreviated for simplicity as $1/\lambda_0$ vs. composition curve) in mixtures of cholesteryl propionate (CP) and nematic compounds of which one side of

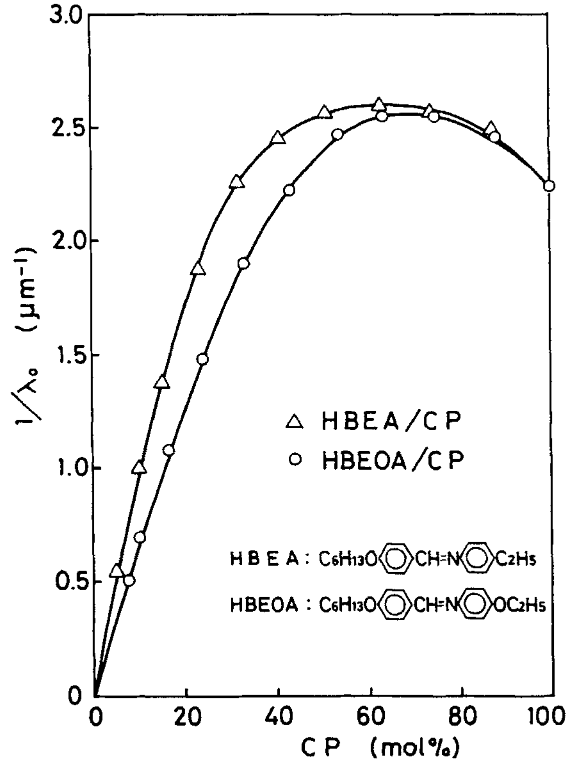
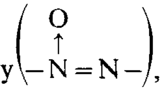


FIGURE 1 Dependence of the $1/\lambda_0$ on composition in the mixtures of nematics and cholesteryl propionate (CP)—Effects of the terminal group of nematic components on $1/\lambda_0$ vs. composition curve (I).

the terminal groups is different from each other. The measurement of λ_0 was carried out at 5°C below the cholesteric-isotropic liquid phase transition temperature for each composition. Since variation of λ_0 on temperature was rather small in such mixtures, the effect of the measuring temperature on the shape of $1/\lambda_0$ vs. composition curve was negligible. As indicated in these figures, $1/\lambda_0$ vs. composition curves deviate strongly from a straight line, and the curvature increases in the order of the terminal groups of the nematic components as cyano($-C{\equiv}N$), alkoxy($-OC_nH_{2n+1}$), alkyl($-C_nH_{2n+1}$).

Let us next describe the effects of central group of nematic molecules on $1/\lambda_0$ vs. composition curve. We studied nematic compounds of which the central group is azoxy  $\left(-\overset{\overset{O}{\uparrow}}{N}=N-\right)$, azo($-N=N-$), Schiff base ($-CH=N-$) and no substituent (biphenyl compound). Figures 4, 5 and 6 show the $1/\lambda_0$ vs. composition curves in the mixtures of CP and nematic compounds, of which

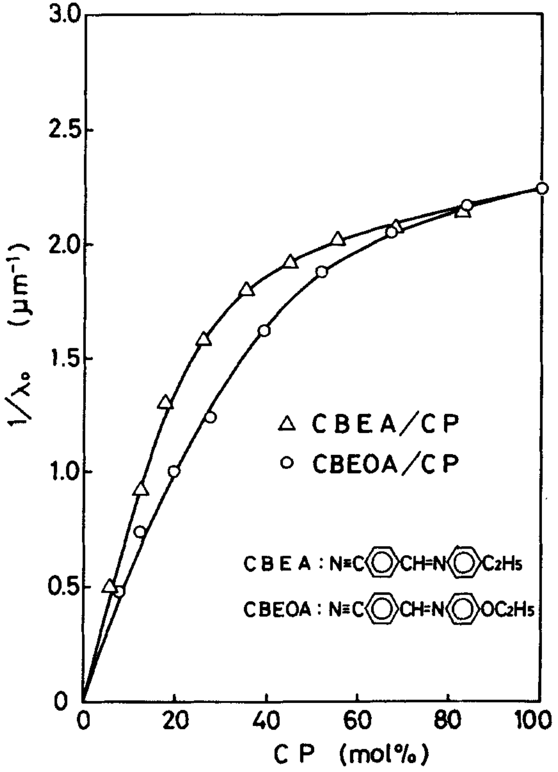


FIGURE 2 Dependence of the $1/\lambda_0$ on composition in the mixtures of nematics and CP—Effects of the terminal group of nematic components on $1/\lambda_0$ vs. composition curve (II).

