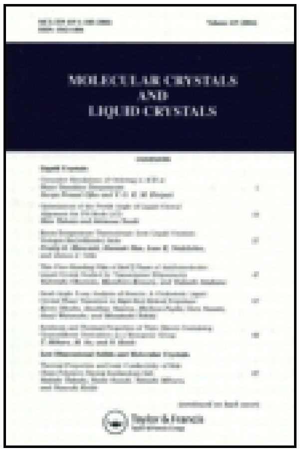

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Liquid Crystallinities of Some Homologous Series Having Bent Linkages-CO-,-O-,-S-, and -CH_2-

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Liquid Crystallinities of Some Homologous Series Having Bent Linkages —CO—, —O—, —S—, and —CH_2—

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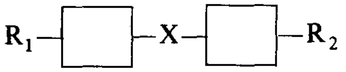
Some related series of liquid crystalline materials having bent linkages —CO—, —O—, —S—, and —CH_2— have been prepared. The thermal properties are discussed in geometrical and electronic terms of molecular structure.

INTRODUCTION

It is known that linearity, rigidity, and polarizability are the most important factors for a molecule to display liquid crystalline properties.[1] The general molecular structure for a liquid crystal material is



where the rectangles usually constitute an aromatic ring and/or cyclohexyl system, and R_1 and R_2 are alkyl, alkoxy, halogens, etc. The linkage X is usually —CH=CH—, —CH=N—, —COO—, —N=N—, etc., which are useful in the enhancement of linearity and polarizability of the molecule, thus increasing the stability of the mesophase. However, some linkages —CO—, —O—, —S—, —CH_2— have been known to be unfavorable for the thermal stability of the mesophase because these lead to a bent geometry of the molecular structure.[2] In fact the liquid crystal materials having these linkages are quite rare.[3] Recently we reported that some cholesteryl 4-substituted benzoates having these linkages formed relatively stable cholesteric phases.[4]

In this present paper we have tried to prepare some nonsteroid liquid crystalline materials having these linkages. The thermal properties will be discussed in relation to the geometrical and electronic structures of the molecule in connection with the Maier–Saupe model.

EXPERIMENTAL

Method

The transition temperatures were determined using a Nikon Model POH polarizing microscope fitted with a Mettler FP 52 heating stage and control unit. The transition entropies were calculated by the equation; $\Delta S = \Delta H/T$, where the transition enthalpies ΔH were measured with a Daini-Seikosha SSC 560 differential scanning calorimeter, indium (99.9%) being used as a calibration standard with a heating rate of 5 °C/min.

Preparation

4-*n*-Alkyl and 4-*n*-alkoxyphenols were purchased from Kanto–Kagaku Co. 4-*n*-Decylbenzoic acid and 4-*n*-decyloxybenzaldehyde were purchased from Tokyo-Kasei Co. 4-*n*-Alkyl-4′-hydroxybiphenyls were obtained according to the literature.[5] The preparations of 4-*n*-alkylphenyl-X-benzoic acids where X = —CO—, —O—, —S—, and —CH_2— have been reported in a previous paper.[6] 4-(4-Alkyl- and 4-(4-alkoxyphenoxycarbonyl)phenols were obtained by the condensation of 4-hydroxybenzoic acid and the corresponding phenols, according to the method of van Meter *et al.*[7] Ij was prepared by a Friedel-Craft benzoylation of 4-*n*-heptylterphenyl obtained by the method of Sadashiva *et al.*[8] The final products were prepared by standard methods.[9] Purification was attained by column chromatography over silica-gel (200 mesh) using an elution solvent of ether-pet.ether (2 : 98–10 : 90), followed by recrystallization from absolute ethanol or a solvent mixture of absolute ethanol and benzene. The purification of IVb was carried out by repeated recrystallization from absolute ethanol.

