J. Phys. Chem. 1986, 90, 666-671

Thermal Properties of Cholesteryl and β-Sitosteryl Esters: The Effect of the Rigid Core on the Thermal Stabilities of Cholesteric and Smectic A Phases

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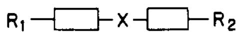
(Received: May 29, 1985; In Final Form: August 22, 1985)

The effect of a central linkage X on the thermal stabilities of the cholesteric and smectic A phases of cholesteryl and β-sitosteryl esters of 4-aryl-X-benzoic and 4-aryl-X-cyclohexanecarboxylic acids (X = -COO-, -CH=N-, -N=N-, -CO-, etc.) has been examined. In both series, the cholesteric–isotropic and smectic A–cholesteric transition temperatures and the transition enthalpies are discussed in terms of the molecular structures and also the angular correlation parameter J_{22} of the carboxy functions. The transition enthalpies for the smectic A–cholesteric transition are also discussed in terms of the McMillan theory.

Introduction

Thermotropic liquid crystals usually have a lath or a rodlike molecular shape, and the general structure is given by



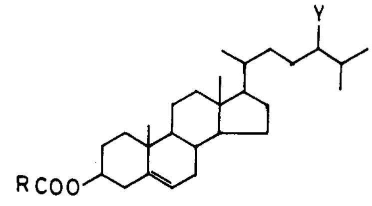
The molecules consist of a relatively hard core (usually unsaturated and/or saturated rings), flexible terminal groups R_1 and R_2 such as alkoxy, alkyl chains, and sometimes small substituents such as cyano, nitro, and halogen, and a central linkage X such as -CH=CH-, -CH=N-, -N=N-, and so on. It is known that linearity, rigidity, and polarizability of the molecule are of primary importance for the mesomorphic properties.[1] The electrical and geometrical properties of the central linkage are especially important in determining mesophase stability. Although an effectiveness for the central linkage X in promoting nematic (cholesteric)–isotropic transition temperatures has been well discussed,[2] it is very difficult to find good quantitative or qualitative correlations between the mesophase stability and physical parameters such as polarizability and dipolarity of a molecule. It may be as a result that usually a subtle change in the molecular structure results in a dramatic change in thermotropic behavior as evidenced by transition temperatures, enthalpies, and entropies, and this would make difficult any qualitative analysis of the substituent effect. We consider that steroid derivatives are the most suitable for the purpose, because they have such a bulky structure that a partial replacement does not change gross characteristics such as molecular geometry and conformation and also molecular organization in the mesophases.

In this paper, we describe the thermal properties of some aryl esters of cholesterol and β-sitosterol, as shown in Chart I. The thermotropic behaviors of these esters are discussed in terms of the electric and geometrical effects of the central linkages.

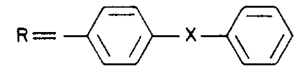
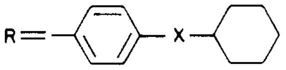
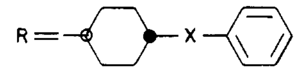
Experimental Section

Methods. Transition temperatures were determined by using a Nikon POH polarizing microscope fitted with a Mettler FP 52 heating stage and control unit. Transition enthalpies were measured with a Daini-Seikosha SSC-560 differential scanning calorimeter. Indium and tin (99.9%) were used as the calibration standards with a heating rate of 5 °C min^{-1} (mp 156.0 °C (ΔH = 3.26 kJ mol^{-1}) and 231.9 °C (ΔH = 7.02 kJ mol^{-1})). Transition entropies were calculated from the equation $\Delta S = \Delta H/T$.

CHART I



I Cholesteryl-R (Y=H)
II β-Sitosteryl-R (Y=C_2H_5)

compd	linkage X	J_{22}
	R= 	
a	-CH=C(CH_3)-	0.78
b	-CH=CH-	0.58
c	-CH=N-	0.53
d	none	0.43
e	-COO-	0.40
f	-CO-	0.30
g	-O-	0.18
h	-S-	0
i	-CH_2-	-0.17
j	-N=N-	
k	-CONH-	
l	-CH_2CH_2-	
	R= 	
m	-COO-	0.43
n	-CO-	
o	-CO-	
	R= 	
p	-CO-	

Materials. Cholesterol and β-sitosterol were purchased from Nakarai Chemical Co. and were purified by column chromatography on silica gel with a mixture of *n*-pentane–ether (98:2) as the developing solvent, followed by recrystallization from absolute ethanol (mp 149.4 and 142.2 °C, respectively).

Stilbene-4-carboxylic acid, α-methylstilbene-4-carboxylic acid, and diphenylethane-4-carboxylic acid were prepared by hydrolysis of 4-cyanostilbene, 4-cyano-α-methylstilbene,[4] and 4-cyanodiphenylethane,[5] respectively. 4-Cyclohexylbenzoic acid was prepared by acetylation of phenylcyclohexane, followed by hypobromite oxidation.[6] 4-(Benzoyloxy)benzoic acid and 4-cyclo-

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(1) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals", Academic Press, London, 1962.