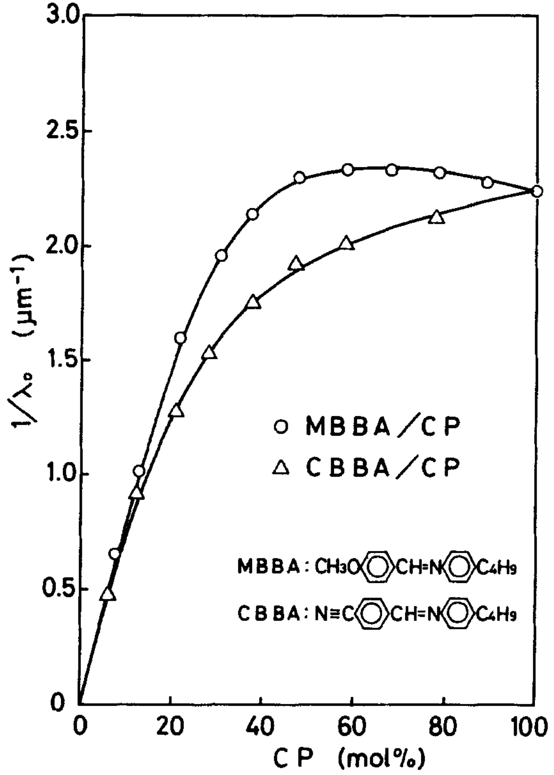


FIGURE 3 Dependence of the $1/\lambda_0$ on composition in the mixtures of nematics and CP—Effects of the terminal group of nematic components on $1/\lambda_0$ vs. composition curve (III).

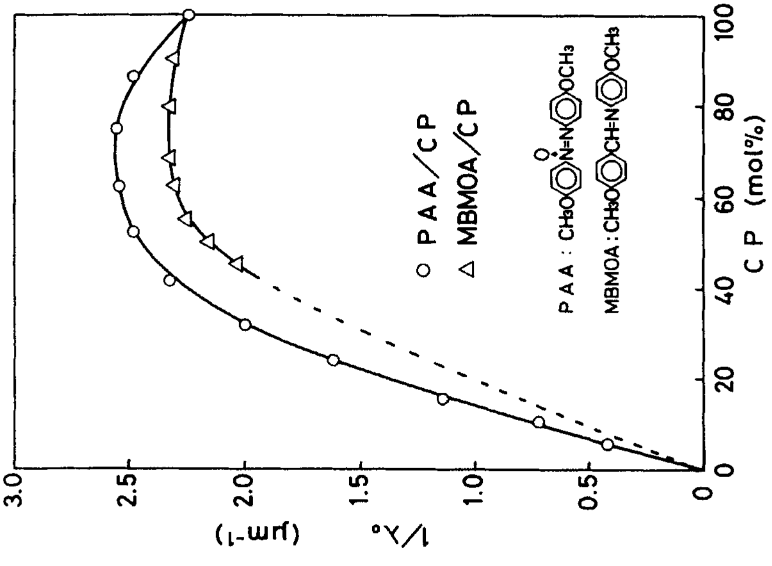


FIGURE 4 Dependence of the $1/\lambda_0$ on composition in the mixtures of nematics and CP—Effects of the central group of nematic components on $1/\lambda_0$ vs. composition curve (I).

