Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

New cholesteric liquid crystals induced by intermolecular hydrogen bonding

Yanqing Tian; Xiaohe Xu; Yingying Zhao; Xinyi Tang; Tiejin Li

To cite this Article Tian, Yanqing , Xu, Xiaohe , Zhao, Yingying , Tang, Xinyi and Li, Tiejin(1997) 'New cholesteric liquid crystals induced by intermolecular hydrogen bonding', Liquid Crystals, 22: 1, 87 — 96

To link to this Article: DOI: 10.1080/026782997209711

URL: http://dx.doi.org/10.1080/026782997209711

LIQUID CRYSTALS, 1997, VOL. 22, NO. 1, 87–96

New cholesteric liquid crystals induced by intermolecular hydrogen bonding

by YANQING TIAN*, XIAOHE XU, YINGYING ZHAO, XINYI TANG
and TIEJIN LI

Department of Chemistry, Jilin University, Changchun 130023, China

(Received 8 June 1996; accepted 14 August 1996)

New cholesteric liquid crystals induced by intermolecular hydrogen bonding between 3-cholesteryloxycarbonylpropanoic acid (MCB) and 4-(4-alkoxybenzoyloxy)-4′-stilbazoles (*n*SZ); between MCB and *N*-(4-pyridylmethylidiene)anilines (*n*-PMA) were prepared. Their liquid crystalline properties were investigated by DSC, polarized optical microscopy and X-ray diffraction. Cholesteric and smectic phases were observed. In order to study the influence of covalent and non-covalent bonding upon the liquid crystal behaviour several new covalently bonded *N*-[4-(3-cholesteryloxycarbonylpropionyloxy)benzylidiene]-4-alkoxy anilines were investigated.

1. Introduction

Since Kato *et al.* [1] synthesized a new liquid crystal induced by intermolecular hydrogen bonds between a substituted pyridine (proton acceptor) and a carboxylic acid (proton donor) in 1989, many liquid crystals including molecular liquid crystals, main chain liquid crystalline polymers, side chain polymer liquid crystals, and ferroelectric liquid crystals have been prepared successfully using the intermolecular hydrogen bond [1–18], because the hydrogen bonding is one of the power tools for assembling molecules and building organized molecular structures [19]. However, there are relatively few reports on chiral liquid crystals synthesized by using intermolecular hydrogen bonding [8–10, 18], and to our knowledge, no liquid crystals containing cholesteryl groups have been prepared in such a way. The aim of this work was to synthesize new cholesteric liquid crystals by choosing 3-cholesteryloxycarbonylpropanoic acid (MCB) as the proton donor and the easily prepared 4-(4-alkoxybenzoyloxy)-4′-stilbazoles (*n*SZ) and *N*-(4-pyridylmethylidiene)anilines (*n*-PMA) as the proton acceptors (see schemes 1 and 2) and study their phase transitions by DSC, polarized optical microscopy and X-ray diffraction. The results show that all of these complexes are cholesteric liquid crystals. In order to investigate the influence of covalent and non-covalent bonds upon the liquid crystalline behaviour, three new covalently bonded *N*-[4-(3-cholesteryloxycarbonylpropionyloxy)benzylidiene]-4-alkoxyanilines were prepared. We found that the phase transition temperatures for the three covalently bonded liquid crystals are higher than those of the analogous intermolecular hydrogen bonded complexes.

2. Results and discussion

2.1. *Synthesis*

The liquid crystals investigated in this paper were prepared according to schemes 1, 2 and 3.

The proton acceptors *n*SZ were purified by recrystallization from ethanol then cyclohexane and exhibited nematic and smectic phases. The proton acceptors *n*-PMA were not mesogenic, but all of the complexes induced by intermolecular hydrogen bond exhibited cholesteric and smectic phases. The liquid crystal transition temperatures are given in tables 1, 2 and 3.