(2) G. W. Gray and P. A. Winsor, "Liquid Crystals and Plastic Crystals", Vol. 1, Wiley, New York, 1974.

(3) G. R. Luckhurst and G. W. Gray, "The Molecular Physics of Liquid Crystals", Academic Press, London, 1979.

(4) G. W. Gray and A. Mosley, *Mol. Cryst. Liq. Cryst.*, **37**, 213 (1976).

(5) D. Coates and G. W. Gray, *J. Chem. Soc., Perkin Trans. 2*, 863 (1976).

(6) L. T. Sandborn and E. W. Bousquet, "Organic Syntheses", Collect. Vol. I, Wiley, New York, 1941, p 526.

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TABLE I: Transition Temperatures, Enthalpies, and Entropies of Compounds I[e]

	solid–S_A, –Ch, or –I			S_A–Ch or –I			Ch–I		
compd	T	ΔH	ΔS	T	ΔH	ΔS	T	ΔH	ΔS
Ia	137.0	22.6	55.2	129.4	0.10	0.25	[311]		
Ib[a]	182.4	23.6	51.7				[386]		
Ic	173.1	32.5	72.7				[350]		
Id	182.1	26.4	58.1				291.6	1.38	2.44
Ie[b]	173.4	33.2	74.4				295.1	1.88	3.31
If[c]	134.2	18.0	44.1				210.3	0.50	1.03
Ig[d]	154.3	30.8	71.9				176.5	0.29	0.62
Ih	135.7	29.6	72.3				(91.5)	0.17	0.47
Ii	173.8	36.8	82.3				[100]		
Ij	191.3	26.7	59.8	(191.0)	0.99	2.15	[365]		
Ik	265.3	42.6	79.1				[342]		
Ii	158.9	32.2	74.5				244.8	1.04	2.03
Im	196.8	31.6	67.3				247.7	0.93	1.79
In	212.9	32.3	66.5				259.2	1.10	2.07
Io	208.9	36.8	76.4				(204.8)	0.72	1.51
Ip	177.5	37.1	82.3	(105.8)	0.08	0.21	217.6	0.67	1.49

[a] This compound underwent a crystal–crystal transition at 127.6 °C. [b] This compound underwent a crystal–crystal transition at 164.8 °C. [c] This compound underwent a crystal–crystal transition at 119.5 °C. [d] This compound underwent a crystal–crystal transition at 143.1 °C. [e] The round and square brackets indicate the monotropic and extrapolated transition temperatures, respectively. Units: T, °C, ΔH, kJ mol^{-1}; ΔS, J K^{-1} mol^{-1}.

TABLE II: Transition Temperatures, Enthalpies, and Entropies of Compounds II[c]

	solid–S_A, –Ch, or –I			S_A–Ch or –I			Ch–I		
compd	T	ΔH	ΔS	T	ΔH	ΔS	T	ΔH	ΔS
IIa	135.9	29.5	72.1	176.7	0.35	0.78	257.7[a]	0	0
IIb	190.6	26.0	56.1	228.4	0.26	0.52	[339]		
IIc	201.9	39.8	83.8	[149]			[302]		
IId	156.4	20.2	47.3	192.2	1.01	2.21	269.1	0.47	0.89
IIe	198.9	40.9	86.5	[143]			275.2	0.99	1.81
IIf	127.4	29.6	73.8	132.7	0.66	1.63	170.3	0.33	0.74
IIg	145.7	38.2	91.2	(105.5)	0.92	2.43	(125.1)	0.28	0.70
IIh	118.5	36.7	93.8	(66.9)[a]			[48]		
IIi	160.1	37.2	85.9	[72]			[50]		
IIj[b]	193.0	14.7	31.4	237.9	2.27	4.43	[310]		
IIk	284.8	44.2	79.2				289.3[a]		
IIi	139.8	27.9	67.4	153.0	0.58	1.36	206.8	0.68	1.42
IIm	186.3	28.9	62.9	(151.6)	0.52	1.22	202.4	0.56	1.18
IIn	200.9	30.3	63.9	(190.0)[a]			217.8	0.65	1.32
IIo	197.7	35.2	74.8	[175]			[163]		
IIp	117.4	17.4	44.7	156.4	1.79	4.17	185.7	0.26	0.56

[a] This transition was not detected on a DSC thermogram. [b] This compound underwent a crystal–crystal transition at 162.7 °C. [c] The round and square brackets indicate the monotropic and extrapolated transition temperatures, respectively. Units: T, °C; ΔH, kJ mol^{-1}; ΔS, J K^{-1} mol^{-1}.