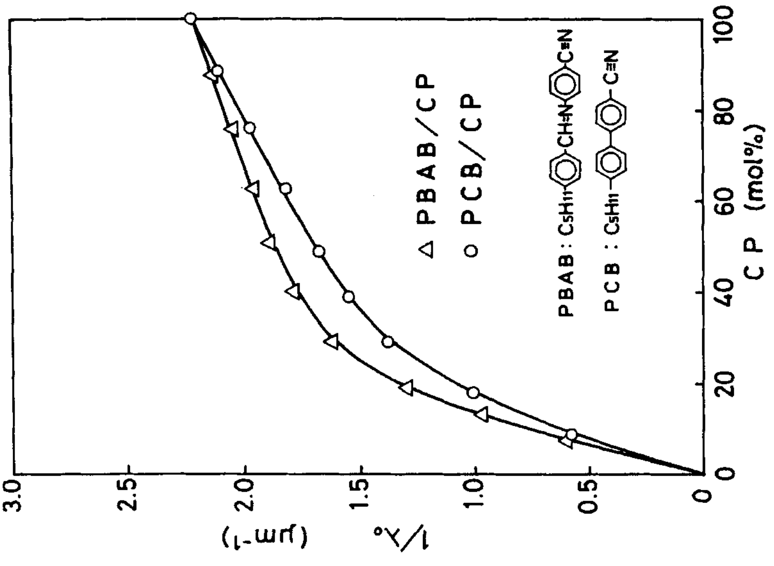


FIGURE 5 Dependence of the $1/\lambda_0$ on composition in the mixtures of nematics and CP—Effects of the central group of nematic components on $1/\lambda_0$ vs. composition curve (II).

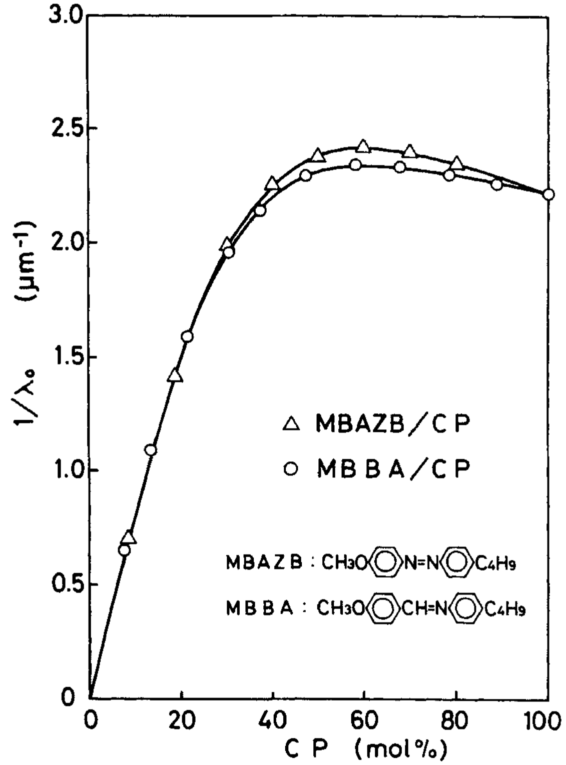


FIGURE 6 Dependence of the $1/\lambda_0$ on composition in the mixtures of nematics and CP—Effects of the central group of nematic components on $1/\lambda_0$ vs. composition curve (III).

the terminal groups are the same and the central group is different from each other. In the MBMOA-rich regions of MBMOA/CP mixtures (Figure 4), λ_0 could not be measured, since the mixed compound did not have a liquid crystal phase. It is shown from the results indicated in these figures that the curvature of $1/\lambda_0$ vs. composition curves increases in the order of the central groups as biphenyl, Schiff base, azo, azoxy.

3.2 Relationship between the helical pitch dependence on composition and the phase diagram

We classify phase diagrams of various nematic-cholesteric mixtures into three types for convenience. Typical examples of the three types are shown in Figures 7(a), (b) and (c). The feature of each type is summarized as follows:

Type a—In this mixture, the smectic-cholesteric phase transition temperature becomes higher than those of components at an intermediate

