Molecular Structure and Smectic Properties. Part 1. The Effect of Linkages on Smectic A Thermal Stability in Three Aromatic Ring Compounds Linked by Ester Groups

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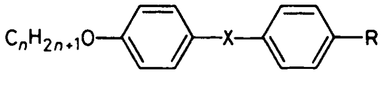
The thermal properties of phenyl 4-(4-alkoxybenzoyloxy)benzoates (**1**), 4-alkoxyphenyl 4-benzoyloxybenzoates (**2**), 4-(4-alkoxybenzoyloxy)benzoyloxyxylenes (**3**), and phenyl 4-(4-alkoxyphenoxycarbonyl)benzoates (**4**) have been examined. In spite of the structural similarity, the smectic nature of the series is quite different. Series (**1**) shows a stable smectic A phase starting with the hexyloxy homologue. Series (**2**) and (**3**) do not show any smectic phases, and the potential smectic stabilities evaluated from the binary phase diagrams are quite low. Although series (**4**) shows no smectic phase because of higher melting points, this series intrinsically possesses a smectic A nature, where the potential smectic A–nematic transition temperatures are as high as those of series (**1**). The difference in the smectic nature for these four series is discussed in terms of the geometrical and electrocstatic properties of the molecules, and a new basis for the thermal stability of the smectic A phase has been proposes.

Many liquid crystals have a hard core where both terminal positions are substituted by flexible alkyl chains, and the entire molecule possesses geometrical symmetry. Frequently, one of the terminal alkyl groups is replaced by relatively small substituents such as hydrogen, halogen, nitro, and cyano groups. In the unsymmetrically substituted molecules, the mesomorphic properties are fairly complex, and are strongly dependent on the electrostatic and geometrical nature of a linkage. A typical molecular structure is shown below:

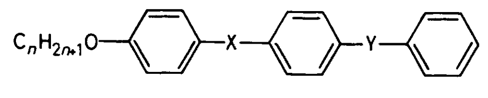


X = —COO—, —CH═N—
R = H, alkoxy, halogen, CN

In the ester systems (X = –COO–, R = halogen), the smectic nature of the molecules is strongly dependent on the orientation of the ester linkage with respect to the alkoxy group. That is, the molecules having X = –COO– are smectogenic, but the related compounds having X = –OOC– are non-mesogenic.[1,2] A similar trend is also observed in the azomethine systems (R = halogen, CN), *i.e.* the molecules having a –CH=N– linkage show more stable smectic phases than those in which the linkage is –N=CH–.[2]

When R is also an alkoxy group, the smectic nature is determined by the relative bulkiness of two alkoxy groups.[3,4] When R = CN, the molecular arrangement in the smectic A phase is also affected by the orientation of the ester linkage.[5] A similar trend has been observed in other systems incorporating biphenyl[6–8] and fluorene skeletons.[9,10] The effect of linkages such as ester and azomethine groups has been tentatively explained in terms of the electrostatic dipole–dipole and dipole–induced dipole interactions.[11] However, these results apparently suggest that the smectic properties of the molecules are strongly affected not only by the electrostatic interactions but also the geometrical circumstances.

In this paper, we have studied the mesomorphic properties of the following four series. Four series have one alkoxy group, and



	X	Y
(1)	–COO–	–COO–
(2)	–OOC–	–OOC–
(3)	–COO–	–OOC–
(4)	–OOC–	–COO–

(n = 5–14)

are different only in the orientation of two ester linkages with respect to the terminal alkoxy group.

The thermal properties of the smectic A phase will be discussed in terms of the electrostatic interactions around the cores and the molecular geometries, and a new aspect for the smectic nature of the molecules has been developed.

