The effect of a lateral substituent on the mesomorphic properties of 4-cyanophenyl 4-(4-alkyloxybenzoyloxy)benzoates

Yoshihide Masuda[a]; Yoshiaki Sakurai[a]; Hisanori Sugiura[a]; Shiro Míyake[a]; Shunsuke Takenaka[a]; Shigekazu Kusabayashi[a]

[a] Chemical Process Engineering, Faculty of Engineering, Osaka University, Suita, Osaka, Japan

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The effect of a lateral substituent on the mesomorphic properties of 4-cyanophenyl 4-(4-alkyloxybenzoyloxy)benzoates

by YOSHIHIDE MASUDA, YOSHIAKI SAKURAI, HISANORI SUGIURA, SHIRO MIYAKE, SHUNSUKE TAKENAKA*
and SHIGEKAZU KUSABAYASHI

Chemical Process Engineering, Faculty of Engineering, Osaka University,
Suita, Osaka 565, Japan

The thermal properties of 4-cyanophenyl 4-(4-alkyloxybenzoyloxy)benzoates having a lateral substituent have been examined. Commencing with the nonyloxy homologue the hydrogen derivative shows a smectic A phase having a partially bilayered arrangement (S_{Ad}). When the substituents are introduced at position X, the S_{Ad} phase commences from the octyloxy homologue, and the chlorine and bromine derivatives show an additional S_{Ad} phase in the low temperature region. When the substituents are introduced at position Y, the S_{Ad} phase commences either from the undecyloxy or the dodecyloxy homologue, and the nitro derivative shows two tilted phases in the low temperature region. Compounds having a methoxy group at position Z have difficulty in forming the S_{Ad} phase. The effect of the substituent on the thermal properties of the smectic phases has been discussed in terms of the electrostatic and structural properties of the substituents. A driving force for the formation of the partially bilayered arrangement is also discussed.
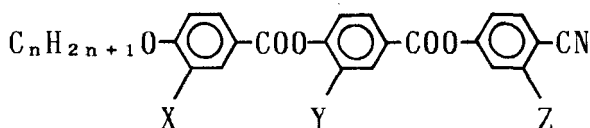
1. Introduction

The effect of a lateral substituent on mesomorphic properties has been examined by several authors. Generally, the lateral substituent is known to be unfavourable for mesomorphic phenomena [1, 2], since it decreases both the anisotropy of polarizability and the anisometry of the molecule.

Generally for non-polar liquid crystals the effect of the substituent on the thermal properties of nematic and smectic A phases has been discussed in terms of the change in the nematic–isotropic (T_{NI}) and smectic A–nematic ($T_{S_A N}$) transition temperatures. Gray *et al.*, for example, found that the nematic–isotropic transition temperatures for some benzoic acids have a good correlation with the van der Waals radii for substituents attached at the lateral position of the molecules [3]. On the other hand, the effect of the lateral substituent on the thermal properties of S_A and S_C phases is fairly complex. In non-polar liquid crystals, substituents such as halogens, alkyloxy, and alkyl groups tend to decrease $T_{S_A N}$ [4–7]. Conversely, polar substituents such as nitro and cyano groups decrease $T_{S_A N}$ due to intermolecular steric hindrance [5], but these can sometimes increase it due to polar interactions [5, 6, 8]. However, $T_{S_A N}$ values cannot be so easily correlated with the physical parameters of substituents. This might be due to the fact that $T_{S_A N}$ is strongly dependent on the molecular structure with regards to the packing effect and local polar interactions [9, 10].

* Author for correspondence.

In polar liquid crystals, the effect of the lateral substituent on the thermal properties of S_A and S_C phases is very complex, since the lateral substituent sometimes affects not only the transition temperature but also the molecular arrangement in the phases [11–16]. As far as we know, any systematic investigation for the substituent effect has not been made.