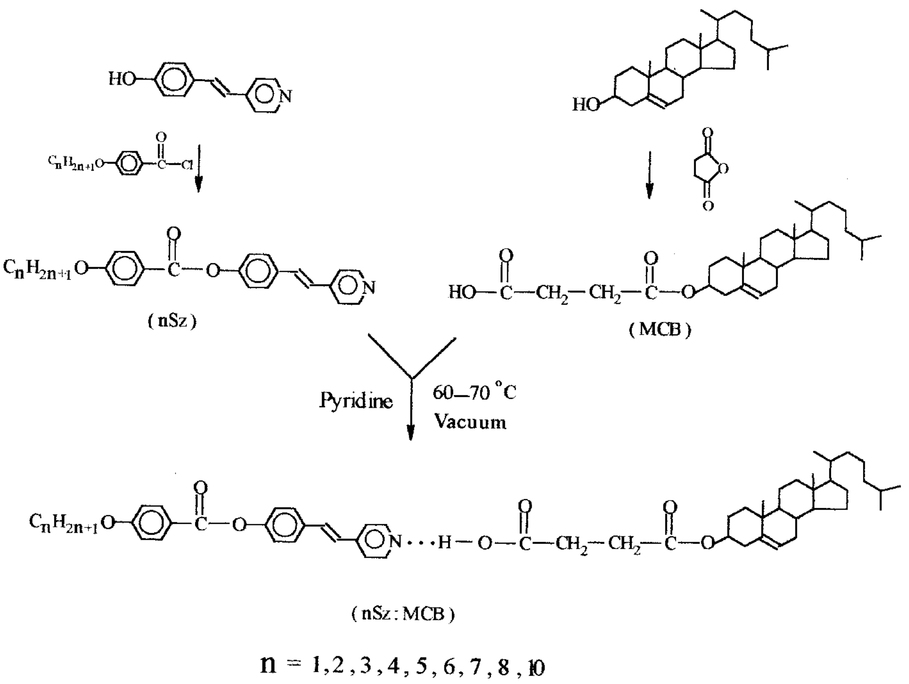
2.2. *Mesomorphic properties*

2.2.1. *Compounds* nSZ

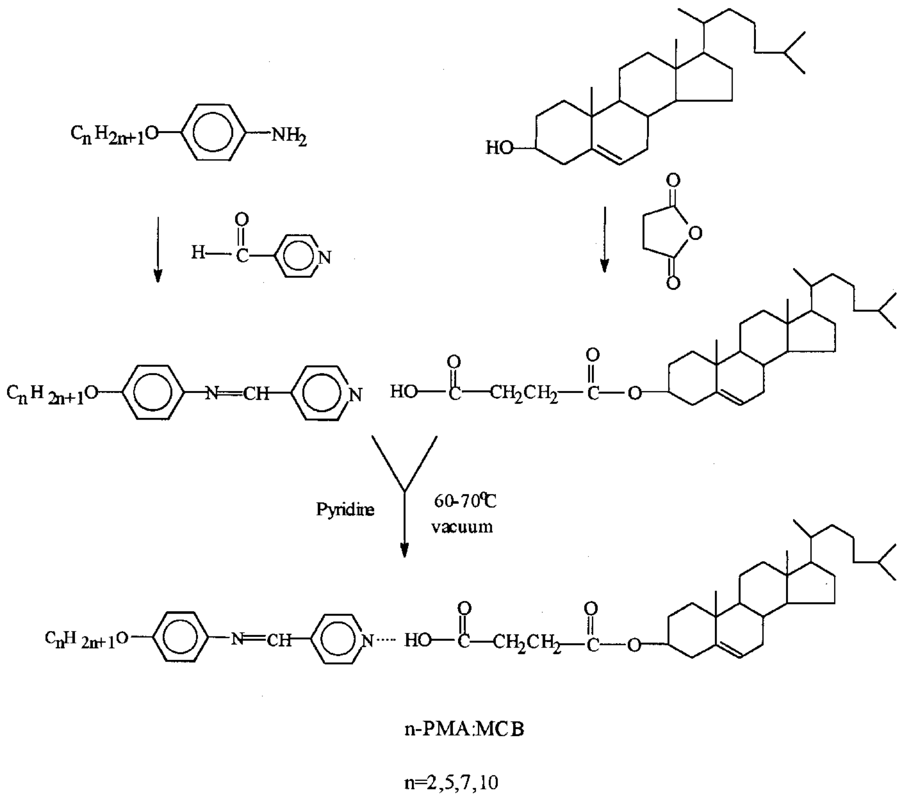
According to the DSC and polarized optical microscopy studies, we found that the compounds 1SZ, 2SZ and 3SZ showed an enantiotropic nematic phase. The phase transitions of 1SZ (Cr 166°C N 216°C I) and 2SZ (Cr 167°C N 212°C I) are in accord with those reported in the literature (Cr 168°C N 216°C I for 1SZ [1], Cr 165°C N 213°C I for 2SZ [2]. For the compounds 4SZ and 5SZ, both on the heating and cooling sequences, besides the nematic phase, a smectic A phase could also be observed with a homeotropic texture, but at the edge of slides; this S_A phase appeared with a focal-conic texture. For compounds 6SZ and 7SZ (their DSC curves can be seen in figure 1), their S_A phases appeared with focal-conic textures, and another monotropic smectic phase (S_I) appeared with an atypical texture (indistinguishable from the crystalline texture) could also be

---

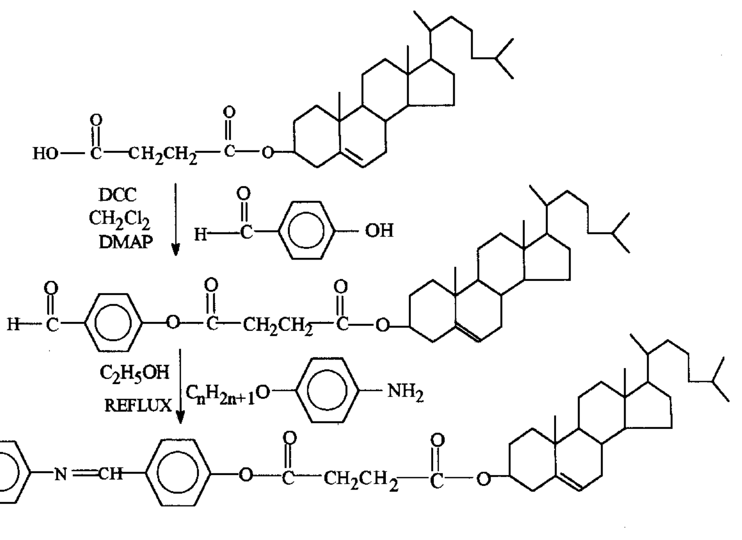
*Author for correspondence.



Scheme 1.



Scheme 2.



CCPBA-n
n=2,5,7

Scheme 3.

observed (X-ray study identifies that it is a smectic phase). For compounds 8SZ [20] and 10SZ, the nematic phase disappeared. On the heating sequence, only the S_A phase with a focal-conic texture could be observed, but on the cooling sequence the two compounds showed not only S_A phases but also S_I phases. The transition temperatures of these compounds (*n*SZ) are shown in table 1.

X-ray diffraction studies were also used to identify the mesophases. Figure 2 shows the X-ray diffraction diagram of 7SZ. A weak and broad reflection at the wide angle (associated with the lateral packing) and a sharp reflection at the low angle (associated with the smectic layers) are shown by the curves, respectively. Curve (*a*) presents a diffuse reflection at about 4·64 Å and a very weak diffuse peak at 33·92 Å, which is characteristic of a nematic phase. Both curves (*b*) and (*c*) show a very sharp first order reflection peak at 33·03–33·38 Å, a second order reflection peak at 15·72–15·91 Å, and a weak diffuse reflection at about 4·60 Å. Using polarized optical microscopy, a focal-conic texture could be seen for this compound in this temperature range. Both

Table 1. Transition temperatures and enthalpies for the compounds of MCB and *n*SZ