The purity of the products was checked by an elemental analysis and thin layer chromatography on Merck Silica-Gel 60, TLC plate, chloroform being used as a developing solvent. 4-Pentylphenyl 4-(3-cyano-4-octyloxybenzoyloxy)benzoate was prepared by the method of J. C. Dubois *et al.*[10]

Results

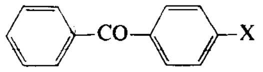
The thermal properties for the related series of I, II, III, and IV are summarized in Tables I, II, III, and IV, respectively. Some compounds do not exhibit any liquid crystal phases. For the comparative study, the virtual N–I transition temperatures were determined by extrapolation of the N–I transition,[11] as shown in Figure 1. For example, Ib has a virtual N–I temperature of ca. 18°C, 74°C below the melting point (see Figure 1a).

Although Id formed a nematic phase, the nematic–isotropic transition could not be detected by the DSC thermogram due to overlapping of the recrystallization peak.

The smectic phase was identified by co-miscibility with the standard materials 4-pentylphenyl 4-(3-cyano-4-*n*-octyloxybenzoyloxy)benzoate and 4-cyanobenzylidene-4′-*n*-octyloxyaniline (CBOOA) exhibit the smectic A and nematic phases. In Figure 1c, the smectic A–nematic

TABLE I

Transition temperatures (°C) and entropies (JK^{-1} $mole^{-1}$)



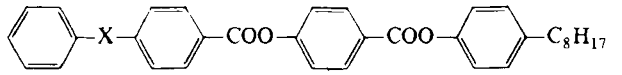
	X	C		N		I	ΔS_{N-I}
Ia	$-COO-C_6H_4-OC_4H_9$	.	113.0	—	[25]	.	
Ib	$-OCO-C_6H_4-OC_5H_{11}$	.	92.0	—	[18]	.	
Ic	$-CH{=}CH-COO-C_6H_4-C_5H_{11}$	.	104.5	—	(52.5)	.	1.5
Id	$-CH{=}CH-COO-C_6H_4-OC_4H_9$	.	119.0	—	(73.3)	.	—
Ie	$-COO-C_6H_4-COO-C_6H_4-OC_2H_5$	.	164.2	.	215.5	.	1.3
If	$-COO-C_6H_4-COO-C_6H_4-C_5H_{11}$	.	122.4	.	181.7	.	1.3
Ig	$-COO-C_6H_4-COO-C_6H_4-C_8H_{17}$	(1).	134.5	.	159.0	.	1.3
Ih	$-COO-C_6H_4-COO-C_6H_4-C_{12}H_{25}$	(2).	125.7	.	149.5	.	1.6
Ii	$-COO-C_6H_4-C_6H_4-C_8H_{17}$	.	155.0	—	(141.7)	.	—
Ij	$-C_6H_4-C_6H_4-C_7H_{15}$	.	200.1	—	[118]	.	

(1) and (2) These compounds underwent smectic A–nematic transitions at 118.0°C and 136.9°C, respectively.

The values in the brackets and parentheses indicate the virtual and monotropic transition temperatures, respectively. $-C_6H_4-$ indicates a para-phenylene group.

TABLE II

Transition temperatures (°C) and entropies (JK^{-1} $mole^{-1}$)



	X	C		S_A		N		I	ΔS_{N-I}
IIa	—CO—	.	134.5	.	(118.0)	.	157.0	.	2.2
IIb	—O—	.	110.0	—		.	112.8	.	1.5
IIc	—S—	.	118.4	—		—	[58]	.	
IId	—CH_2—	.	112.7	—		—	[75]	.	

The values in the brackets indicate the virtual transition temperatures.

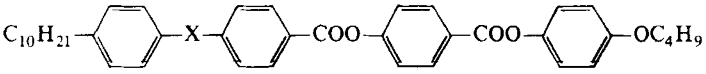
transition temperatures show almost a straight line, indicating that the smectic phase for Ih is the smectic A modification, presumably with a monolayer alignment of the molecules. The smectic A phases for both Ih and CBOOA are also miscible with showing weak convex curve (Figure 1d), whereas CBOOA forms an anti-parallel dimer of the molecules in the nematic and smectic A phases.[12] Some derivatives such as IIIa, IIIc, IVa, IVb, IVi, and IVj exhibit other smectic properties, but the classification has not yet been performed.