Experimental

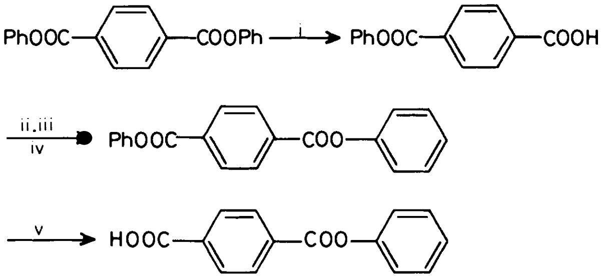
Materials.—The materials for series (1)–(3), phenyl 4-hydroxybenzoate, 4-(benzoyloxy)benzoate, and 4-(benzoyloxy)phenol, respectively, were easily obtained by a general method,[12,13] in which a benzyl group was used as a protecting group for the hydroxy and carboxy groups of hydroquinone and 4-hydroxybenzoic acid, and was removed by a catalytic hydrogenation with palladium–carbon (10% w/w). In contrast, 4-(phenoxycarbonyl)benzoic acid, the starting material for series (4), was not easy to obtain by partial esterification of terephthaloyl chloride.[14] In the present work, 4-phenoxycarbonyl)benzoic acid was prepared according to the Scheme.

Dibenzyl terephthalate, obtained by an esterification of terephthaloyl chloride with phenol, was hydrogenated with palladium–carbon in toluene–ethanol (1:1). After 37% of the theoretical amount of hydrogen had been taken up, the catalyst was filtered off. 4-(Benzyloxycarbonyl)benzoic acid was easily purified from the reaction micture by column chromatography on silica gel, followed by recrystallization from ethanol. At this stage, terephthalic acid, 4-(benzyloxycarbonyl)benzoic acid,

Table 1. Transition temperatures of series (**1**)–(**4**) (T/°C).

	Series (**1**)				Series (**2**)			Series (**3**)			Series (**4**)		
n	C	S_A	N	I	C	N	I	C	N	I	C	N	I
5	146	*a*	146		129	147		122	157		157	(145)	
6	127	(115)	143		122	142		118	151		156	(144)	
7	130	(124)	142		123	136		123	143		154	(142)	
8	118	129	140		118	135		117	142		153	(138)	
9	118	131	140		115	128		121	140		151	(136)	
10	114	131	140		114	127		121	136		152	(136)	
11	120	134	136		115	124		126	133		152	(135)	
12	114	135	135		116	123		127	131		150	*b*	
13	120	134			118	121		124	129		151	*b*	
14	113	133			117	120		122	128				

C, S_A, N, and I represent crystal, smectic A, nematic, and isotropic phases, respectively. Parentheses indicate monotropic transitions. [a] The smectic A–nematic transition temperature extrapolated from a binary phase diagram with the hexyloxy homologue is *ca.* 100 °C. [b] Recrystallization preceded the formation of the nematic phase.



Scheme. *Reagents:* i, H_2–Pd–C; ii, PCl_5–$SOCl_2$; iv, PhOH; v, H_2–Pd–C.

and dibenzyl terephthalate were obtained in the ratio of 1:2:6 (w/w). Thereby, dibenzyl terephthalate was completely recovered. For example, dibenzyl terephthalate (20 g) gave 4-(benzyloxycarbonyl)benzoic acid, (4.0–4.5 g), m.p. 179–180 °C. 4-(Benzyloxycarbonyl)benzoyl chloride was obtained by the reaction of 4-(benzyloxycarbonyl)benzoic acid and phosphorus pentachloride in thionyl chloride (twice the amount of the acid). This method gave a better yield, usually in excess of 90%. The acid chloride was treated with phenol in a solvent mixture of pyridine–toluene (1:1), to give benzyl phenyl terephthalate. The benzyl group of benzyl phenyl terephthalate was removed by catalytic hydrogenation with palladium–carbon, to give 4-(phenoxycarbonyl)benzoic acid, mp. 242 °C. The chlorination of 4-(phenozycarbonyl)benzoic acid was also achieved by the reaction of phosphorus pentachloride in thionyl chloride (twice the amount of the acid). The acid chloride was treated with the corresponding 4-alkoxyphenols, to give the homologous series (**4**). The products were purified by repeated column chromatography on silica gel, followed by recrystallization. The identification of the products was carried out by elementary analysis and thin layer chromatography on silica gel.