Compound	Transition temperature/°C [Enthalpy/kJ^{-1} mol^{-1}]								
MCB	Cr	177–179							I
1SZ	Cr	166					N	216	I
2SZ	Cr	167					N	212	I
3SZ	Cr_1	132·6 [0·2]	Cr_2	154·8 [29·3]			N	192·7 [0·2]	I
4SZ	Cr	136·4 [21·8]			S_A	146·1 [0·7]	N	192·7 [0·4]	I
5SZ	Cr	111·1 [18·7]			S_A	148·0 [0·5]	N	185·3 [0·4]	I
6SZ	Cr	116·6 [24·0]	(S_I	89·5) [−1·7]	S_A	164·0 [1·3]	N	177·0 [0·4]	I
7SZ	Cr	112·9 [26·8]	(S_I	99·0) [−1·8]	S_A	171·5 [2·1]	N	174·1 [0·8]	I
8SZ	Cr	106·3 [19·5]	(S_I	86·9) [−2·3]	S_A	172·9 [3·1]			I
10SZ	Cr	108·7 [22·6]	(S_I	89·8) [−1·3]	S_A	175·0 [4·1]			I

Cr: crystal; S_A: smectic A; N: nematic; I: isotropic; S_I: unidentified smectic phase. Parentheses denote a monotropic transition.

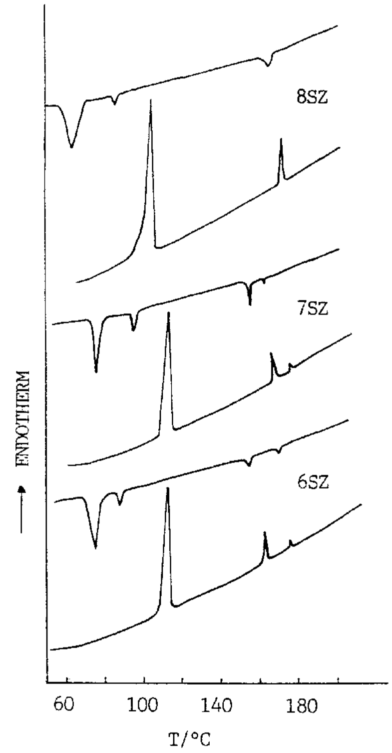


Figure 1. DSC curves of 6SZ, 7SZ and 8SZ.

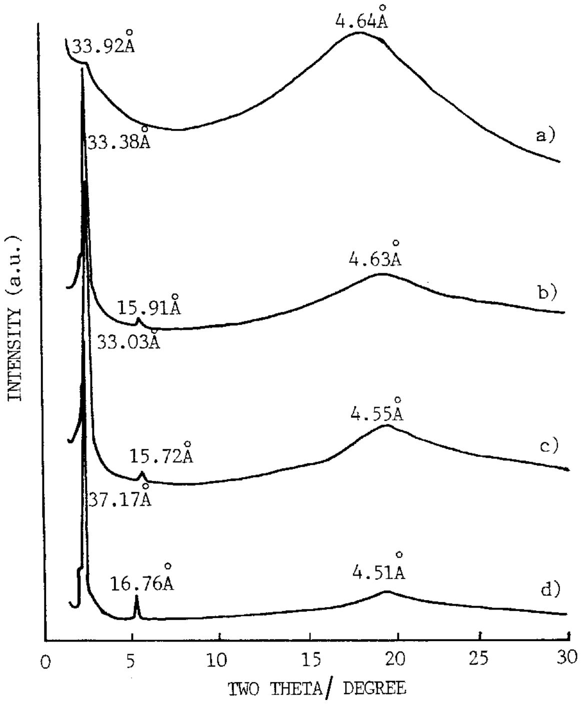


Figure 2. X-ray diffractograms for compound 7SZ at different temperatures: (*a*) nematic phase at 173°C (heating), (*b*) smectic A phase at 150°C (heating), (*c*) smectic A phase at 130°C (heating) and (*d*) smectic 1 phase at 87°C (cooling).

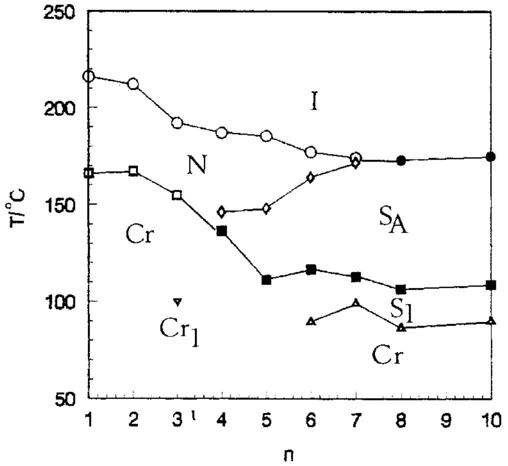


Figure 3. The phase behaviour for the *n*SZ series.

results are consistent with a smectic phase. When the temperature was lowered to 87°C on the cooling sequence, the sharp first order reflection increased to 37·17 Å; this is also strong evidence for a smectic phase. What should be noticed is the layer thicknesses (*d* spacing, the first order reflection) of the compound are longer than its molecular length (according to standard molecular bond angles and lengths in the all-*trans* conformation, *L* is 27 Å for 7SZ). Generally speaking, if *d* is longer than *L*, the molecular arrangement should be bilayered. On the other hand, this bilayer arrangement for molecular liquid crystals is caused by strong dipole groups, such as nitro or cyano groups [21]. However, no such groups are present in this compound, so further experiment (AFM, neutron diffraction etc.) will be performed in order to identify the molecular arrangement.

Figure 3 illustrates the phase behaviour for the *n*SZ series. The transition temperatures do not show an odd–even effect, the clearing points decrease with increasing alkoxy chain length. However, the SA–N transition temperatures increase with increasing alkoxy chain length, and as a result, the temperature ranges of the nematic phases narrow and the SA phase ranges become wider.