DISCUSSION

Nematic–isotropic transition temperatures—In the present series, the compounds are simply classified into two classes, i.e., the one being

TABLE III

Transition temperatures (°C) and entropies (JK^{-1} $mole^{-1}$)



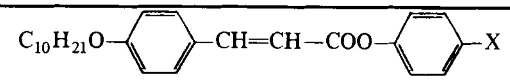
	X	C		S_A		N		I	ΔS_{N-I}
IIIa	—CH=CH—	(1).	134.3	—	[301]	—	[343]	.	
IIIb	—	.	127.5	.	261.9	.	295.1	.	1.3
IIIc	—COO—	(2).	151.2	.	227.2	.	294.2	.	1.6
IIId	—CO—	.	129.7	.	137.0	.	139.3	.	3.6
IIIe	—O—	.	118.6	—		.	121.1	.	2.2
IIIf	—S—	.	107.7	—		—	[35]	.	
IIIg	—CH_2—	.	103.0	—		—	[70]	.	

(1) and (2) These compounds underwent smectic–smectic A transitions at 212.7°C, and 143.2°C, respectively.

The values in the brackets indicate the virtual transition temperatures.

TABLE I

Transition temperatures (°C) and entropies (JK^{-1} mole^{-1})



$C_{10}H_{21}O-C_6H_4-CH{=}CH-COO-C_6H_4-X$

	X	C		S_A		N		I	ΔS_{S_A-N}	ΔS_{N-I}
IVa	$-CH{=}CH-C_6H_5$	(1).	144.3	.	172.6	.	214.6	.	1.1	2.2
IVb	$-CH{=}N-C_6H_5$	(2).	96.2	.	169.8	.	188.5	.	3.8	2.6
IVc	$-C_6H_5$	(3).	126	.	151	.	170	.		
IVd	$-COO-C_6H_5$	.	108.5	.	166.3	.	175.2	.	4.2	2.3
IVe	$-OCO-C_6H_5$	.	111.0	.	(94.2)	.	175.5	.	0.4	2.6
IVf	$-CO-C_6H_5$	.	119.1	.	(84.1)	—	[82]	.		
IVg	$-O-C_6H_5$	.	84.5	.	(72.2)	—	[71]	.	12	
IVh	$-CH_2-C_6H_5$	.	53.2	.	(37.1)	—		.	10	
IVi	$-N{=}N-C_6H_5$	(4).	86.8	.	153.3	.	179.2	.	3.0	2.7
IVj	$-CH_2CH_2-C_6H_5$	(5).	97.9	.	114.4	.	126.9	.	3.3	4.6
IVk	$-C_6H_{11}$	.	126.4	—	(110.0)	—	(124.0)	.	—	3.2

(1) and (2) These compounds underwent smectic–smectic A transitions at 126.3°C, and 99.1°C, respectively. (3) J. C. Dave and R. A. Vola, *Mol. Cryst. Liq. Cryst.*, **28**, 269 (1974). (4) and (5) These compounds underwent smectic–smectic A transitions at 87.4°C and 81.9°C, respectively. The values in the brackets and parentheses indicate the virtual and monotropic transition temperatures, respectively. $-C_6H_5$, and $-C_6H_{11}$ indicate phenyl and cyclohexyl groups, respectively.

regarded as a linear molecule and the other a bent molecule. Figure 2 indicates the dimensions for Ia, Ic, Ij, and IIId–IIIg where trans rather than cis conformations have been used because the former results in a more linear, rod-like molecular shape, a general requisite for mesophase stability. In the figures, the dotted lines indicate the long molecular axes passing though the gravity centers of the aromatic rings, except for the terminal benzoyl group.

Ia and Ib do not show any mesomorphic properties, and their virtual nematic–isotropic transition temperatures are quite low. The gravity center of the phenyl ring at the benzoyl function is far apart from the dotted line, and the ratio of the molecular length/breadth should be the smallest within the present series (Figure 2).