hexylcarbobenzoic acid were prepared from 4-hydroxybenzoic acid and benzoyl chloride or cyclohexanecarboxylic acid chloride.[7] 4-(Benzoylamino)benzoic acid was prepared by the reaction of 4-aminobenzoic acid and benzoyl chloride.[8] Azobenzene-4-carboxylic acid was purchased from Tokyo Kasei Co. The preparation of diphenyl-4-carboxylic acid, 4-benzoylbenzoic acid, 4-phenoxybenzoic acid, 4-(phenylthio)benzoic acid, and *trans*-4-benzoylcyclohexanecarboxylic acid has been described in a previous paper.[9] Cholesterol and β-sitosterol were interacted with the acid chlorides in dry pyridine at room temperature, giving the corresponding esters,[9] except for Ic and IIc. Ic and IIc were prepared by the interaction of cholesteryl and β-sitosteryl 4-aminobenzoates with benzaldehyde.[10] All esters were purified by column chromatography on silica gel, followed by recrystallization from absolute ethanol or a solvent mixture of absolute benzene and ethanol. The purity was checked by elementary analysis and thin-layer chromatography (E. Merck, Silica Gel 60 F_{254}, TLC plates).

Results

The transition temperatures, enthalpies, and entropies for the cholesteryl esters (I) and β-sitosteryl esters (II) are shown in Tables I and II. The cholesteric phases of I and II show a typical focal conic texture. The smectic phases, showing a typical fan-shaped texture, were identified as a smectic A modification by an examination of the binary-phase diagrams in which cholesteryl myristate was used as a standard.[14,15] For example, Figure 1a shows a miscibility diagram for a mixture of IIg and cholesteryl myristate. The smectic A–cholesteric (S_A–Ch) transition temperatures show an ideal-solution behavior, indicating that the smectic phase for IIg is correctly assigned as being a S_A modification.

Some derivatives decompose at above 250 °C without any indication of a sharp transition from the cholesteric phase to the isotropic liquid. Therefore, we determined the virtual transition temperatures by extrapolation from the phase diagrams of the binary mixtures of these esters and cholesteryl benzoate (T_{mp} = 145.6 °C; $T_{Ch\text{-}I}$ = 181.6 °C).[11] For example, the cholesteric phase for Ic disappeared gradually at around 290 °C on the first heating. In the phase diagram for a mixture of Ic and cholesteryl benzoate (Figure 1b), the Ch–I transition temperatures increase almost linearly with increasing concentration of Ic in the range between 0 and 70 mol %, show a large deviation thereafter, and then become a plateau at ca. 290 °C. These abnormal features indicate that compound Ic decomposes around 290 °C. Generally, the nematic–isotropic (N–I) transition temperatures in the binary-

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(7) W. R. Young, I. Haller, and D. C. Green, *J. Org. Chem.*, **37**, 3707 (1972).

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(9) M. Koden, S. Takenaka, and S. Kusabayashi, *Bull. Chem. Soc. Jpn.*, **55**, 2460 (1982).

(10) J. S. Dave and G. Kurian, *Mol. Cryst. Liq. Cryst.*, **24**, 347 (1973).

(11) V. C. Wiegand, *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys. Biol.*, **4**, 249 (1949). Cholesteryl benzoate: T_{mp} = 149 °C, $T_{Ch\text{-}I}$ = 180 °C. Id: T_{mp} = 179 °C, $T_{Ch\text{-}I}$ = 290 °C.

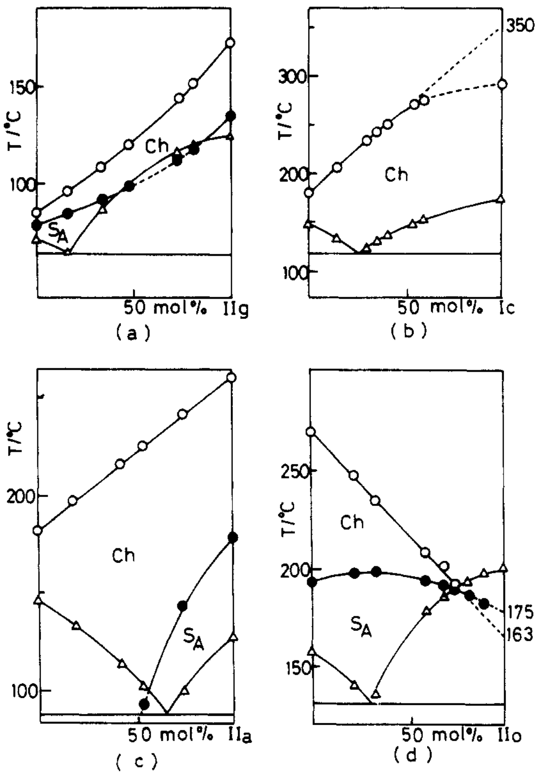


Figure 1. Miscibility diagrams for mixtures of (a) cholesteryl myristate (left) and IIg (right), (b) cholesteryl benzoate (left) and Ic (right), (c) cholesteryl benzoate (left) and IA (right), and (d) IId (left) and IIo (right). In (a), (c), and (d), the S_A–Ch (I) transitions indicated by the dotted lines are monotropic. Extrapolated transition temperatures are indicated.

phase diagram show a linear correlation with composition, when the components have similar thermal properties. Therefore, we assume that the extrapolated value (350 °C) is close to the true transition temperature for Ic, though this value may be slightly high compared with the value (ca. 300 °C) for cholesteryl 4-[(4-alkoxybenzylidene)amino]benzoates.[10]

The latent heat for the Ch–I transition of IIa is so small that the transition could not be detected by the DSC thermogram. However, the miscibility diagram (Figure 1c) for a mixture of cholesteryl benzoate and IIa indicates that the Ch–I transition for IIa occurs at 257.7 °C. All values in square brackets in Tables I and II were obtained similarly.