In this paper, we describe the effect of the lateral substituent on the thermal properties of nematic, smectic A and smectic C phases for the 4-cyanophenyl 4-(4-alkyloxybenzoyloxy)benzoates, as shown below.

$$C_nH_{2n+1}O-\bigcirc-COO-\bigcirc-COO-\bigcirc-CN$$

$$X \qquad Y \qquad Z$$

Compound	X	Y	Z
1	Cl	H	H
2	Br	H	H
3	OCH_3	H	H
4	NO_2	H	H
5	Cl–Cl	H	H
6	H	Br	H
7	H	OCH_3	H
8	H	NO_2	H
9	H	H	OCH_3
10	H	H	H
11	H	CH_3	H

Compounds **10** and **11** have been prepared by Sigaud *et al.* [17] and Sadashiva [18], respectively. The present results will be discussed in terms of the structural and electronic properties of the molecules.

2. Experimental
2.1. *Materials*

The 4-hydroxy-3-*R*-benzoic acids (R = Cl, Br, OCH_3, NO_2, and –Cl, Cl) are commercially available, and were alkylated with the corresponding *n*-alkylbromides in cyclohexanone. Compounds 1–5 were prepared by a two step esterification of 4-alkyloxy-3-*R*-benzoic acids, as mentioned in an earlier paper [10]. Compounds 6–8 were also prepared by a two step esterification of 4-hydroxy-3-*R*-benzoic acids. Compound **9** was prepared by the esterification of 4-(4-alkyloxybenzoyloxy)benzoyl chlorides [10] and 4-bromo-3-methoxyphenol in dry pyridine, followed by cyanation according to the literature method [19]. Purification of the materials was carried out by repeated column chromatography on silica-gel and recrystallization. The identification of the materials was carried out by elemental analysis and NMR. The *N*-[4-(4-alkyloxybenzoyloxy)benzylidene]-4-cyanoanilines (alkyloxy = octyloxy and decyloxy) [20], 4-alkylphenyl 4-(4-cyanobenzoyloxy)benzoates (alkyl = hexyl and octyl) [21], 4-octylphenyl 4-(4-nitrobenzoyloxy)benzoate [22], *N*-[4-(4-octyloxyphenoxycarbonyl)benzylidene]-4'-cyanoaniline [20] were prepared according to the literature method.

2.2. *Method*

The phase transitions were observed by using a Nikon Model POH polarizing microscope fitted with a Mettler FP-52 heating stage.

3. Results

The transition temperatures for compounds **1–11** are summarized in tables 1–3. For comparison the transition temperatures of the 4-cyanophenyl 4-(4-alkyloxybenzoyloxy)benzoates (**10**) and the 4-cyanophenyl 4-(4-alkyloxybenzoyloxy)-3-methylbenzoates (**11**) [18] are also shown in table 3.

The S_A phase for compound **10** is known to have a partially bilayered arrangement of the molecules (S_{Ad}) [18].

Table 1. The transition temperatures for compounds **1–5**.

Compound	X	n	C		S_{Ad}		N_{re}		S_{Ad}		N		I
1	Cl	7	•	122°C	(•	68°C)					•	200°C	•
		8	•	116°C	(•	77°C	•	88°C)	•	144°C	•	199°C	•
		9	•	115°C	(•	85°C)			•	167°C	•	186°C	•
2	Br	7	•	126°C	(•	63°C)					•	197°C	•
		8	•	116°C	(•	73°C	•	82°C)	•	137°C	•	187°C	•
		9	•	96°C	(•	83°C)			•	155°C	•	181°C	•
		10	•	97°C	(•	81°C)			•	162°C	•	171°C	•
3	OCH₃	6	•	111°C							•	173°C	•
		7	•	117°C							•	165°C	•
		8	•	112°C			(•	49°C)	•	139°C	•	163°C	•
		9	•	117°C					•	151°C	•	159°C	•
		10	•	115°C						157°C			•
4	NO₂	7	•	123°C							•	178°C	•
		8	•	110°C					•	110°C	•	163°C	•
		9	•	111°C					•	136°C	•	157°C	•
		10	•	116°C					•	148°C	•	152°C	•
5	Cl, Cl	8	•	114°C						150°C	•	158°C	•
		9	•	105°C					•	151°C	•	151°C	•
		10	•	112°C					•	148°C			•

C, S_{Ad}, N_{re}, N and I indicate crystal, partially bilayered smectic A, reentrant nematic, nematic, and isotropic phases, respectively. Parentheses indicate a monotropic transition.