As is evident from the model in Figure 2, an introduction of the vinyl group will elongate the core portion, and reduce the bend at the terminal group. This might be the cause of an appearance of the nematic phase for Ic and Id. For Ie–Ih, the bend at the terminal function seems to be quite small relative to the core, and these exhibit high stability of the nematic phases.

A note worthy fact is that Ii exhibits a monotropic nematic phase and Ij does not exhibit any mesophases, whereas both compounds have four aromatic rings. The reason is that Ii contains only one ester

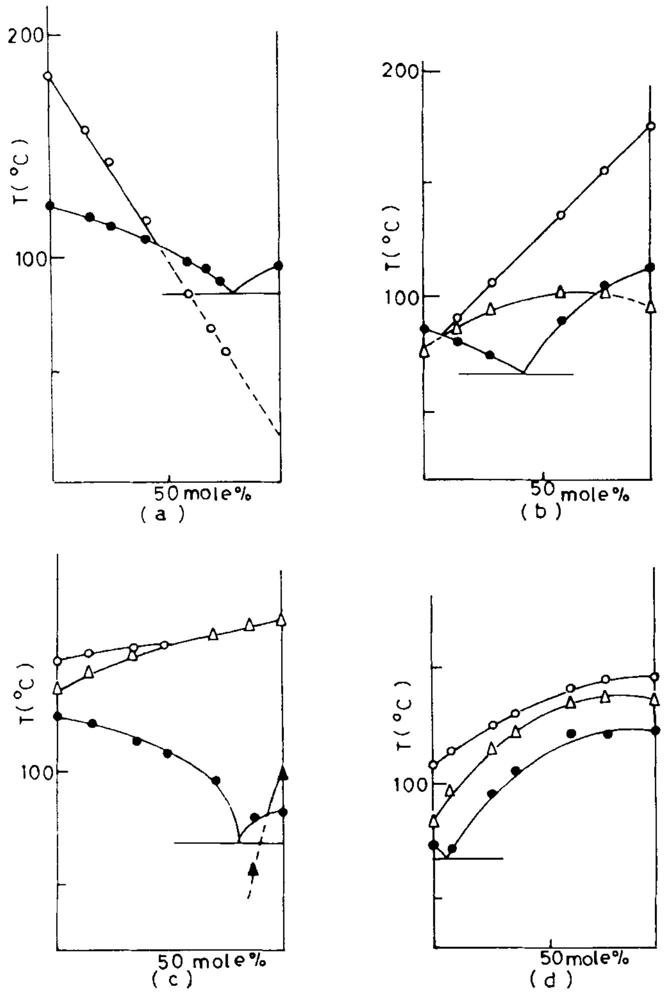


FIGURE 1 The phase diagrams for the binary systems of (a) If (on left) and Ib (on right); (b) IVg (on left) and IVe (on right); (c) Ih (on left) and 4-pentylphenyl 4-(3-cyano-4-*n*-octyloxybenzoyloxy)benzoate (on right); (d) CBOOA (on left) and Ih (on right); ○: nematic–isotropic; △: smectic A–nematic (isotropic); ●: crystal–smectic A (nematic, isotropic); and ▲: smectic C–smectic A transitions, respectively.

group which increases the polarity and polarizability of the molecule, and Ij no polar group except the benzoyl ketone. In addition, the terminal alkyl and benzoyl groups in Ij may be unfavorable for the linearity of the entire molecule, as shown in Figure 2c.

The effect of the linkage X upon the thermal stability of the nematic phase is examined in Table 2.