Although some compounds did not show any mesophase, for the purpose of this comparative study, the transition temperatures were roughly evaluated by the extrapolation from the miscibility diagrams. For example, compound IIo exhibits only a smectic A phase; the S_A–I transition occurs at 175 °C. In the miscibility diagram (Figure 1d), the virtual Ch–I transition also occurs at 163 °C.

Although the transition temperatures for Ij and IId are very different from reported values,[12,13] we believe that our values are more close to the true transition temperatures.

Discussion

Cholesteric–Isotropic Transition. In the present series, the change in molecular geometry associated with replacing the central linkage can be regarded as negligible, because the cholesteryl and β-sitosteryl groups and the two phenyl and/or cyclohexyl groups are so large. In addition, all molecules have no very polar group, so that it can be assumed that the molecular arrangement in the cholesteric and smectic A phase is almost unchanged by replacing the central linkage. Under these conditions, the polarizability of the entire molecule is assumed to be of primary importance in determining the thermal stability of the cholesteric phase.

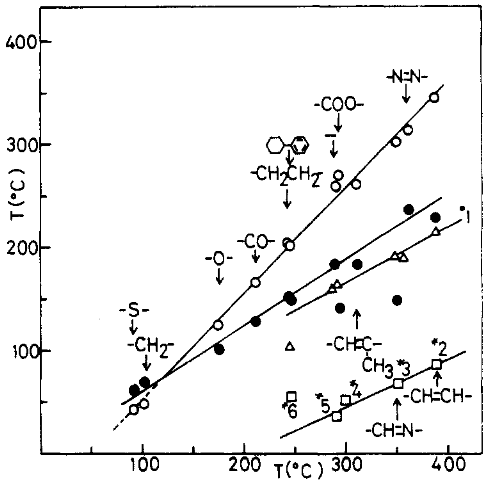


Figure 2. Plots of Ch–I transition temperatures for cholesteryl esters (I) against Ch–I (○) and S_A–Ch (I) (●) transition temperatures for II, N–I (△) transition temperatures for III, and N–I (□) transition temperatures for IV: *1, N. H. Tinh, A. Zann, and J. C. Dubios, *Mol. Cryst. Liq. Cryst.*, **53**, 43 (1979); *2, R. J. Cox and N. J. Clecak, *Mol. Cryst. Liq. Cryst.*, **37**, 263 (1976); *3, C. Tani, *Appl. Phys. Lett.*, **19**, 241 (1976); *4, D. Coates and G. W. Gray, *Mol Cryst. Liq. Cryst.*, **37**, 249 (1976); *5, G. W. Gray, *J. Phys.*, **36**, C1-338 (1975); *6, T. Szezucinski and R. Dabrowski, *Mol. Cryst. Liq. Cryst.*, **88**, 53 (1982).

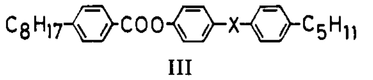
The effective order of the central linkages for the thermal stabilities of the cholesteric phases in Tables I and II can be summarized as

$$-CH{=}CH- > -N{=}N- > -CH{=}N- > -CONH- > -CH{=}C(CH_3)- > -COO- > \text{none} > -CH_2CH_2- > -CO- > -O- > -S- > -CH_2-$$

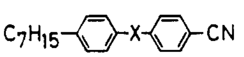
The order is roughly consistent with that reported for another system.[1-3] The last four linkages are known to be so-called "nonmesogenic" central linkages. These linkages result in increases in the molecular breadth, decreasing the mesophase stabilities.

In Figure 2, Ch (N)–I transition temperatures for some liquid crystals are compared with the Ch–I values for cholesteryl esters (I). The Ch–I transition temperatures for the β-sitosteryl esters (II) show a linear correlation with a slope of unity, indicating that these two related series have very similar structural and electric characteristics.

For the related series III and IV, the N–I transition temperatures tend to form straight lines, where the slopes are apparently less than unity. However, some of them show a marked deviation from the lines. For the cyano compounds VI, the N–I transition temperatures for the phenylcyclohexane compounds show a positive deviation (ca. 50 °C) from the straight line. The enhanced nematic stability has been accounted for in terms of the difference in the molecular arrangement in the mesophases.[16] In both III and IV, the N–I transition temperatures for the compounds incorporating a $-CH_2CH_2-$ linkage show a negative deviation from the straight lines, i.e., 30 and 50 °C, respectively. The following facts are noteworthy in this connection. In the cholesteryl and β-sitosteryl



III



IV

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(12) E. M. Barrall II, J. F. Johnson, and R. S. Porter, *Mol. Cryst. Liq. Cryst.*, **8**, 27 (1969). Ij: T_{mp} = 192.4 °C, T_{Ch-I} = 185.3 °C.