2.2.2. *Complexes* n*SZ:MCB*

The existence of intermolecular hydrogen bonds in the complexes of *n*SZ:MCB can be confirmed by FTIR spectroscopy. For example, MCB has two carbonyl bonds (1731 cm^{-1} and 1710 cm^{-1}, corresponding to the ester carbonyl and carboxylic absorption, respectively), and compound 6SZ has an ester carbonyl absorption at 1722 cm^{-1}. For the complex 6SZ:MCB the two ester carbonyl bands merge into one (1729 cm^{-1}), while the carboxylic carbonyl band changes to 1718 cm^{-1} due to the formation of an intermolecular hydrogen bond. The

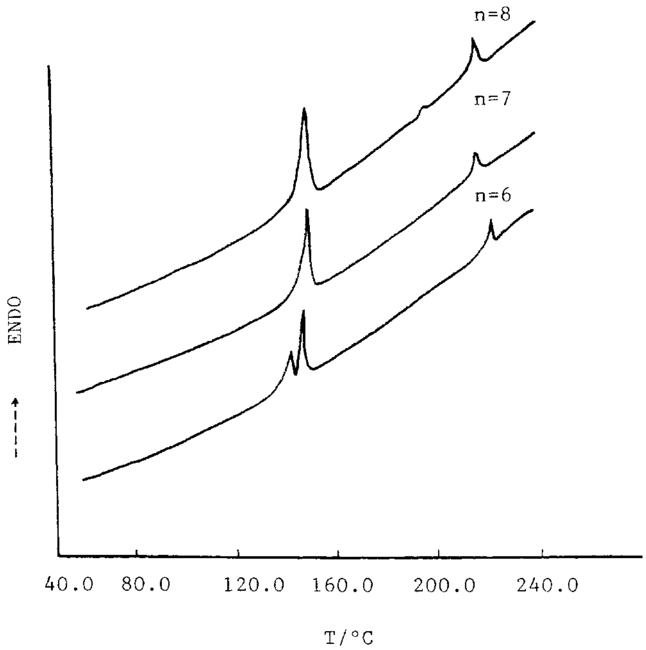


Figure 4. DSC curves of *n*SZ:MCB (*n*=6, 7 and 8).

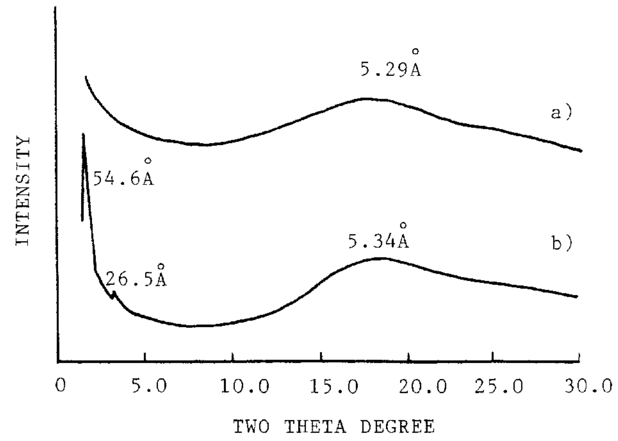


Figure 5. The X-ray diffraction diagram for complex 7SZ:MCB on heating at 195°C (*a*) (cholesteric phase) and (*b*) 165°C (smectic phase).

appearance of two broad absorption bands centred at 2523 cm^{-1} and 1926 cm^{-1} for 6SZ:MCB is strong evidence for the unionized intermolecular hydrogen bonding [1–10].

The phase transition temperatures of *n*SZ:MCB were investigated by DSC (see figure 4) and polarized microscopy. The results are shown in table 2. All of the *n*SZ:MCB complexes are enantiotropic liquid crystals. They exhibit cholesteric phases which show an oily-streak texture with colour changing on heating and focal-conic textures on cooling [21, 22], and also exhibit a smectic C phase with a silk texture [21].

Figure 5 illustrates the X-ray diffractograms of 7SZ:MCB on heating. Curve (*a*) has only a diffuse reflection at about 5·29 Å. Curve (*b*) has a first order reflection at 54·6 Å, a weak second order reflection at 26·5 Å and a diffuse reflection at about 5·3 Å. With the

Table 2. Transition temperatures and enthalpies for the *n*SZ:MCB complexes

Compound	Transition temperature/°C [Enthalpy/kJ^{-1} mol^{-1}]								
1SZ:MCB	Cr	133·7 [19·9]			S_C	190·0 [–]^b	Ch	229·3 [3·6]	I
2SZ:MCB	Cr	152·2 [24·6]			S_C	186·0^a [–]^b	Ch	234·6 [9·1]	I
3SZ:MCB	Cr	145·6 [37·3]			S_C	187·0^a [–]^b	Ch	224·4 [5·8]	I
4SZ:MCB	Cr_1	132·1 [4·0]	Cr_2	157·0 [22·0]	S_C	183·0^a [–]^b	Ch	231·4 [5·0]	I
5SZ:MCB	Cr	149·2 [47·4]			S_C	185·0^a [–]^b	Ch	226·4 [9·8]	I
6SZ:MCB	Cr_1	144·2 [–]^b	Cr_2	148·5 [24·1]	S_C	190·0^a [–]^b	Ch	222·3 [5·7]	I
7SZ:MCB	Cr	150·7 [24·8]			S_C	187·2 [–]^b	Ch	219·1 [3·7]	I
8SZ:MCB	Cr	151·8 [30·9]			S_C	195·3 [–]^b	Ch	218·7 [5·3]	I
10SZ:MCB	Cr	148·8 [22·6]			S_C	190·6 [–]^b	Ch	209·1 [5·1]	I

Cr: crystal; S_C: smectic C; Ch: cholesteric; I: isotropic.
[a] Value from polarized optical microscopy.
[b] – Enthalpy value too small to measure.

results of the polarized optical microscopy, this indicates a smectic phase in the range of 150°C to 185°C for complex 7SZ:MCB.

Figure 6 illustrates the transition behaviour for *n*SZ:MCB. When $n<6$, Cr–Sc, Sc–Ch and Ch–I transitions show an odd–even effect, but when $n>4$, the Ch–I transition temperatures decrease continuously with increasing alkoxy chain length.