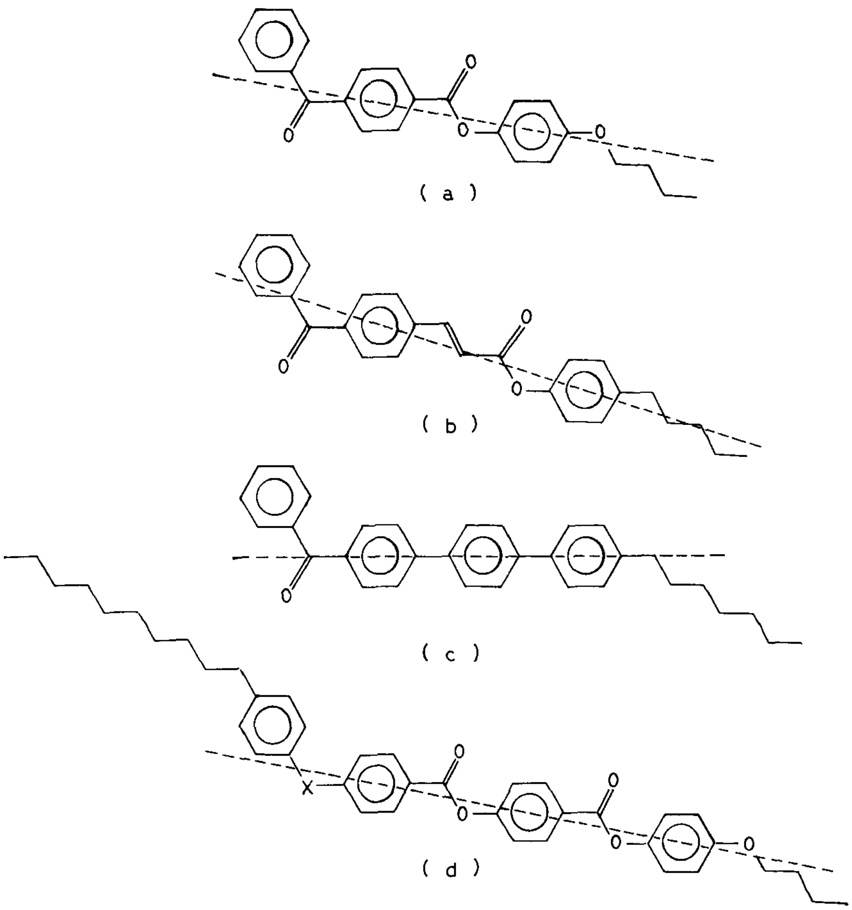
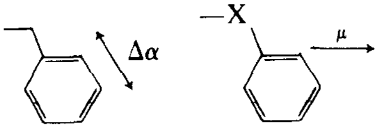


FIGURE 2 Schematic molecular structures for Ia, Ic, Ij, and IIId–IIIg (X = —CO—, —O—, —S—, or —CH_2—).

The effective ratio of the molecular length/breadth can be approximated to be almost constant throughout the series except for IIc, though the angles and bond lengths are considerably different for the cores ph—CO—ph (bond angle = 122°, bond length of the C—ph = 1.46 Å[13]), ph—O—ph (118, 1.41[14]), ph—S—ph (106, 1.75[14a]), and ph—C—ph (111, 1.49[15]). Whereas, the N–I transition temperatures have large differences where IIc and IId do not form a nematic phase. This might be connected to the anisotropic polarizabilities of the phenyl-X-groups. It has been reported that the anisotropic polarizability of the benzoyl group is 6 Å^3 along the longer axis.[16] As we can see from the figure shown below, the anisotropic polarizability of the benzyl group would disperse the anisotropic polarizability of the entire molecule, since the terminal phenyl group has an angle of ca. 60° with respect to the axis passing through the benzoate group. The decrease in the anisotropic polarizability will reduce the dispersion forces, depressing the N–I transition temperature. On the other hand, the relatively large dipolarities arising from the phenyl and carbonyl or ether groups in IIa and IIb have been known to direct towards the direction, as shown below,[17] and increase their anisotropies. The increased dipolarity would increase the polarizability along the direction, enhancing the thermal stability of the nematic phase.



X = —CO—, —O—

The molecular polarizability has been reported to be 244 cm^3 for benzophenone,[18] 80.3 for diphenyl ether,[19] 107.2 for diphenyl thioether,[20] and 59.3 for diphenylmethane.[21] Although we assume that the polarizability is very important in determining the mesophase stability, the effective order of the polarizability does not follow those of the N–I transition temperature for series II.