(13) C. Motoc, Savin, and I. Baciu, *Mol. Cryst. Liq. Cryst.*, **53**, 69 (1979). IId: T_{mp} = 162 °C, $T_{S_A\text{-}Ch}$ = 181 °C, T_{Ch-I} = 232 °C.

(14) J. H. Wendorff and F. P. Price, *Mol. Cryst. Liq. Cryst.*, **24**, 129 (1973).

(15) B. M. Craven and G. T. DeTitta, *J. Chem. Soc., Perkin Trans. 2*, 814 (1976).

(16) A. J. Leadbetter and A. I. Mehta, *Mol. Cryst. Liq. Cryst.*, **72**, 51 (1981).

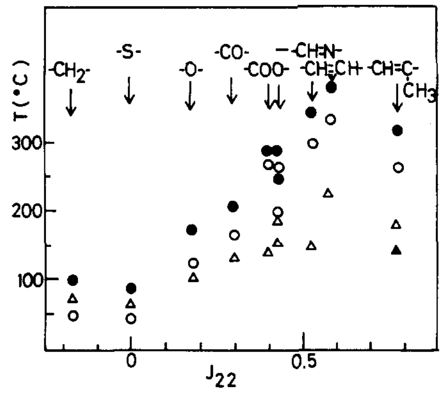


Figure 3. Plots of J_{22} against transition temperatures: Ch–I (●) and S_A–Ch (I) (▲) transition temperatures for compounds I; Ch–I (○) and S_A–Ch (I) (△) transition temperatures for compounds II.

esters, the thermal rotation around this linkage scarcely increases the breadth of the entire molecules, because the steroid cores have sufficiently large molecular breadths. On the other hand, thermal rotation around the $-CH_2CH_2-$ linkage should result in a remarkable increase in their molecular breadths, since the cores of III and IV are considerably smaller than those of the steroids.

Recently, Destrade et al. have proposed a close relation between an angular correlation parameter J_{22} and the mesogenic power for several angular and linear rigid cores. The angular correlation parameters have been measured by means of depolarized Rayleigh scattering of liquids or solutions in an isotropic solvent.[17-19] The expression is

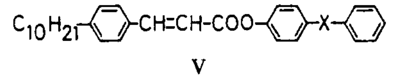
$$J_{22} = Z\langle 3 \cos^2 \theta - 1 \rangle / 2$$

θ is the angle between the symmetric axis of one molecule with Z neighbors. The parameter is known to be in some way proportional to the molecular polarizability. The parameters have been compared with mesogenic powers for some model compounds. Although their results indicate the importance of the parameter for indexing the mesogenic power, they have not succeeded in reaching any quantitative relation.[19]

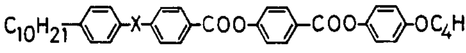
Figure 3 indicates the plots of the Ch–I transition temperatures for the cholesteryl esters (I) and β-sitosteryl esters (II) against J_{22} of the cores. Apparently, the transition temperatures for I and II show very good correlations with J_{22} in the range between $J_{22} = 0$ and 0.7, indicating that the polarizability of the carboxy portion is of primary importance in determining the transition temperatures in the related series.

An interesting fact in Figure 3 is that the transition temperatures increase with increasing J_{22}, where the discontinuity in the plots between If–Ih and Ia–Ie or IIf–IIh and IIa–IIe appears to be quite small, whereas If–Ih and IIf–IIh have appreciably bent geometries. These facts indicate that the steroid skeletons are large enough to cover the increased molecular breadth around the carboxy portions.

For comparative purposes, the plots of the N–I transition temperatures for V and VI against J_{22} are shown in Figure 4. The



V



VI

plots reveal apparent discontinuities and are divided into two classes: the related series having the bent linkages and linear linkages. This trend is very remarkable in VI. The temperature gap is ca. 130 °C for VI and ca. 70 °C for V. In compounds I and II, the temperature gaps appear to be small compared with those for V and VI. These facts indicate very clearly that J_{22} values do not precisely reflect the geometrical factors of the molecules, while the molecular geometry is very important in determining the thermal stability of the mesophase. An interesting fact in this connection is that the Ch–I transition temperatures for IIa and Ia are very low, while the $C_6H_5-CH{=}CH(CH_3)-C_6H_5$ group has a large J_{22} value. The increased molecular thickness around the carboxy portion due to strong repulsive interaction between the methyl and phenyl groups is proposed to account for the depression of the cholesteric stabilities.