From tables 1 and 2, and figures 3 and 6, we can see the phase transition temperatures and mesophases of MCB, *n*SZ and *n*SZ:MCB are very different. 3-Cholesteryloxycarbonyl propanoic acid (MCB) is not a liquid crystal, compounds *n*SZ show nematic and smectic phases, and the *n*SZ:MCB complexes exhibit cholesteric phases. When $n<4$, the melting points (Cr–Sc) of *n*SZ:MCB are lower than the melting points (Cr–N) of *n*SZ, and the clearing points (Ch–I) are higher than the clearing points of *n*SZ. As a result, the mesomorphic ranges of *n*SZ:MCB are wider than those of *n*SZ. Similar results can also be found in the intermolecular hydrogen bonded complex 4BA:2SZ (for example, 4-butyloxybenzoic acid: 4-(4-ethyloxybenzoyloxy)-4′-stilbazole) [1].

2.2.3. n-*PMA*: *MCB complexes*

The aim of this part of work was to investigate the phase changes by choosing non-mesogenic proton donors and acceptors. The IR spectra show that intermolecular hydrogen bonds have formed according to the bands centred at 2525 cm^{-1} and 1925 cm^{-1}. Also, the carboxylic carbonyl band of MCB at 1710 cm^{-1} has changed to 1717 cm^{-1} due to the formation of intermolecular hydrogen bonding [1–10]. The DSC (see figure 7) and optical polarized microscopy studies show that the 1:1 complexes of *n*-PMA:MCB exhibit enantiotropic cholesteric phases even though MCB and *n*-PMA are not liquid crystals in their own right. The phase transition temperatures for the complexes are given in table 3.

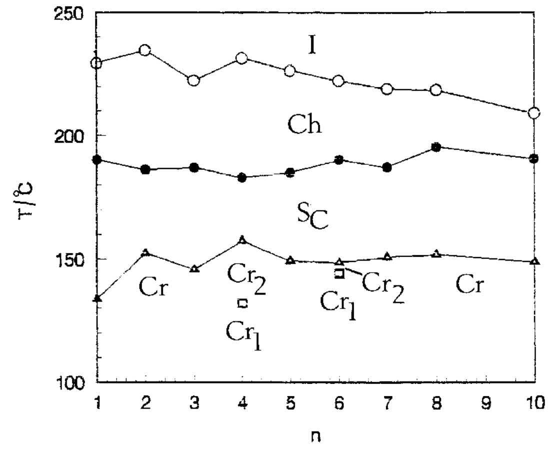


Figure 6. The phase diagram for complexes *n*SZ:MCB.

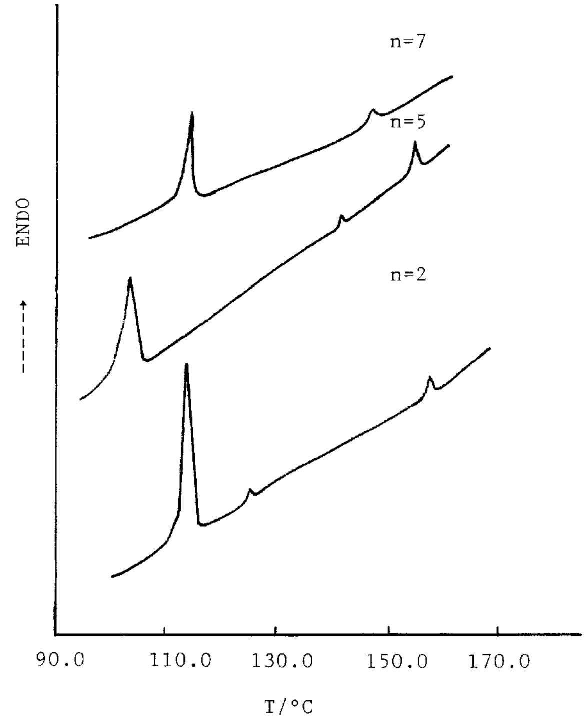


Figure 7. DSC curves of *n*-PMA:MCB ($n=2$, 5 and 7).

From table 3, we find that the phase transition temperatures for complexes *n*-PMA:MCB are very different from those of the individual components. The melting points for the complexes are higher than the melting points of their relative proton acceptors, but lower than that of the proton donor. On the other hand, the clearing points for the complexes are lower than the melting points of the proton donor. On the contrary, the clearing points for *n*SZ:MCB are higher than the melting point of MCB. Under polarized optical microscopy, cholesteric phases with oily streak textures on heating and focal-conic fan textures on cooling, and smectic A phases with pesudoisotropic textures can be seen very clearly. However, it is very strange that for complex 7PMA:MCB the pesudoisotropic texture cannot be observed both on heating and cooling.

2.2.4. *Compounds CCPBA*-n

We also investigated three new covalently bonded molecules *N*-[4-(3-cholesteryloxycarbonylpropionyloxy)benzylidiene]-4-alkoxyanilines (CCPBA-*n*). The molecular structures are similar to these of the intermolecular hydrogen bonded complexes *n*-PMA:MCB, but they are covalently bonded with ester groups (see scheme 3). The aim of this work was to compare the

Table 3. Phase transition temperatures and enthalpies for *n*PMA, MCB, *n*PMA:MCB and CCPBA-*n*

Compound		Transition temperature/°C [Enthalpy/kJ^{-1} mol^{-1}]						
MCB	Cr	177–179	I					
1-PMA	Cr	99–101	I		(Cr	99·7	I)	Ref [23]
5-PMA	Cr	62–64	I		(Cr	66·1	I)	Ref [23]
7-PMA	Cr	70–72	I		(Cr	68·4	I)	Ref [23]
10-PMA	Cr	70–71	I		(Cr	69·1	I)	Ref [23]
2PMA:MCB	Cr	113·8 [32·3]	S_A*	126·0 [–]	Ch	156·6 [4·1]	I	
5PMA:MCB	Cr	103·1 [16·3]	S_A*	140·0 [–]	Ch	149·6 [4·0]	I	
7PMA:MCB	Cr	115·4 [27·6]			Ch	144·9 [3·1]	I	
10PMA:MCB	Cr	110·0 [24·7]	S_A*	120·0 [–]	Ch	141·4 [4·2]	I	
CCPBA-2	Cr	166·7			Ch	256·2	I	
CCPBA-5	Cr	118·5			Ch	243·1	I	
CCPBA-7	Cr	132·1			Ch	234·1	I	