Method.—Transition temperatures were determined using a Nikon Model POH polarizing microscope fitted with a Mettler FP 52 heating stage, and a Daini-Seikosha SSC-560 differential scanning calorimeter. Both systems were usually operated at 5 °C min^{-1} of the heating and cooling rates.

Results

The transition temperatures for the homologous series (**1**)–(**4**) are summarized in Table 1.

All of the series show a nematic (N) phase, while the N phase for series (**4**) is formed monotropically because of higher melting points. The nematic–isotropic (N–I) transition temperatures are similar [average for the heptyloxy to decyloxy homologues; (**1**) (140 °C); (**3**) (140 °C); and (**4**) (140 °C)], except for series (**2**) (132 °C). On the other hand, the smectic properties of the series are strongly dependent on the orientation of the ester linkages. The S_A phase for series (**1**) commences from the hexyloxy homologue, and the S_A thermal stability exceeds the N thermal stability from the tridecyloxy homologue. In addition, the binary phase diagram for a mixture of the pentyloxy and hexyloxy homogues indicated that the pentyloxy homologue intrinsically possesses an S_A phase, where the extrapolated S_A–N transition temperature is 100 °C.

The homologous series, (**2**)–(**4**), do not show any smectic phases. In order to evaluate the S_A–N transition temperatures of these series, the binary phase diagrams were examined and the results are shown in Figure 1

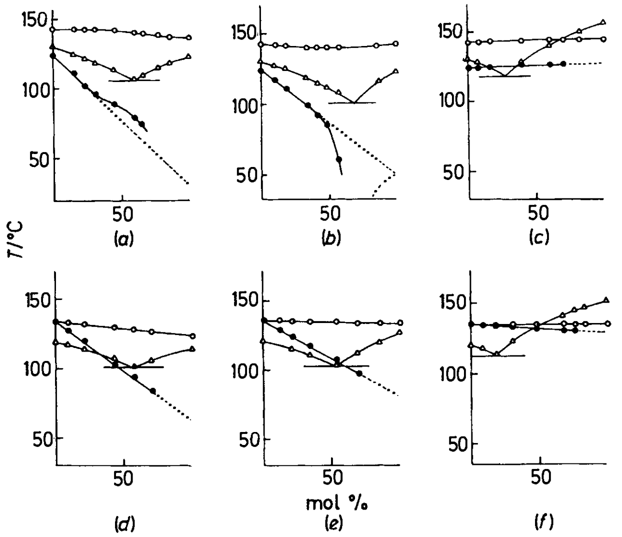


Figure 1. Binary phase diagrams for the mixtures of: (*a*) the heptyloxy homologues of (**1**) (left) and (**2**) (right); (*b*) the heptyloxy homologues of (**1**) (left) and (**3**) (right); (*c*) the heptyloxy homologues of (**1**) (left) and (**4**) (right); (*d*) the undecyloxy homologues of (**1**) (left) and (**2**) (right); (*e*) the undecyloxy homologues of (**1**) (left) and (**3**) (right); (*f*) the undecyloxy homologues of (**1**) (left) and (**4**) (right). ○, nematic–isotropic; ●, smectic A–nematic (isotropic); △, crystal–mesophase (isotropic) transitions; (– – – –) extrapolated transitions.

In the examination, series (**1**) was used as the standard material. In Figure 1(*a*), the S_A–N transition temperatures show