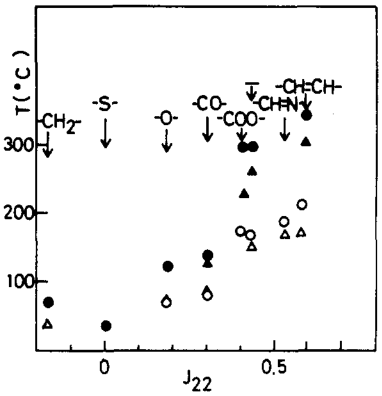


Figure 4. Plots of J_{22} against transition temperatures: N–I (○) and S_A–N (I) (△) transition temperatures for compound V;[20] N–I (●) and S_A–N (I) (▲) transition temperatures for compound VI.[20]

Our interest is whether the good correlation illustrated in Figure 3 is held irrespective of the J_{22} value or not. Recently, Destrade et al. have reported some core groups having extremely large J_{22} values: phenyl pentafluorobenzoate (3.0) and pentafluorphenyl pentafluorobenzoate (2.7).[19] However, the Ch–I transition temperatures for the steroid esters incorporating these linkages should not have very high Ch–I transition temperatures expected from Figure 3. A characteristic of these linkages is that they have large polarizabilities and dipole moments, simultaneously. Although we do not know the reason, the following facts in connection with large dipole moment are noteworthy. In general, liquid crystals having a polar terminal group such as nitrophenyl and cyanophenyl tend to form antiparallel dimers that are more or less interdigitated, in order to cancel their local dipoles; the interdigitated dimers are considered to be responsible for the enhanced mesophase stability.[21] When a substituent is introduced adjacent to the polar group in order to suppress the formation of the dimers, the nematic properties are considerably depressed, while the introduction of the substituent results in an increase in the parallel component of the permittivity.[22,23] Similarly, polar liquid crystals with a tropolone skeleton, where the dipole moment along the molecular axis is 3.5 D, show quite low nematic and smectic stability. The large molecular breadth has been proposed to explain suppression of the formation of antiparallel dimers.[24] Another example is that some liquid crystals incorporating a number of fluorine atoms or a trifluoromethyl group show remarkably low mesophase stabilities, especially in cases of smectic ones.[25-29] It has been known that these groups tend to suppress

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(17) C. Destrade, H. Gasparoux, and F. Guillon, *Mol. Cryst. Liq. Cryst.*, **40**, 163 (1977).

(18) C. Destrade, N. H. Tinh, and H. Gasproux, *Mol. Cryst. Liq. Cryst.*, **59**, 273 (1980).

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the formation of antiparallel dimers formed by the more common polar liquid crystals.[28,29] A characteristic of these substituents is that they have large local dipole moments (fluorobenzene, 1.66 D; trifluoromethylbenzene, 2.63 D[30]) considering their bond lengths and van der Waals radii. Throughout these compounds, we can recognize that the resultant strong dipoles scarcely enhance the mesophase stabilities of the molecules. Thus, molecules having large dipole moments appear to give rise to different mesomorphic properties from those of nonpolar liquid crystals and do not have highly stable mesophases. Therefore, we conclusively assume that the good correlation between $T_{\mathrm{Ch-I}}$ and J_{22} gradually disappears with increasing J_{22}.

The Thermal Behavior of the Smectic A Phase. Recent work has shown that there are four kinds of molecular arrangements in a smectic A phase: monolayer (S_{A1}), bilayer (S_{A2}), antiphase ($S_{\tilde{A}}$), and partially bilayer (S_{Ad}), i.e., having a layer thickness between 1 and 2 times that of the molecular length.[21] Usually, nonpolar liquid crystals give rise to only the S_{A1} phase, and the other arrangements have been found in polar liquid crystals and some binary mixtures. Of course, these S_A phases have different thermal properties. Therefore, it is very important in this work to characterize the smectic phase type for the present compounds. It would be reasonable to assume that the smectic A phase for the present compounds forms only the S_{A1} arrangement of the molecules, because the S_A–N transition temperatures show a linear correlation with additivity in some binary mixtures involving cholesteryl myristate or 4-pentylphenyl 4-[(4-octylbenzoyl-oxy)]benzoate having a S_{A1} phase. The present compounds have very similar molecular geometries, as mentioned above. Therefore, the changes in S_A–Ch (I) transition temperatures should be correlated with the electric properties of the carboxy portions. The plots of the S_A–Ch (I) transition temperatures for the related series II against the Ch–I transition temperatures for I are shown in Figure 2. The plots tend to show a linear correlation, perhaps due to their geometrical and electric similarities. However, the plots for compounds IIc and IIe incorporating relatively large dipole moments (cf. 1.57 D[31] for C_6H_5—CH=N—C_6H_5 and 1.9 D for C_6H_5—COO—C_6H_5[32]) show a remarkable negative deviation. Moreover, the slope in Figure 2 is less than unity. A similar trend is also recognized in Figure 3. Although the S_A–Ch (I) transition temperatures in the figure tend to increase with increasing J_{22}, the changes are less than those for the Ch–I transition temperatures. These facts suggest that the increased dipolarity of the molecules interrupts the monolayer layer arrangement of the molecules.