Table 2. The transition temperatures for compounds **6–8**.

Compound	Y	n	C		S_{C2}		N_{re}		S_{Cd}		S_{Ad}		N		I
6	Br	9	•	95°C									•	164°C	•
		10	•	95°C									•	164°C	•
		11	•	86°C									•	167°C	•
		12	•	82°C			•	93°C			•	135°C	•	158°C	•
7	OCH₃	9	•	116°C									•	153°C	•
		10	•	115°C									•	148°C	•
		11	•	121°C					(•	66°C)	•	127°C	•	144°C	•
		12	•	127°C					(•	64°C)	•	137°C	•	144°C	•
8	NO₂	7	•	103°C									•	168°C	•
		8	•	95°C									•	162°C	•
		9	•	76°C	(•	56°C)							•	156°C	•
		10	•	94°C	(•	60°C)			•	78°C)	•	146°C	•	152°C	•
		11	•	106°C	(•	52°C)			•	84°C)	•	160°C			•
		12	•	95°C	(•	52°C)			•	84°C)	•	159°C			•

C, S_{C2}, N_{re}, S_{Cd}, S_{Ad}, N and I indicate crystal, unknown smectic C, reentrant nematic, partially bilayered smectic C, bilayered smectic A, nematic and isotropic phases, respectively. Parentheses indicate a monotropic transition.
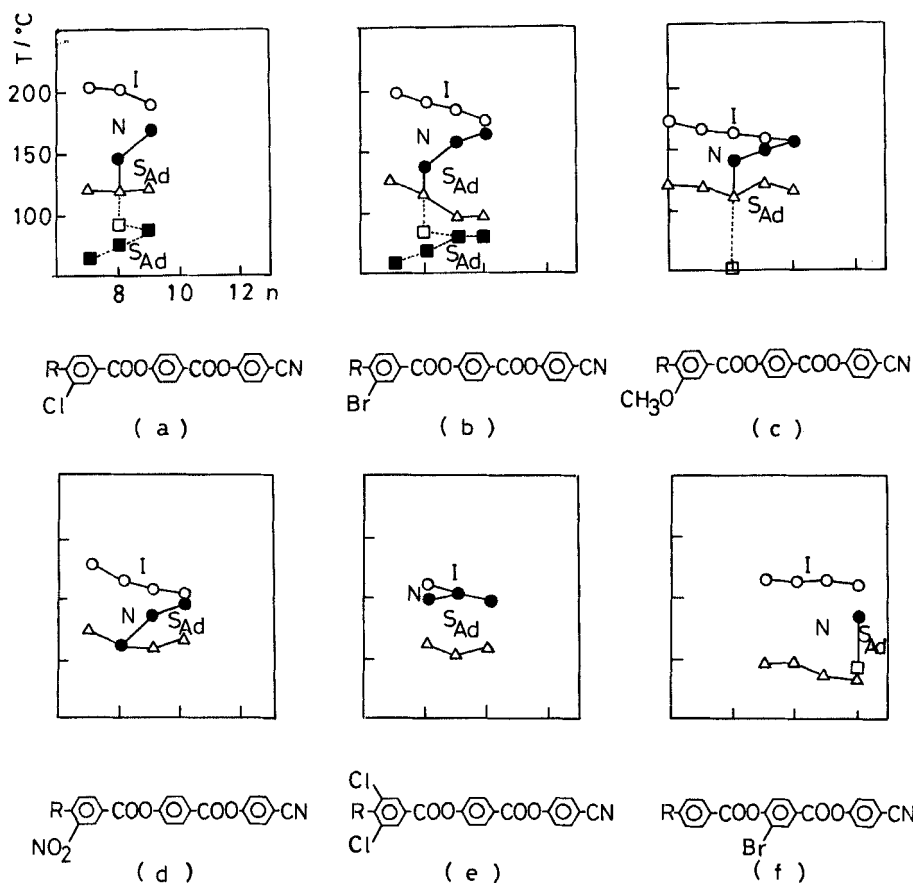
Y. Masuda *et al.*

Figure 1.   A plot of the transition temperatures versus the carbon number (*n*) for compounds:
(*a*) **1**; (*b*) **2**; (*c*) **3**; (*d*) **4**; (*e*) **5**; (*f*) **6**; (*g*) **7**; (*h*) **8**; (*i*) **9**; (*j*) **10**; (*k*) **11**. ($R = C_n H_{2n+1}O$;
dashed lines indicate monotropic transitions and △ indicates melting points).