Cr: crystal; Ch: cholesteric; I: isotropic.
[a] Value from polarized optical microscopy.

phase difference caused by non-covalent and covalent bonds with similar structures. For the three covalently bonded CCPBA-*n*, under polarized optical microscopy, only oily streak textures could be observed on both heating and cooling, indicating only cholesteric liquid crystals. This result is also shown in table 3. From this table, we find that both the melting and clearing points for CCPBA-*n* are higher than those of *n*PMA:MCB, and the liquid crystal temperature ranges are also broader than those of *n*PMA:MCB. As an example, the melting and clearing points for 2PMA:MCB are 113·8°C and 156·6°C, respectively whereas for CCPBA-2 the melting and clearing points are 166·7°C and 256·2°C, respectively. This difference shows that the melting point of CCPBA-2 is 42·9°C higher than that of 2PMA:MCB and the clearing point of CCPBA-2 is 99·6°C higher than that of 2PMA:MCB. As a result, the liquid crystalline range for CCPBA-2 is 46·7°C greater than that for 2PMA:MCB. Meanwhile we find the complexes exhibit cholesteric and smectic phases, but the compounds CCPBA-*n* show only cholesteric phases. This great difference must be caused by the difference in molecular structures. The rigidity of mesogenic group for CCPBA-*n* is stronger than that of *n*PMA:MCB, so the phase transition temperatures for CCPBA-*n* are higher than those of *n*PMA:MCB because of their analogous structures. However, the reason why the liquid crystalline phases of *n*PMA:MCB are more complicated than those of CCPBA-*n* is not clear. Kato *et al.*, reported that the isotropic transition temperature of a covalently bonded OPHOFB is higher than that of intermolecular hydrogen bonded 6-OFBA-8PY and 6-OFBA-8PY shows more LC phases than OPHOFB [13].

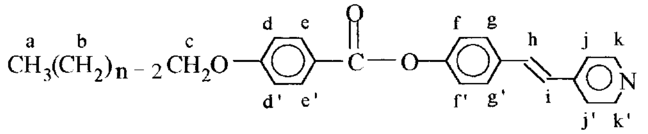
3. Experimental

Cholesterol, 4-methoxybenzoic acid, 4-pyridinecarbaldehyde and succinic anhydride were used as received. The solvents were dried and distilled prior to use. Infrared spectra were recorded using a Nicolet-5DX FTIR spectrometer with a maximum resolution of 2 cm^{-1} using KBr pellets. ^{1}H NMR spectra were measured using a Unity 400 NMR instrument operating at 400 MHz in CDCl$_3$. Elemental analyses were performed with a Perkin–Elmer 240C microanalyser. The textures of the mesophases were characterized by polarized optical microscopy (Zeiss Jena optical microscopy) with a heating stage from HunJiang (China). DSC measurements were conducted on a Perkin–Elmer DSC-7 system with heating and cooling rates of 10°C min^{-1}. X-ray diffraction diagrams were taken using a Philips PW-1700 system. Unoriented powder samples were exposed to CuKα radiation (1·54 Å). The temperature was controlled with a precision of ±1°C.

The 4-hydroxy-4′-stilbazole was prepared according to the known procedure [6, 24]. The 4-alkoxybenzoic acids were synthesized according to the method of Brynmor Jones [25] and purified by recrystallization three times from glacial acetic acid. The phase transitions of these compounds are in accordance with the literature [25].

4-Alkoxybenzoyl chlorides were obtained according

Table 4. Data of ^{1}H NMR spectra for *n*SZ(400 MHz in $CDCl_3$)



n	*a*	*b*	*c*	*dd′*	*ee′*	*ff′*	*gg′*	*h*	*i*	*jj′*	*kk′*
1	3·90	–	–	7·00	8·17	7·23	7·61			7·37	8·60 [6]
1	3·91	–	–	7·01	8·17	7·25	7·59	6·98	7·30	7·36	8·59
2	1·47	–	4·14	6·97	8·15	7·24	7·60	6·98	7·30	7·38	8·59
3	1·07	1·87	4·02	6·98	8·15	7·24	7·59	7·02	7·29	7·37	8·59
4	1·00	1·50–1·82	4·06	6·95	8·15	7·24	7·60	7·01	7·30	7·37	8·59
5	0·95	1·42–1·84	4·05	6·98	8·15	7·24	7·59	7·02	7·29	7·37	8·59
6	0·92	1·36–1·84	4·05	6·98	8·15	7·25	7·60	7·03	7·30	7·40	8·61
7	0·91	1·32–1·85	4·05	6·99	8·15	7·25	7·60	7·02	7·30	7·38	8·58
8	0·89	1·30–1·84	4·05	6·98	8·15	7·25	7·59	7·01	7·29	7·37	8·59
10	0·89	1·27–1·84	4·05	6·98	8·15	7·26	7·59	7·02	7·30	7·37	8·59

to a general procedure and were used without any further distillation.

The 4-(4-octyloxybenzoyloxy)-4′-stilbazole (8SZ) was synthesized according to a slight modification of the literature [6, 20]. 4-Hydroxy-4′-stibazole (3·0 g, 15·2 mmol) was dissolved in dry pyridine (100 ml), and a solution of 4-octyloxybenzoyl chloride (17·3 mmol) in dry THF (20 ml) was added dropwise to the pyridine solution within 30 min at room temperature. After the mixture had been stirred overnight, most of the THF and pyridine was distilled off. The residue was poured into a large amount of crushed ice, the precipitate was filtered and recrystallized twice from ethanol, and twice from cyclohexane. The purity of this compound was checked by thin layer chromatography, elemental analysis and ^{1}H NMR. Yield 80 per cent. Elemental analysis calculated for $C_{28}H_{31}NO_3$: C 78·30, H 7·22, N 3·26. Found: C 78·04, H 7·35, N 3·23 per cent.