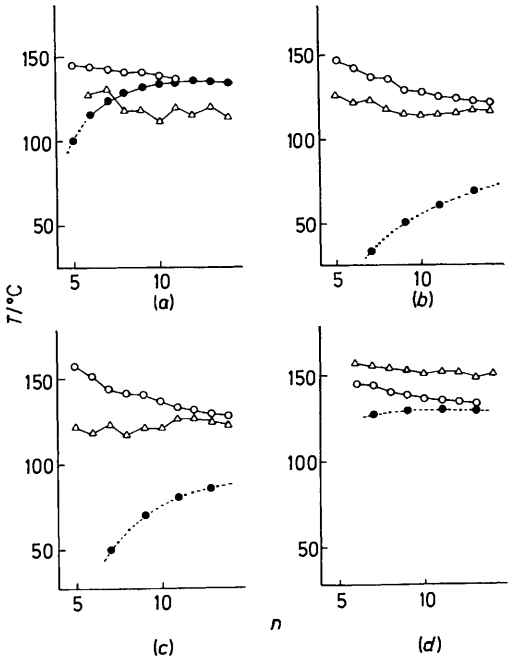


Figure 2. Plots of transition temperatures against the carbon numbers for: (*a*) series (**1**); (*b*) series (**2**); (*c*) series (**3**); and (*d*) series (**4**). ○, nematic–isotropic, ●, smectic A–nematic (isotropic), and △, crystal–mesophase (isotropic) transitions. (● - - - ● - - - ●) extrapolated smectic A–nematic transition temperatures (see Figure 1).

a weak upward convexity around the centre of the diagram. A part of the $\mathrm{S_A}$–N transition was hidden by the crystalline phase of the heptyloxy homologue of (**2**). The convexity around the centre becomes small with elongation of the alkoxy chain, and the $\mathrm{S_A}$–N transition temperatures become almost linear in the binary mixture of the undecyloxy homologues, as shown in Figure 1(*d*). The $\mathrm{S_A}$–N transition temperatures for the heptyloxy and undecyloxy homologues of (**2**) were extrapolated to 35 and 60 °C, respectively. In the extrapolation for the heptyloxy homologue [Figure 1(*a*)], the convexity around the centre was neglected (dotted line in the figure). Similarly, the transition temperatures for the nonyloxy and tridecyloxy homologues were extrapolated to 50 and 80 °C, respectively.

For a binary mixture of the heptyloxy homogues of series (**1**) and (**3**) [Figure 1(*b*)], the $\mathrm{S_A}$–N transition temperatures show a rapid reduction over 50 mol% of the heptyloxy homologue of (**3**), and the extrapolation was very difficult. The trend diminishes with increasing chain length of the alkoxy chain, and the $\mathrm{S_A}$–N transition temperatures become almost linear in the range 0–70 mol% of the undecyloxy homologue of (**3**) [Figure 1(*e*)]. From these results, we can assume that the heptyloxy homologue has a potential $\mathrm{S_A}$–N transition at *ca.* 50 °C obtained by extrapolation [the dotted line in Figure 1(*b*)], but the $\mathrm{S_A}$ phases of both heptyloxy homologues essentially have no affinity, and are discontinuous in the range. Therefore, the $\mathrm{S_A}$–N transition temperature for the heptyloxy homologue was supposed to be 50 °C. Similarly, the N–I transition temperatures for the nonyloxy, undecyloxy, and tridecyloxy homologues were determined to be 70, 80, and 87 °C, respectively. For the binary mixtures of the heptyloxy and undecyloxy homologues of series (**1**) and (**4**) [Figures 1(*c*) and 1(*f*)], the $\mathrm{S_A}$–N transition temperatures show good linearity. From the diagrams, the $\mathrm{S_A}$–N transition temperatures for the heptyloxy and undecyloxy homologues were extrapolated to 128 and 130 °C, respectively. Similarly, the transition temperatures for the nonyloxy and tridecyloxy homologues were extrapolated to 130 and 130 °C, respectively. Thereby, the N–I transition temperature for the tridecyloxy homologue was also extrapolated to 134 °C.

Figure 2 plots the transition temperatures for series (**1**)–(**4**) against the carbon number (*n*) of the alkoxy chain. In Figure 2, the solid and dotted lines indicate the observed and extrapolated transition temperatures, respectively. Although the extrapolated $\mathrm{S_A}$–N transition temperatures for the heptyloxy homologues of series (**2**) and (**3**) may involve a certain amount of error, there is no doubt that these are very poor in the smectic phase.

Discussion

In this work we examine the mesomorphic properties of four series having different orientations of the ester linkages, and draw the following conclusions.