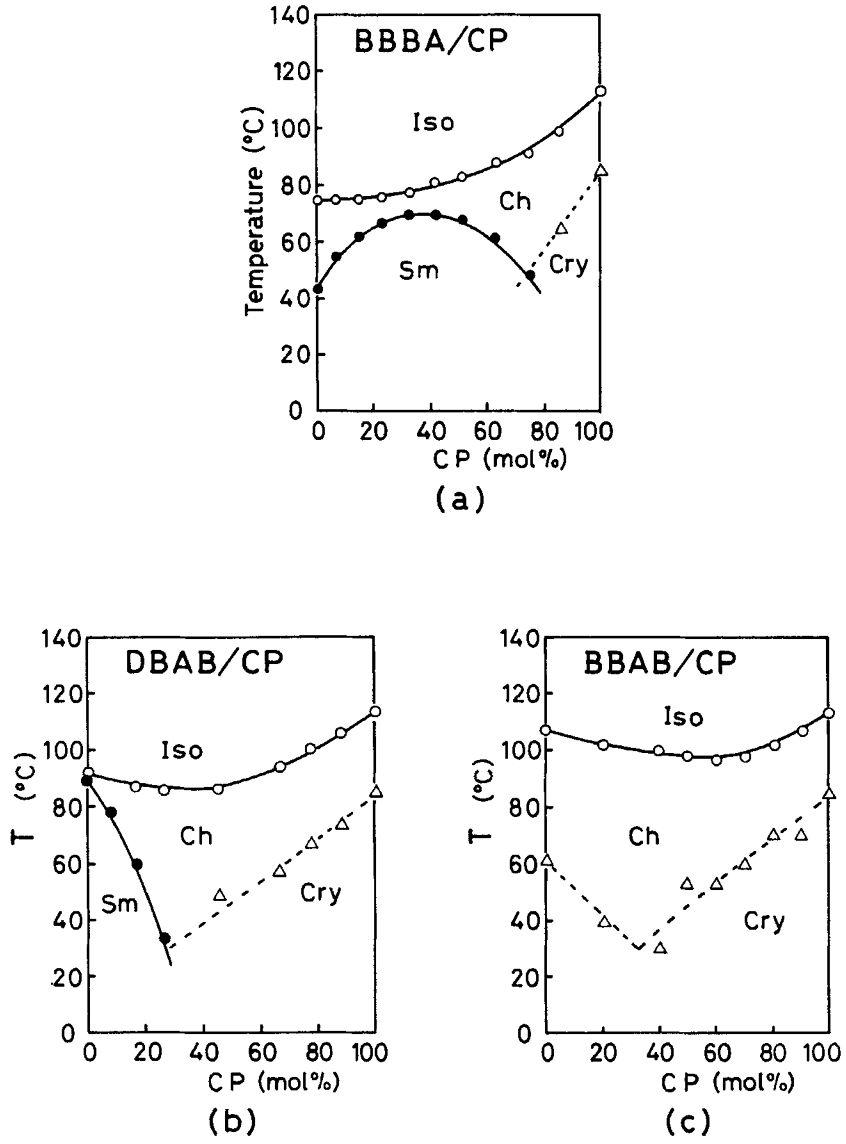


FIGURE 7 Examples of three types of the phase diagram in nematic-cholesteric mixtures: (a) BBBA/CP mixture, (b) DBAB/CP mixture, (c) BBAB/CP mixture. Iso: Isotropic liquid phase, Ch: Cholesteric liquid crystal phase, Sm: Smectic liquid crystal phase, Cry: Crystal phase.

composition and a smectic phase is observable over wide regions of composition and temperature (as shown in Figure 7(a)).

Type b—In this mixture, the smectic-cholesteric phase transition temperature becomes lower than that of a component at an intermediate composition (as shown in Figure 7(b)).

Type c—In this mixture, a smectic phase is not observable and the temperature region of the cholesteric phase is wider than those of components (as shown in Figure 7(c)).

On the other hand, for investigating the correlation between the phase diagram and the shape of the $1/\lambda_0$ vs. composition curve, we also classify the curves into three types as shown in Figure 8. The curve of Type I deviates considerably from a straight line and takes a maximum value at an appropriate composition, a typical example of which is BBBA/CP mixture. The curve of Type III does not deviate strongly from a straight line, a typical example of