It is known that the thermal stability of a nematic phase is strongly dependent on the anisotropies of molecular geometry and electronic nature of the molecule. Maier and Saupe considered the difference in free energy (ΔF) between the nematic (cholesteric) phase and the isotropic phase, taking into account the attractive dispersion forces.[22]

This leads to

$$T_{\mathrm{N-I}} = A/4.54\,\mathrm{k}V^2 \tag{1}$$

where k and V are Boltzmann's constant and the molecular volume, respectively. The electronic terms of the molecule are incorporated in the factor A which is apparently proportional to the square of the anisotropy of the molecular polarizability.[23]

$$A \approx (\Delta\alpha)^2 \tag{2}$$

where $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$, $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the polarizabilities along the parallel and perpendicular directions with respect to the long molecular axis, respectively. On the other hand, recent studies suggest that the entropy contribution to ΔF due to steric intermolecular repulsions (repulsive forces) is also important and an expression which considers both contributions is

$$\Delta F = -An^2 - BTn^2 - TS(n) \tag{3}$$

where n and S represent the order parameter and the orientational entropy, respectively.[24] For a phase transition at constant volume ($\Delta F = 0$), the expression for the N–I transition temperature is

$$T_{\mathrm{N-I}} = 2A/(4.54k - 2B) \tag{4}$$

A precise expression for B cannot easily be given, but it seems plausible that B is in some way proportional to the effective length/breadth ratio of the molecule. Thus, the anisotropies of electronic and geometrical terms of the molecule are very important in determining the mesomorphic properties. In a practical sense, however, both terms tend to vary simultaneously, and it is not so easy to evaluate the relative importance of both terms.

The thermal stability of the nematic phase for the related series of III and IV are compared with the related series of cholesteryl 4-substituted benzoates for the cholesteric–isotropic transition temperatures (Ch–I). In Figure 3, the N–I transition temperatures are plotted for series III and IV as well as the Ch–I transition temperatures for β-sitosteryl 4-substituted benzoates against the Ch–I transition temperatures for cholesteryl 4-substituted benzoates.[25] It can be seen from eq. 4 that the N–I transition temperatures are a function of both A and B terms. If the geometrical and electronic contributions are similar to those for the cholesteryl esters, one would expect the plot to show a straight line with a slope of unity. The plot for β-sitosteryl esters is just the case.

It would be reasonable to assume that the horizontal axis is in some way proportional to the anisotropic polarizability of the entire molecule, if the change in the molecular volume by replacing the linkage X is practically small compared with the molecular volume, i.e., B being constant in Eq. 4. for the related series III and IV, however, the plots show apparent discontinuities and can be simply divided into two classes, i.e., the one being constituted of the linear molecules and the other so-called 'bent' ones. The discontinuity between two classes is 20°C or less for series IV and more than 150°C for series III. The small value for series IV indicates that the geometrical bend, i.e., the bent angle of ca. 60°, is negligibly small for the stability of the nematic phase. In contrast, the large discontinuity for series III indicates that