Recent work has shown the importance of a longitudinal molecular dipole in determining the molecular arrangement in mesophases.[33-35] Our extended model for the depression of the smectic stabilities is shown in Figure 5. In this model, we refer to only the dipole correlations in order to simplify, though the geometry of molecule is also important for the mesomorphic phenomena, as mentioned above.

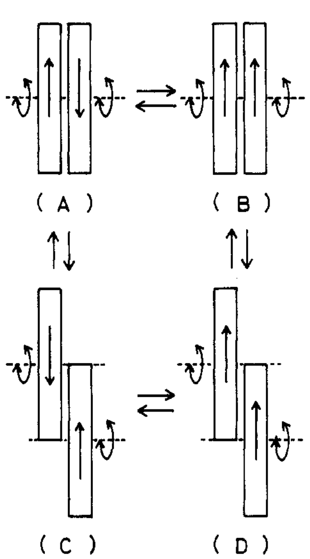

Figure 5. Possible molecular arrangements in a smectic A phase and the dipole correlations. Rectangles and arrows indicate mesogenic molecules and longitudinal components of dipole moments, respectively.

In nematic (cholesteric) and smectic A phases in which the dipole correlations are as shown above, the molecules would rotate less freely around the longitudinal axis. It would be reasonable to assume that the molecules at elevated temperature stay in each state for a period of a microsecond. Energetically, [A] and [B] should be the most stable, since their molecular volumes are less than the others. Under these conditions, the dipole–dipole interaction is attractive in the pair [A] but repulsive in [B]. The dipole–dipole interaction in [C] should be weaker than in [B], since the interaction energy is proportional to R^{-3} (R is the distance between dipoles). For nonpolar liquid crystals, in general, the molecules in the S_{A1} phase stay in an equilibrium between [A] and [B]. However, the pair [B] would gradually become unstable with increasing molecular dipolarity, and at last [B] becomes less stable than [C]. Such conditions i.e., an increase in the populations of [C] and [D], would result in the nematic arrangement of the molecules. At low temperature, on the other hand, the population of [A], the most stable configuration, should increase, since the molecular motion becomes slow, increasing the smectic character of the entire system.

Liquid crystals having a cyano or a nitro group at the terminal generate a very strong longitudinal dipole. In order to cancel the strong local dipole, such molecules form tight antiparallel dimers having the [C] and/or [A] configurations. However, it is not possible for the antiparallel pairs to form the smectic ordering, since the pairs still keep the strong dipole of the entire molecule. The pairs form the smectic ordering (S_{Ad} or S_{A1}) only when the molecules have a sufficiently long alkyl or an alkoxy chain. The alkyl or the alkoxy group is assumed to increase the short-range interaction around the saturated chain and to decrease the repulsive dipole–dipole interaction around the cores by increasing the intermolecular distance. The formation of the S_{A2} type's arrangement of the molecules is also explicable by a similar model.[36]

In the present work, compounds IIa, IIb, IId, and IIj, in which the core groups are rigid but not polar, give rise to stable S_A phases. On the other hand, compounds IIc and IIe, in which the core groups –CH=N– and –COO– have relatively large longitudinal dipoles, show a remarkable negative deviation from the straight line in Figure 2. Similarly, compounds IIo and IIp give rise to the more stable S_A phase than IIf and IIg. In these cases, the cores of the formers are less polar than those of the latter. Compound IIl, having a flexible and nonpolar linkage –CH_2CH_2–, gives rise to a more stable S_A phase than IIc and IIe. In compounds IIf–IIi, the bent geometries decrease the cholesteric stabilities but still produce S_A phases. These results are reasonably explained in terms of the dipole correlation model in Figure 5. The thermal properties of the smectic A phase have been successfully formulated by McMillan[37] by introducing the concept of a density wave to Maier–Saupe theory. He introduced a new

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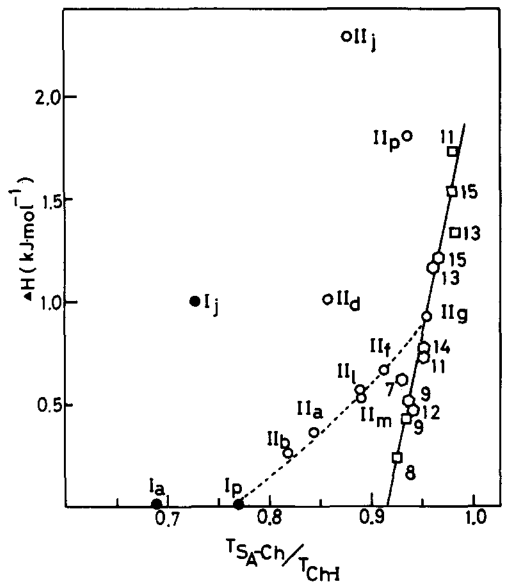

Figure 6. Plots of transition enthalpies against the ratio of $T_{S_A\text{-}Ch}/T_{Ch\text{-}I}$ for compound I (●), compound II (○), cholesteryl alkanoates (J. Y. C. Chu, *J. Phys. Chem.*, **79**, 119 (1975)) (□), and cholesteryl ω-phenylalkanoates (J. L. W. Pohlmann, W. Elser, and P. R. Boyd, *Ml. Cryst. Liq. Cryst.*, **20**, 87 (1973)) (○). Numbers indicate the carbon numbers in the alkyl chains.

parameter σ (interaction strength) which was in some way proportional to the ratio of the molecular length of the hard-core portion to the layer spacing in a smectic A phase, and is a criterion for the thermal stability of the smectic A phase. He found that some S_A–N transitions become second order; i.e., the latent heat for the transition vanishes.