(*a*) For series (**1**) the smectic A phase begins with the hexyloxy homologue. The thermal stability of the $\mathrm{S_A}$ phase increases on ascending the series and exceeds that of the N phase from the tridecyloxy homologue.

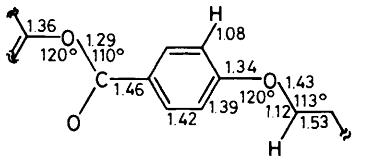
(*b*) Series (**2**) and (**3**) are very poor in the smectic phase even in the higher members. The potential smectic A phase for the low members of series (**3**) appears to be strongly characterized, and the $\mathrm{S_A}$–N transition temperatures in the binary phase diagrams frequently show remarkable non-linear behaviour.

(*c*) Series (**4**) has higher melting points than those of the other series. Although the homologues do not show any smectic phases, they intrinsically possess high smectic nature. The thermal stability of the potential $\mathrm{S_A}$ phase is almost independent of the chain length of the alkoxy group and does not exceed that of the nematic phase even if the alkoxy chain is of considerable length.

(*d*) The smectic properties decrease in the order (**4**) > (**1**) > (**2**) > (**3**), and the characteristics are maintained even in the higher members.

It would be reasonable to assume that non-polar interactions, such as van der Waals forces around the core and alkyl groups, are of primary importance in determining the smectic thermal stability. At the same time, it is also known that polar interactions (dipole–dipole and dipole–induced dipole) are also very important in enhancing the thermal stabilities of the smectic phases.[15,16] The present results also suggest that the smectic properties are strongly dependent on the orientation of the ester linkages. In order to clarify the smectic nature of the molecules, we have to know the geometrical and electrostatic nature of the molecules, and the molecular arrangement in the smectic A phase.

Firstly, the bulk molecular structures of the present series were estimated by calculation. The following parameters were used for the calculation. The results are shown in Figure 3. Here, the relative conformation around the ester linkages was supposed to be *trans*, and the alkyl group has a zig-zag conformation and is fully extended. A twist around the ester groups (*ca.* 60°[17]) was ignored.



As is evident from Figure 3, the alternation of the ester linkages results in a remarkable change in the molecular geometries. It is well known that the molecules in the N and $\mathrm{S_A}$ phases keep their intra- and inter-molecular rotational freedom. Therefore, we must consider the rotational conformers around the terminal alkoxy group. In Figure 3, the alkoxy group occupies the space between the real and dashed conformers. We

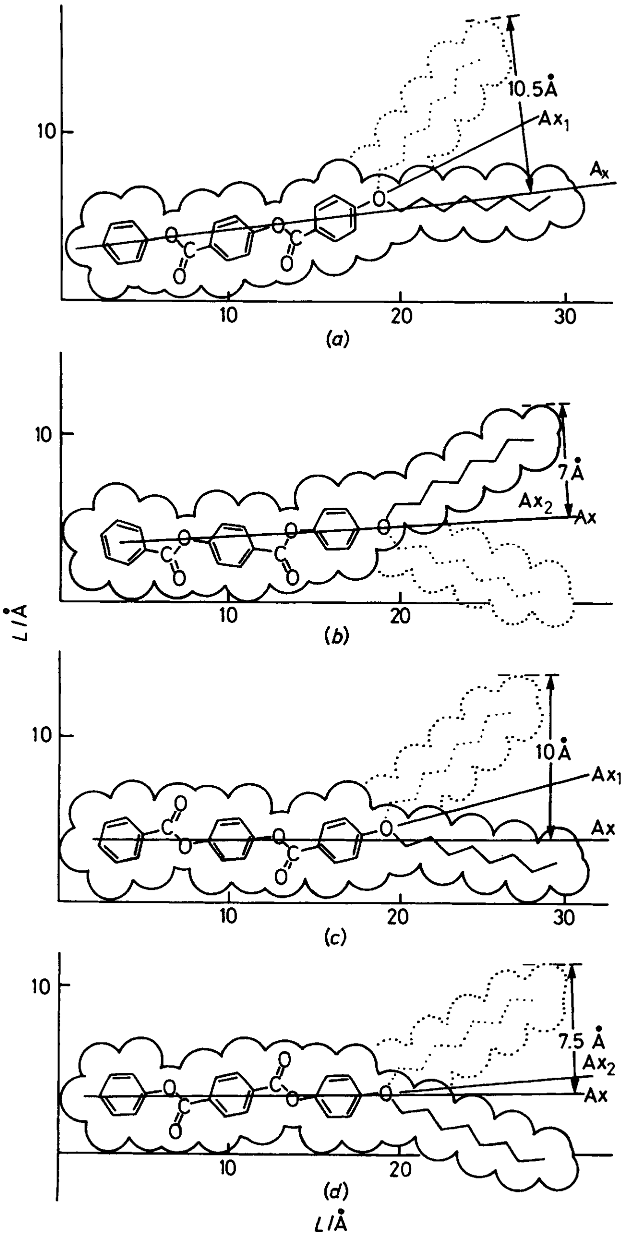
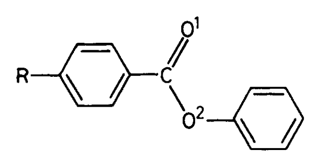