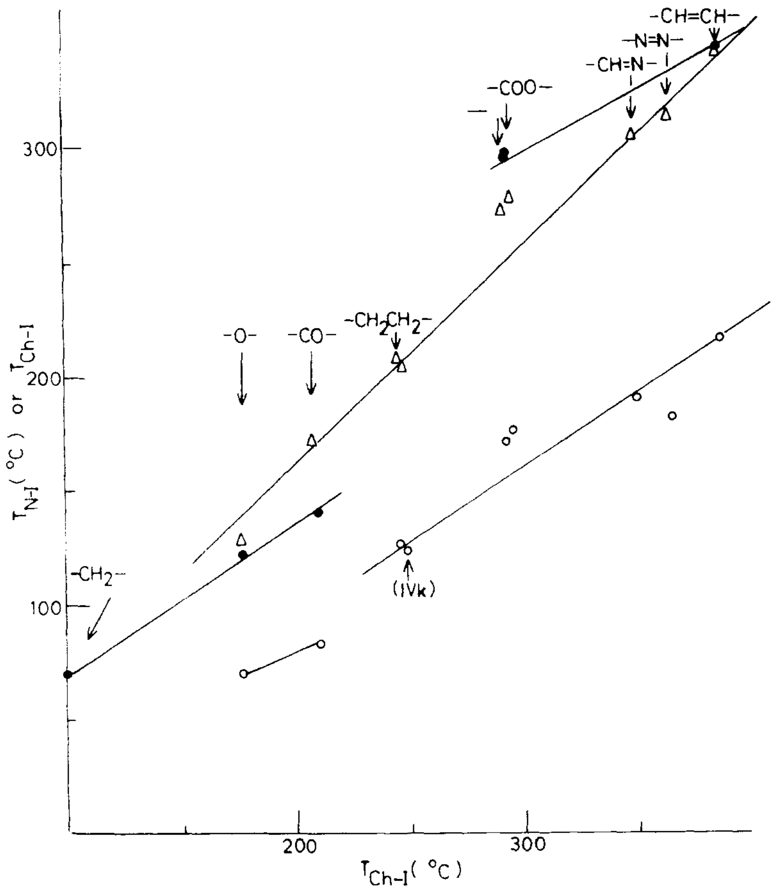
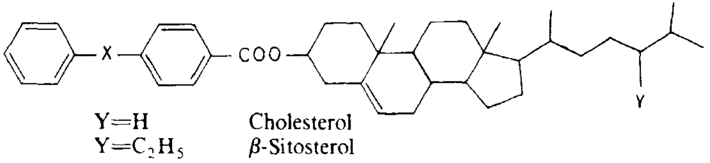


FIGURE 3 The plots of the nematic–isotropic transition temperatures for III (●) and IV (○) and the cholesteric–isotropic transition temperatures for β-sitosteryl 4-substituted benzoates (△) against the cholesteric–isotropic transition temperatures for cholesteryl 4-substituted benzoates.



the alkyl chain being slanted is very much unfavorable for the nematic stability. As is evident from Figure 2d, the terminal *n*-decyl group must increase considerably the molecular breadth due to the bent linkages —CO—, —O—, —S—, and —CH_2—. That is, the bent geometry near the center of the molecule is quite unfavorable for the stability of the nematic phase.[26]

In fact, Dewar *et al.* have led the similar conclusion from the consideration of symmetric thiophene and furan compounds for the nematic–isotropic transition.

For series III and IV the slopes are apparently less than that for the β-sitosteryl esters, and are almost similar throughout the series. The ratio of $T_{\text{N-I}}/T_{\text{Ch-I}}$ for series III or IV is given by

$$\frac{T_{\text{N-I}}}{T_{\text{Ch-I}}} = \frac{\dfrac{2A}{4.54k - 2B}(\text{for series III or IV})}{\dfrac{2A}{4.54k - 2B}(\text{for cholesteryl esters})} \tag{5}$$

As discussed above, we suppose that both B terms are almost constant, because the change in the molecular volume by replacing the linkage X is quite small compared with the entire molecular volume. Then, the ratio is simply given by

$$T_{\text{N-I}}/T_{\text{Ch-I}} = A\ (\text{series III or IV})/A\ (\text{cholesteryl esters}) \tag{6}$$

The plots for series III and IV show good correlation, indicating that the B terms for both series III and IV, and the cholesteryl esters can be approximated to be constant. The change in the A term by replacing the linkage X in series III and IV is less than that for the cholesteryl esters, because the expansion of the conjugated system for the former series is larger than that for the latter. Therefore, it is a matter of course that the slopes for both are less than unity. For series III, the slopes for the linear and bent molecules are similar to each other, whereas these plots have large discontinuities, indicating that the N–I transition temperatures are determined mainly by the A term, i.e., the anisotropy of the molecular polarizability.

Smectic A–nematic (isotropic) transition temperatures—The thermal stability of the smectic A phase is also essentially a function of both anisotropic polarizability and geometry of the molecule.