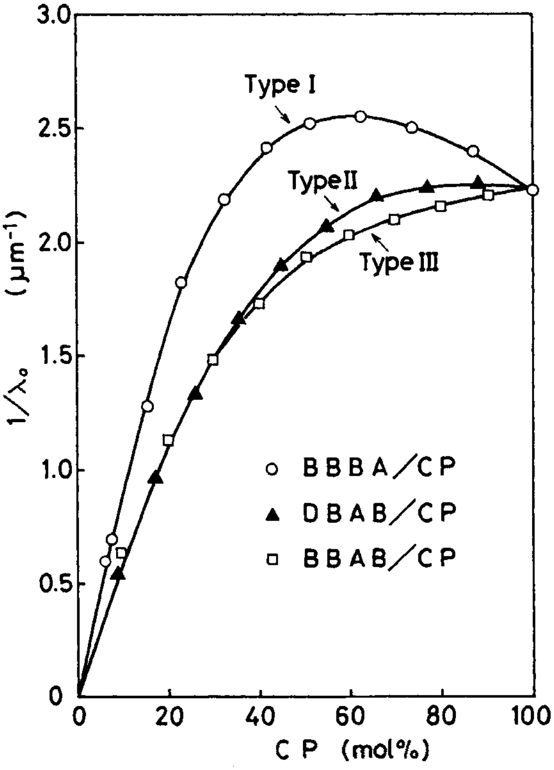


FIGURE 8 Examples of three types of the $1/\lambda_0$ vs. composition curve in nematic-cholesteric mixtures.

which is BBAB/CP mixture. The curve of Type II shows a medium curvature between those of Type I and Type III, where, at high concentrations of cholesterics, a saturation is observed, a typical example of which is DBAB/CP mixture.

Tables III, IV and V show the type of phase diagram and $1/\lambda_0$ vs. composition curve, which is classified, as mentioned above, for various nematic-cholesteric mixtures. The mixtures shown in Table III consists of nematics (EBBA, BBBA, HBAB and PCB) and various cholesteryl esters, of which the length of side chain combining with 3β-carbon site is different from one another. The mixtures shown in Tables IV and V consist of various

TABLE III

The relationship between phase diagram and $1/\lambda_0$ vs. composition curve in the mixtures of nematics and cholesteryl fatty acid ester compounds.

Nematic component	Cholesteric component		Type of phase diagram	Type of $1/\lambda_0$ curve
	n			
EBBA	0	CF	c	I
EBBA	1	CA	a/c	I
EBBA	2	CP	a	I
EBBA	8	CN	b	II
EBBA	15	CPa	b	III
BBBA	0	CF	a	I
BBBA	1	CA	a	I
BBBA	2	CP	a	I
BBBA	4	CV	a	I
BBBA	6	CH	a	II
BBBA	8	CN	a/b	II
BBBA	11	CL	b	III
BBBA	13	CMy	b	III
BBBA	15	CPa	b	III
BBBA	17	CS	b	III
HBAB	0	CF	c	I
HBAB	1	CA	c	I
HBAB	2	CP	c	II
HBAB	8	CN	b	III
HBAB	15	CPa	b	III
PCB	0	CF	c	I
PCB	1	CA	c	II
PCB	2	CP	c	III
PCB	8	CN	b	III
PCB	15	CPa	b	III

[a] Cholesteric component: $C_nH_{2n+1}OCOC_{27}H_{45}$

TABLE IV

The relationship between phase diagram and $1/\lambda_0$ vs. composition curve in the mixtures of various nematics and cholesteryl chloride. In the mixture shown the mark Ⓘ, $1/\lambda_0$ vs. composition curve deviates extremely from a straight line.

Nematic component	Cholesteric component	Type of phase diagram	Type of $1/\lambda_0$ curve
MBBA	CC	c	Ⓘ
EBBA	CC	a	Ⓘ
PBBA	CC	a	Ⓘ
BBBA	CC	a	Ⓘ
EBAB	CC	c	I
BBAB	CC	c	I
HBAB	CC	c	I
DBAB	CC	b	I
PAA	CC	c	I
POAB	CC	a	Ⓘ
BAB	CC	a	Ⓘ
HAB	CC	a	Ⓘ
PCB	CC	c	I
HCB	CC	c	I
HBEA	CC	a	Ⓘ
HBEOA	CC	a	Ⓘ
CBEA	CC	c	I
CBBA	CC	c	I
CBEOA	CC	c	I

nematics and cholesterics (CC or CP). From these tables, we can obtain the following results:

1) As shown in Table III, the shorter side chain length the cholesteric component molecules have, the more the $1/\lambda_0$ vs. composition curve shows a tendency to Type I. In particular, as shown in Table IV, all mixtures of nematics and CC with a short side chain are classified into Type I.