The remaining 4-(4-alkoxybenzoyloxy)-4′-stibazoles (*n*SZ) were prepared in a similar way. The ^{1}H NMR data are shown in table 4. The elemental analyses data for *n*SZ are given in table 5.

Table 5. Elemental analyses (per cent) for the compounds *n*SZ

	C		H		N	
Compound	Cal	Exp.	Cal	Exp.	Cal	Exp.
3SZ	76·86	76·75	5·89	5·80	3·90	3·72
4SZ	77·19	76·82	6·20	6·18	3·75	3·54
5SZ	77·50	77·15	6·50	6·27	3·62	3·43
6SZ	77·78	77·56	6·78	6·51	3·49	3·27
7SZ	78·05	77·68	7·04	6·90	3·37	3·09
8SZ	78·30	78·04	7·22	7·35	3·26	3·23
10SZ	78·52	78·57	7·50	7·78	3·16	3·27

3-Cholesteryloxycarbonylpropanoic acid (MCB) was prepared according to the following procedure: a solution of cholesterol (3·87 g, 10 mmol), succinic anhydride (1·00 g, 10 mmol) and triethylamine (1·100 g, 10 mmol) in dry acetone (60 ml) was heated at reflux for 20 h. The acetone was then evaporated and the resulting precipitate recrystallized twice from glacial acetic acid. Yield 70 per cent. m.p. 177–179°C (175–178°C) [26]. IR: 1731 cm^{-1}, (ester carbonyl), 1710 cm^{-1} (acid carbonyl). Elemental analysis: calculated for $C_{31}H_{50}O_4$: C 76·50, H 10·27. Found: C 76·21, H 10·09 per cent.

N-(4-pyridylmethylidiene)anilines (*n*PMA) were prepared by the condensation of an equimolar mix of 4-pyridinecarbaldehyde and 4-alkoxyaniline in hot ethanol. These final compounds were purified by recrystallization twice from hexane. The yields were in the range of 70–75 per cent.

Elemental analysis for 2-PMA, calculated: $C_{14}H_{14}N_2O$, C 74·31, H 6·24, N 12·37. Found: C 74·02, H 6·45, N 12·62 per cent.

^{1}H NMR for 5-PMA: 8·49 (s, 1 H, –CH=N–), 8·74 and 7·76 (d, 4 H, pyridyl, $J=6{\cdot}0$ Hz), 7·29 and 6·95 (d, 4 H, phenyl, $J=8{\cdot}4$ Hz), 3·99 (t, 2 H, $-CH_2O-$, $J=6{\cdot}4$ Hz), 1·83–1·41 (m, 6 H, $-(CH_2)_3-$), 0·94 (t, 3 H, $-CH_3$, $J=7{\cdot}2$ Hz).

Elemental analysis for 7-PMA calculated: $C_{19}H_{24}N_2O$, C 77·03, H 8·16, N 9·46. Found: C 76·78, H 8·35, N 9·49 per cent. ^{1}H NMR for 7-PMA: 8·48 (s, 1 H, –CH=N–), 8·74 and 7·74 (d, 4 H, pyridyl, $J=6{\cdot}0$ Hz), 7·29 and 6·94 (d, 4 H, phenyl, $J=8{\cdot}4$ Hz), 3·99 (t, 2 H, $-CH_2O-$, $J=6{\cdot}4$ Hz), 1·82–1·32 (m, 10 H, $-(CH_2)_5-$), 0·90 (t, 3 H, $-CH_3$, $J=6{\cdot}8$ Hz).

Elemental analysis for 10-PMA, calculated: $C_{22}H_{30}N_2O$, C 78·05, H 8·94, N 8·28. Found: 78·03, H 9·31, N 8·45 per cent.

The liquid crystals (*n*SZ:MCB and *n*PMA:MCB) were obtained according to the same literature procedure [1–7]. Equal molar quantities of *n*SZ or *n*-PMA and MCB were dissolved in dry pyridine. The pyridine was evaporated under vacuum at 60–70°C and the residual complexes cooled to room temperature for investigation.

4-(3-Cholesteryloxycarbonylpropionyloxy)benzaldehyde was prepared according to the following method: 3-cholesteryloxycarbonylpropanoic acid (MCB) (2·50 g, 5·1 mmol) and 4-hydroxybenzaldehyde (0·8 g, 6·5 mmol) were dissolved in 30 ml dry CH_2Cl_2 containing pyridine (1·8 ml) and a small amount of DMAP, DCC (2·08 g, 10 mmol) was then added to this mixture at room temperature. The mixture was stirred at r.t. for 24 h, and the white precipitate (DCU) was removed by filtration. After the solvent was evaporated under reduced pressure, the residue was purified by silica gel column chromatography (cyclohexane:ethyl acetate 7:1 as eluent), and 1·60 g of a white solid was obtained. Yield 53 per cent IR: 1770 cm^{-1} and 1737 cm^{-1} (ester carbonyl), 1705 cm^{-1} (aldehyde carbonyl). This compound was also a liquid crystal: Cr 116·7°C (22·76 kJ mol^{-1}) S 127·4°C (1·30 kJ mol^{-1}) Ch 134·1°C (1·59 kJ mol^{-1}) I. Elemental analysis: calculated for $C_{38}H_{54}O_5$: C 77·25, H 9·22, Found: C 77·39, H 9·59 per cent.

N-[4-(3-Cholesteryloxycarbonylpropionyloxy)benzylidiene]-4-alkoxyanilines (CCPBA-*n*) were obtained by refluxing an ethanolic solution containing equimolar quantities of 4-(3-cholesteryloxycarbonylpropionyloxy)-benzaldehyde and 4-alkoxyaniline. The precipitates obtained were filtered hot then recrystallized twice from ethyl acetate. Yields 60–70 per cent. The purity of these compounds can be warranted by ^{1}H NMR and elemental analyses.