Extending the Maier–Saupe model to the smectic A phase, however, McMillan has presented a simple molecular model for smectic A phase of liquid crystals, where he has introduced a new parameter to evaluate the interacting forces along the lateral direction of molecule, an interacting strength α which is a function of the molecular length and the layer spacing in a smectic A phase.[27]

The S_A–N (I) transition temperatures for the related series of IV are plotted against the S_A–Ch (I) transition temperatures for the corresponding β-sitosteryl 4-substituted benzoates in Figure 4.

It would be reasonable to assume that the β-sitosteryl esters have so bulky structures that the change in the molecular volume by replacing

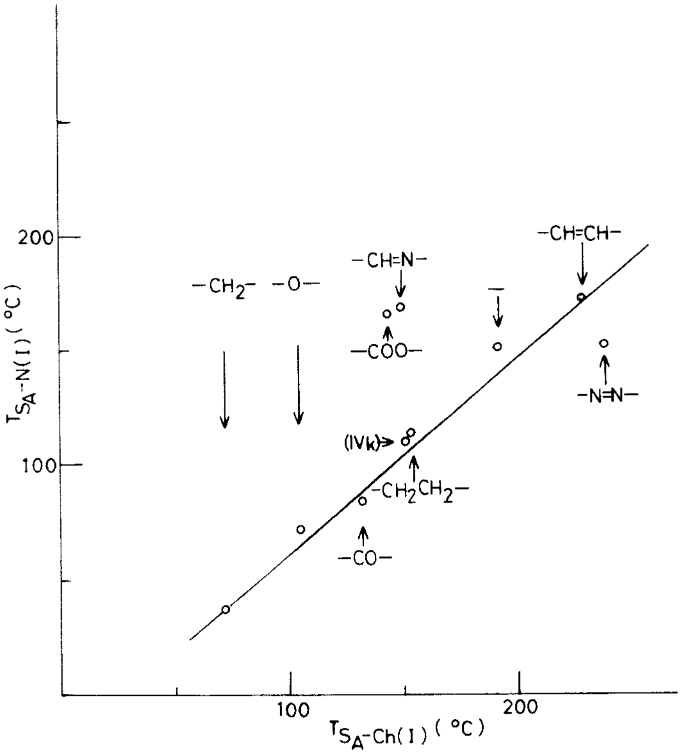


FIGURE 4 The plot of the smectic A—nematic (isotropic) transition temperatures for IV against the smectic A-cholesteric (isotropic) transition temperatures for β-sitosteryl 4-substituted benzoates.

the linkage X is negligibly small, as mentioned in the previous section. Therefore, the horizontal axis, i.e., the S_A–Ch (I) transition temperatures can be considered to be in some way proportional to the anisotropic polarizability of the molecule, though it is difficult to evaluate the effect of the interaction strength α on the thermal stability of the smectic A phase. The S_A–N (I) transition temperatures for series IV, except for IVb, IVd, and IVi, tend to be proportional to the S_A–Ch (I) transition temperatures for the β-sitosteryl esters, without showing any discontinuities. This fact indicates that the bent geometry in the related series of IV is less sensible for the thermal stability of the smectic A phase than that of the nematic phase.

Gray *et al.* reported that the even-odd effect on the thermal stability for the S_A–N transition temperatures in a homologous series of ω-phenylalkyl 4-(4-phenylbenzylideneamino)cinnamates was more moderate than that for the N–I transition temperatures.[28]

The slope in Figure 4 is less than unity, presumably due to the same reason mentioned in the previous section.

A noteworthy fact in the figure is that IVb and IVd show marked positive deviations from the straight line, and IVi shows negative one. These trends are more remarkable than those for the N–I transition temperatures in Figure 3.

A fact in common between three is that the linkages —COO—, —CH=N—, and —N=N— have relatively strong dipole moments along both parallel and perpendicular directions of the molecule, while the dipole moments for —N=N— along both directions just cancel within the linkage. Although it is difficult to discuss the effect of the dipole moment on the thermal stability of the smectic A phase, some authors have pointed out that the dipole across the long molecular axis is important in determining certain smectic properties.[29]

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