2) As shown in Tables III and V, a certain correlation is observed between the type of $1/\lambda_0$ vs. composition curve and the type of phase diagram in the mixtures of nematics and cholesterics with a long side chain.

TABLE V

The relationship between phase diagram and $1/\lambda_0$ vs. composition curve in the mixtures of various nematics and cholesteryl propionate.

Nematic component	Cholesteric component	Type of phase diagram	Type of $1/\lambda_0$ curve
MBBA	CP	c	I
EBBA	CP	a	I
BBBA	CP	a	I
EBAB	CP	c	III
BBAB	CP	c	III
HBAB	CP	c	III
DBAB	CP	b	II
PAA	CP	c	I
POAB	CP	a	I
BAB	CP	a	I
HAB	CP	a	I
PCB	CP	c	III
HCB	CP	c	III
HBEA	CP	a	I
HBEOA	CP	a	I
CBEA	CP	c	III
CBBA	CP	c	III
CBMOA	CP	c	III
CBEOA	CP	c	III
MBAZB	CP	c	I
MHAZB	CP	c	I

Mixtures classified into Type-a in the phase diagram tend to belong to Type I in the $1/\lambda_0$ vs. composition curve.

Though all mixtures of CC and nematics are classified into Type I in $1/\lambda_0$ vs. composition curve, the curvature of the curve is recognized to be correlated with the type of its phase diagram, as shown in Table IV and Figure 9. That is, the curvature becomes larger in the mixtures classified into Type-a than those classified into Type-b or Type-c in phase diagram.

4 DISCUSSION

As the results mentioned above, the curvature of $1/\lambda_0$ vs. composition curve in nematic-cholesteric mixtures depends on the molecular structure of the

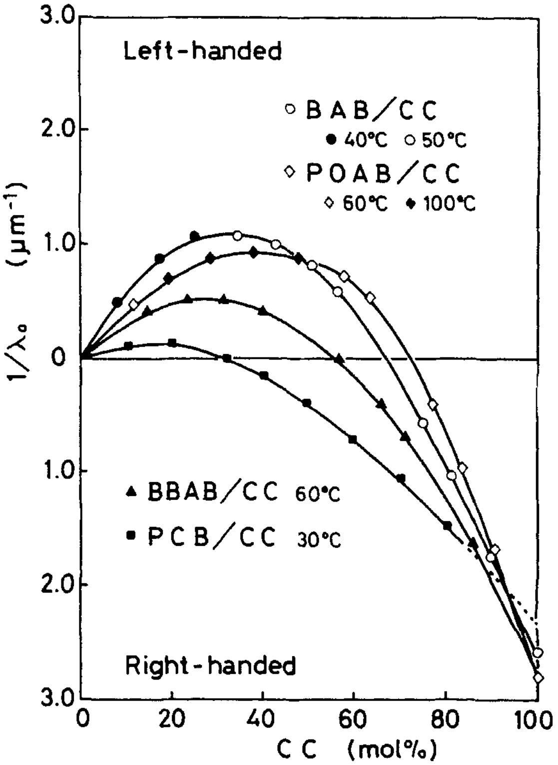


FIGURE 9 Dependence of $1/\lambda_0$ on composition in the mixtures of various nematics and cholesteryl chloride (CC).

components. Furthermore, the higher the smectic-cholesteric phase transition temperature in these mixtures than those of the components is, the more remarkably the curvature is. In this section, such a correlation is discussed in detail.

The properties of liquid crystals in connection with the molecular structure, for example, the strength of intermolecular interaction, have been discussed from the thermal stability of a smectic phase and the value of liquid crystal-isotropic liquid phase transition temperature (T_i).[11] That is, the appearance of smectic phase is considered to indicate that the lateral intermolecular interaction is much stronger than the terminal interaction, and the value of T_i is considered to indicate the whole strength of the lateral and terminal intermolecular interactions.