For CCPBA-2: IR: 1763 cm^{-1} and 1731 cm^{-1} (ester carbonyl), 1628 cm^{-1} (–CH=N–). Elemental analysis: calculated for $C_{46}H_{63}NO_5$: C 77·81, H 8·94, N 1·97. Found: C 77·66, H 9·08, N 1·83 per cent. ^{1}H NMR: 8·46 (1 H, s, –N=CH–), 7·91, 7·23, 7·19, 6·92 (8 H, d, phenyl), 5·38 (1 H, d, –CH–), 4·64 (1 H, m, –OCH–), 4·06 (2 H, q, –OCH$_2$–), 2·90, 2·73 (4 H, t, –COCH$_2$CH$_2$CO–), 2·35–0·67 (46 H, m, aliphatic chains). Cr 166·7°C Ch 256·2°C I.

For CCPBA-5, IR: 1761 cm^{-1} and 1730 cm^{-1} (ester absorption), 1627 cm^{-1} (imine absorption). Elemental analysis: calculated for $C_{49}H_{69}NO_5$, C 78·25, H 9·25, N 1·86. Found, C 78·45, H 9·19, N 2·02 per cent. Cr 118·5°C Ch 243·1°C I.

For CCPBA-7. Elemental analysis calculated for $C_{51}H_{73}NO_5$, C 78·52, H 9·43, N 1·80. Found: C 78·72, H 9·47, N 1·98 per cent. Cr 132·1°C Ch 234·1°C I.

4. Summary

In summary, in this paper we prepared three series of liquid crystals with cholesteryl groups and the results show that these series are cholesteric liquid crystals. The results also show that the phase transition temperatures for the covalently bonded liquid crystals are higher than those of their analogous intermolecular hydrogen bonded complexes.

This work was supported by National Natural Science Foundation of China and the Polymer Physics Laboratory of Changchun Institute of Applied Chemistry.

References

[1] Kato, T., and Frechet, J. M. J., 1989, *J. Am. chem. Soc.*, **111,** 8533.

[2] Kato, T., and Frechet, J. M. J., 1990, *Macromolecules*, **23,** 360.

[3] Kato, T., Kichara, H., Uryu, T., Fujishima, A., and Frechet, J. M. J., 1992 *Macromolecules*, **25,** 6836.

[4] Yu, L. J., and Wu, J. M., 1991, *Mol. Cryst. liq. Cryst.*, **198,** 407.

[5] Grant, A., Griffin, A. C., Taylor, P. L., Yeates, S. G., and Smyth, M. G., 1994, Proceedings of the International Conference on Liquid Crystal Polymers, Beijing, China, p. 146.

[6] Kumar, U., Kato, T., and Frechet, J. M. J., 1992, *J. Am. chem. Soc.*, **114,** 6630.

[7] Kato, T., Uryu, T., and Fumiko, K., 1993, *Liq. Cryst.*, **14,** 1311.

[8] Yu, L. J., 1993, *Liq. Cryst.*, **14,** 1303.

[9] Kumar, U., Frechet, J. M. J., Kato, T., Ujile, S., and Itmura, K., 1992, *Angew. Chem. Int. Ed. Engl.*, **31,** 1531.

[10] Tian, Y. Q., Su, F. Y., Zhao, Y. Y., Luo, X. Y., Zhao, X. G., and Zhou, E. L., 1995, *Liq. Cryst.*, **19,** 743.

[11] Alexander, C., Jariwala, C.-P., Lee, C. M., and Griffin, A. C., 1994, *Makromol. Chem. Macromol. Symp.*, **77,** 283.

[12] Wilson, L. M., 1994, *Macromolecules*, **27,** 6683.

[13] Kato, T., Fukumasa, M., and Frechet, J. M. J., 1995, *Chem. Mater.*, **7,** 368.

[14] Sidevatou, Z., Paleos, C. M., and Skoulios, A., 1995, *Mol. Cryst. liq. Cryst.*, **265,** 19.

[15] Pourcain, C. B., and Griffin, A. C., 1995, *Macromolecules*, **28,** 4416.

[16] Kato, T., Kihara, H., Kumar, U., Uryu, T., and Frechet, J. M. J., 1994, *Angew. Chem. Int.* Ed. Engl., **33,** 1644.

[17] Kato, T., Hihota, N., Fujishima, A., and Frechet, J. M. J., 1996, *J. Polym. Sci. Polym. Chem.*, **34,** 57.

[18] Kato, T., Hihara, H., Uryu, T., Ujiie, S., Iimura, K., Frechet, J. M. J., and Kumar, U., 1993, *Ferroelectrics*, **148,** 161.

[19] Paleo, C. M., and Tsiourvas, D., 1995, *Angew. Chem. Int. Ed, Engl.*, **34,** 1696.

[20] Nash, J. A., and Gray, G. W., 1974, *Mol. Cryst. liq. Cryst.*, **25,** 299. It is interesting that the phase transition temperatures and the mesophases of 8SZ in table 1 (Cr 106·3 S$_1$ 86·9 S$_A$ 172·9 I) differ from those reported by Nash and Gray (Cr$_2$ 95·7 Cr$_1$ 117 N 214 I). The purity of this compound can be warranted by IR, ^{1}H NMR and elemental analysis.

[21] Gray, G. W., and Goodby, J. W., 1984, *Smectic Liquid Crystals* (Glasgow and London: Leonard Hill).

[22] Dong, C. C., Sun, Z. M., and Li, G. Z., 1990, *Mol. Cryst. liq. Cryst.*, **185,** 35.

[23] Marcos, M., Ros, M. B., Serrano, J. L., Esteruelas, M. A., Sola, E., Oro, L. A., and Barbera, J., 1990, *Chem. Mater.*, **2,** 748.

[24] Chiang, M. C., and Hartung, W. H., 1944, *J. org. Chem.*, **10,** 21.

[25] Jones, B., 1935, *J. chem. Soc.*, 1874.

[26] Pouzar, V., Drasar, P., Cerny, I., and Havel, M., 1984, *Synth. Commun.*, **14,** 501.