Figure 3. The calculated molecular geometries for the octyloxy homologues of series (**1**)–(**4**). The circles indicate the van der Waals radii for respective atoms (C = 1.4, H = 1.0, and O = 1.5 Å).

suppose here that the average rotational axis of the entirety of the molecules passes throgh the centre of both terminal aromatic rings (Ax in Figure 3).

Phenyl 4-(4-benzoyloxy)benzoate [the core of series (**1**) and (**2**)] is intrinsically bow shaped due to the bend around the ester groups. The rotational axis of the alkoxy group (Ax_1) for series (**1**) forms an angle of *ca.* 20° to the axis Ax so that the elongation of the alkoxy group would increase the bent geometry. Thereby, the molecular breadth around the terminus of the octyloxy chain is *ca.* 10.5 Å, and the bend increases as the series is ascended. Therefore, we can conclude that series (**1**) has an intrinsically bent geometry. In contrast, the rotational axis of the alkoxy group (Ax_2) for series (**2**) is almost parallel to the axis Ax so that the alkoxy group extends parallel to the long axis of the core. Thus, the molecular breadth around the terminus of the octyloxy chain is *ca.* 7 Å. Therefore, series (**2**) has a linear geometry, and the elongation of the alkoxy chain increases the linearity.

Table 2. Dipole moments and charge of the ester group.



R	μ_{obs}/D	μ_{calc}[a]/D	Charge C	O$_1$	O$_2$
H	1.9[b]	2.12	0.397	−0.387	−0.231
CH_3O		1.77	0.402	−0.392	−0.232
C_6H_5COO		4.02	0.395	−0.383	−0.230
C_6H_5OOC	[c]	0.14	0.390	−0.379	−0.228

[a] In the calculation, the twist around the ester group was assumed to be 60°. [b] Ref. 4. [c] The molecule was supposed to have C_2 symmetry. The dielectric anisotropy for 4-octyloxyphenyl terephthalate in the nematic phase is reported to be −0.63.[20]

1,4-Dibenzoyloxybenzene [the core of series (**3**)] has a C_2 symmetry. However, the rotational axis of the alkoxy group (Ax_1) forms an angle of *ca.* 15° to the axis Ax. The molecular breadth around the terminus of the octyloxy chain is thus *ca.* 10 Å. Therefore, series (**3**) is also a bent molecule when the alkoxy chain is long.

1,4-Diphenoxycarbonylbenzene [the core of series (**4**)] also has C_2 symmetry. However, the rotational axis of the alkoxy group (Ax_2) arranges parallel to axis Ax. Thereby, the molecular breadth around the terminal of the octyloxy chain is *ca.* 7.5 Å. Therefore, series (**4**) has a linear geometry even if the alkoxy chain is of considerable length.