In Figure 6 are plotted the latent heats for the S_A–Ch transitions against the $T_{S_A\text{-}Ch}/T_{Ch\text{-}I}$, where the latent heats for cholesteryl ω-phenylalkanoates and cholesteryl alkanoates are also plotted for comparison. The latent heats for the cholesteryl ω-phenylalkanoates and cholesteryl alkanoates tend to converge on the solid line and intersect at 0.92. Although the value is different from the predicted value (0.87) by McMillan, the smectic properties roughly follow the McMillan theory. Similarly, the latent heats on the dotted line in Figure 6 for the present compounds tend to decrease with increase in the ratio. The ratios of $T_{S_A\text{-}Ch}/T_{Ch\text{-}I}$ for compounds Ia and Ip are 0.69 and 0.77, respectively, at which the latent heat for the former is ca. 100 J mol^{-1} and 80 J mol^{-1} for the latter, suggesting the second-order nature of the S_A–Ch transitions. As far as we know, the second-order-type transition from S_A to Ch (N) phases in nonpolar liquid crystals is rare, though S_{Ad}–N and S_{A1}–N transitions in polar liquid crystals frequently show the second-order nature.[21] The dotted line intersects at 0.77, which is quite small compared with the predicted value by McMillan. On the other hand, the latent heats for the present compounds show remarkable deviations from the dotted line. For example, the latent heats for Ij and IIj are 2.15 and 4.43 kJ mol^{-1}, while the ratios of $T_{S_A\text{-}Ch}/T_{Ch\text{-}I}$ are 0.73 and 0.88, respectively. Strictly speaking, therefore, the smectic properties for the present compounds do not follow McMillan theory. A polar interaction around the aryl portions is proposed to explain the abnormal behaviors for the smectic phase.

Conclusion

The Ch–I transition temperatures for cholesteryl and β-sitosteryl esters provide good criteria for the prediction of mesophase stability. Although the J_{22} parameters are also good parameters for the prediction, these sometimes do not properly reflect molecular parameters dependent upon geometrical and electric factors. The smectic stability even in nonpolar liquid crystals is strongly affected by a polar interaction involving the aryl and linking groups.

Search for Tricritical Points in Ternary Systems: Water–Oil–Nonionic Amphiphile

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(Received: July 8, 1985; In Final Form: October 8, 1985)

In a recently published paper we have suggested considering the phase behavior of ternary systems of the class H_2O–oil–nonionic amphiphile as a near-tricritical phenomenon. In this paper we demonstrate how to search for the tricritical points in such systems. We show that they can be reached, at least in principle, either by increasing the pressure, by changing the hydrophobicity of the oil or the amphiphilicity of the amphiphile within a homologous series, or by adding an appropriate electrolyte. Furthermore, we summarize the features of the phase behavior, in particular the three-phase temperature interval, its mean temperature and the efficiency of the amphiphile as they depend on the amphiphilicity of the amphiphile and the hydrophobicity of the oil, in order to supply the basis for a consistent theory of the microstructure of such systems.

Introduction

As we have shown in a series of papers,[1-5] the phase behavior of ternary systems of the class H_2O (A)–oil (B)–nonionic amphiphile (C) is determined by the interplay of the (lower) miscibility gap of the binary system A–B with the (lower) gap of the system B–C and the upper loop of the system A–C. The phase diagrams of these three binary systems are shown schematically in Figure 1 which shows the unfolded phase prism of the ternary system with the Gibbs triangle as base and temperature T as ordinate. On the left one can see the phase diagram in the conventional density (wt %–T) representation, while on the right it is in field representation ξ–T, where ξ_i is a measure of the activity of component i.[5] In this representation the miscibility gaps reduce to lines terminating in the critical points. We should emphasize, however, that these lines are, in general, neither straight nor do they lie in the center of the ξ–T diagrams.

The UCP of the (lower) A–B gap lies well above the boiling point of the mixture. The UCST T_α of the (lower) B–C gap lies, in general, close to 0 °C, its position depending strongly on the chemical nature of both the oil and the amphiphile. The (upper) loop of the A–C system can be looked at as a vertical section through a "nose" in c–T–p space.[5] Accordingly, the loop may show up (as assumed in Figure 1) or may only "lurk" behind the c–T plane at 1 bar. The LCST T_β of the loop lies, in general, between

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