Concerning nematic compounds such as used in our experiments, the relation between the molecular structure and the thermal stability of smectic phase is concluded from the data given in references as follows. The smectic thermal stability increases in the order of the terminal groups as cyano, alkoxy, alkyl.[12,13] The smectic thermal stability of azoxy compounds is higher than that of azo or Schiff base compounds in relation to the central group.[14,15] Furthermore, the smectic thermal stability of biphenyl compounds is almost the same degree as that of Schiff base compounds.[13,16] On the other hand, concerning the relation between the molecular structure of nematic compounds and the temperature T_i, the value of T_i shows a tendency to increase in the order of biphenyl, Schiff base, azo, azoxy compounds.[13,14,16]

It is seen from the above discussions that the lateral intermolecular interaction of nematic compounds increases in the order of the terminal groups as cyano, alkoxy, alkyl, and in the order of the central groups as biphenyl, Schiff base, azo, azoxy. By comparing such an order of the strength of the lateral intermolecular interaction with an order of the curvature of $1/\lambda_0$ vs. composition curve, as mentioned in Section 3.1, it is seen that the both results coincide with each other. Therefore, it is concluded that the stronger the lateral intermolecular interaction is, the more remarkably the curvature of $1/\lambda_0$ vs. composition curve is.

As described in Section 3.2, this curvature is closely related to the thermal stability of smectic phase in the mixtures. The relation is consistent with the concept of the important role of lateral intermolecular interactions in the specific dependence of helical pitch on composition.

Recently the specific dependence of helical pitch in nematic-cholesteric mixtures has been studied theoretically by many workers.[4,7,8] They suggest that an intermolecular interaction seems to be an important factor to explain the helical pitch dependence on composition. Our experimental results also prove that their suggestions hold good.

5 CONCLUSION

We observed the dependence of the selective reflection wavelength $\lambda_0(=np)$ on composition in many nematic-cholesteric mixtures and discussed the characteristics in relation to the molecular structure of components. Furthermore, we investigated the correlation between the λ_0 dependence on composition and phase diagram in the mixtures. It is concluded from these investigations that the specific dependence of helical pitch on composition in nematic-cholesteric mixtures is closely related to the lateral intermolecular interaction.

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References

1. G. H. Heilmeier and J. E. Goldmacher, *Appl. Phys. Lett.*, **13**, 132 (1968).
2. R. Cano and P. Chatelain, *C.R. Acad. Sci. Paris*, **253B**, 1815 (1961).
3. T. Nakagiri, H. Kodama, and K. K. Kobayashi, *Phys. Rev. Lett.*, **27**, 564 (1971).
4. H. Stegemeyer and H. Finkelmann, *Chem. Phys. Lett.*, **23**, 227 (1973).
5. H. Kozawaguchi and M. Wada, *Japan. J. appl. Phys.*, **14**, 651 (1975).
6. F. D. Saeva and J. J. Wysocki, *J. Amer. Chem. Soc.*, **93**, 5928 (1971).
7. J. M. Pochan and D. D. Hinman, *J. phys. Chem.*, **78**, 1206 (1974).
8. H. Hanson, A. J. Dekker, and F. van der Woude, *J. chem. Phys.*, **62**, 1941 (1975).
9. V. G. Rumyantsev, P. D. Berezin, L. M. Blinov, and I. N. Kompanets, *Sov. Phys. Crystallogr.*, **18**, 697 (1974).
10. W. U. Müller and H. Stegemeyer, *Ber. Bunsenges. phys. Chem.*, **77**, 20 (1973).
11. G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals" (Acad. Press, London 1962).
12. K. Murase, Kenkyu Jitsuyoka Hokoku (E.C.L. Tech. Jour.) NTT, Japan, **21**, 1159 (1972) (in Japanese).
13. J. Billard, J. C. Dubois, and A. Zann, *J. Physique*, **36**, CI-355 (1975).
14. J. van der Veen, W. H. Jeu, A. H. Grobben and J. Boven, *Mol. Cryst. and Liq. Cryst.*, **17**, 291 (1972).
15. J. S. Dave and P. R. Patel, *Mol. Cryst.*, **2**, 103 (1966).
16. G. W. Gray, *J. Physique*, **36**, CI-337 (1975).