Secondly, we have to consider the polar interactions involving dipoles in the S_A phase. In the present series, the dipole moments mainly arise from the ether and ester oxygens. The dipole moment for phenyl benzoate and anisole are reported to be 1.9 and 1.24 D, respectively.[18] The values, of course, vary by the electrostatic interactions between the ester group and a substituent attached at the *para* position of the aromatic ring. In order to estimate the local dipole moments of the ester groups, we tried to calculate the charge around the ester group by the MNDO method,[19] and the results are shown in Table 2.

As we can assume from Table 2, the dipolarity around the ester group at position Y decreases in the order of (**3**) > (**1**), (**2**) > (**4**). The order is the opposite of that of the S_A thermal stability, indicating that the increase in the dipolarity around the ester group lowers the S_A thermal stability. In order to understand the role of dipoles around the ester groups, we must consider the molecular arrangement in the S_A phase.

It would be reasonable to assume that the S_A phase for the present series has a monolayer arrangement of the molecules, since the present molecules involve no very polar substituent. In the smectic A phase, the molecules are known to have a translational order, though the molecular arrangement within the layer is disorder. A momentary molecular arrangement in the S_A phase is indicated in Figure 4. Of course, the molecules maintain their rotational freedom and inter-layer movement. As molecules approach one another and pack side by side, there are two typical arrangements of molecules with respect to their neighbours; that is, head-to-tail (*a*) and head-to-head (*b*) arrangements, though both arrangements, in practice, are impossible to distinguish. The ratio of the head-to-tail to the head-to-head arrangements must be different from system to system, and must vary according to the electostatic and geometrical nature of the molecule.

In arrangement (*a*), the head and tail portions arrange

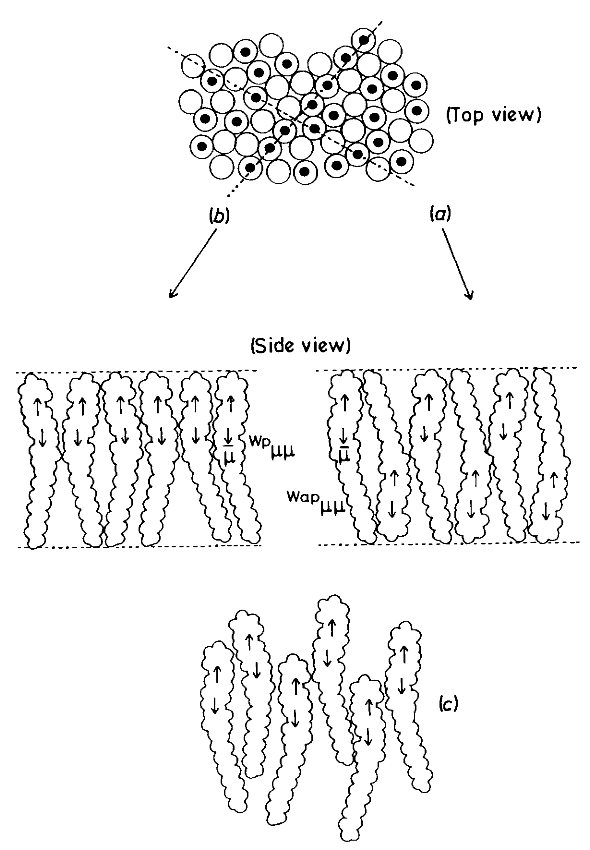


Figure 4. The molecular arrangement models in the nematic and smectic A phases: (*a*) the head-to-head; (*b*) head-to-tail arrangements in smectic A phase. The molecules indicate the dodecyloxy homologue of series (**3**) so that the orthogonal arrangement is not allowed. Arrows indicate the longitudinal components of the dipoles arising from the ester groups.

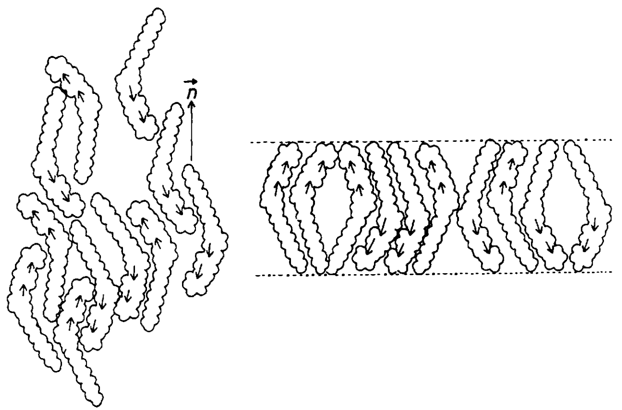


Figure 5. Possible molecular arrangements of the tridecyloxy homologue of series (1) in the N and S_A phase. In practice, the homologues do not show the nematic phase.

alternately. The dipoles incorporated in the cores inevitably arrange in an antiparallel fashion so that the dipole–dipole interaction ($Wap_{\mu\mu}$) is attractive for the layer arrangement. However, the interaction is a function of the chain length of the alkoxy group. When the alkoxy chain is sufficiently long; for example, C_{12}–C_{14}, the dipoles in arrangement (*a*) are too far apart to undergo effective interactions. In arrangement (*b*), on the other hand, the dipoles are always parallel, and the distance between dipoles is very weakly dependent on the alkoxy chain length. Therefore, the dipole–dipole interaction ($Wp_{\mu\mu}$) is always large and repulsive for the layer arrangement.

$$Wp_{\mu\mu} \gg Wap_{\mu\mu} \approx 0$$

Therefore, the repulsive dipole–dipole interaction ($Wp_{\mu\mu}$) in arrangement (*b*) is very important in the determinination of the smectic properties of the molecules. Certainly in the present series the effect of the linkages on the smectic properties is recognized even in the higher members.

When the dipoles in the core are sufficiently large, the molecules slip out of the layer, to give, for example, arrangement (*c*). This molecular rearrangement would reduce the translational order, increasing the nematic nature of the state. Considering thus, the longitudinal component of the dipoles in the monolayer arrangement is always repulsive for the layer formation.

Finally, this model is applied to the present results. The highly smectic nature for series (**1**) is assumed to arise primarily from the packing effects of the bent molecule. As shown in Figure 5, the S_A thermal stability is strongly dependent on the alkoxy-chain length in connection with the bent geometry.

In order to illustrate the smectic properties of the bent molecules, the molecular-arrangement models in the S_A and N phases for the tridecyloxy homologue of series (**1**) are depicted in Figure 5.

The homologue does not form the nematic arrangement. As we can assume from Figure 5, the increased molecular volume caused by the bending might be reduced by the tighter packing in the S_A phase, whilst it apparently reduces the orientational order in the N phase. A similar model for the L-shaped molecules has been proposed by Gray *et al.*[21,22] In such systems, the disappearance of the translational order may simultaneously induce orientational order, giving rise to an S_A–I transition. The higher members of series (**1**) are examples of this.

The situation is reversed in series (**2**). Although series (**2**) has a core identical with that of series (**1**), the molecule has a linear geometry, and in addition, the ester groups have effective dipole moments. Therefore, the repulsive dipole–dipole interaction around the ester groups in the arrangement (*a*) lowers the translational order, giving rise to the wide-range nematic phase.

Series (**3**) has similar electrostatic properties to series (**2**), while the overall shape of the molecule is somewhat bent. Therefore in series (**3**) it is difficult to form the layer arrangement, giving the wide-range nematic phase.

Series (**4**) has the best linearity, and the ester groups are less polar. For the layer arrangement of non-polar rod-like molecules, Kimura *et al.*,[23] have pointed out the importance of the excluded volume effect. In this system, the disappearance of translational order is not accompanied by the simultaneous loss of orientational order so that the nematic phase is formed even if the alkoxy chain is of considerable length.

In conclusion, we wish to emphasize that the alternation of linkages such as ester and azomethine, is accompanied by not only a change in the electrostatic but also the geometrical circumstances, and the subtle change in geometry strongly affects the smectic nature of the molecule. Although the polar interactions have been always considered to be the basis of the layer formation, the effect of polar interactions on the smectic properties is not so simple, and must be re-examined very carefully.

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