Table 3.   The transition temperatures for compounds **9–11**.

Compound	Z	n	C		N_{re}		S_{Ad}		N		I
9	OCH_3	9	●	70°C					●	90°C	●
		10	●	72°C					●	85°C	●
		11	●	73°C					●	83°C	●
10	Br	8	●	123°C					●	233°C	●
		9	●	122°C	(●	117°C)	●	199°C	●	229°C	●
		10	●	106°C	(●	95°C)	●	208°C	●	221°C	●
		11	●	103°C	(●	86°C)	●	212°C	●	217°C	●
		12	●	102°C	(●	84°C)	●	215°C	●	215°C	●
11	CH_3	11	●	101°C					●	168°C	●
		12	●	101°C	(●	76°C)	●	147°C	●	162°C	●

C, N_{re}, S_{Ad}, N and I indicate crystal, reentrant nematic, partially bilayered smectic A,
nematic and isotropic phases, respectively. Parentheses indicate a monotropic transition.
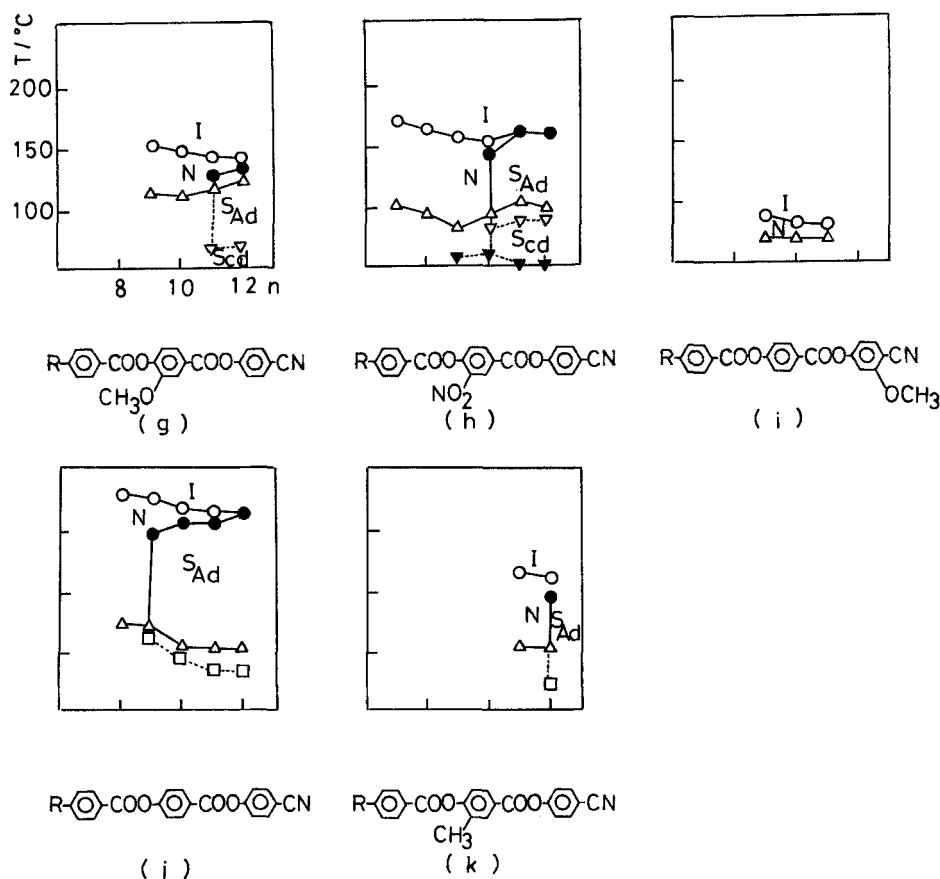
Figure 1 *(continued)*.

For compounds **1** and **2** the S_A–S_A transition for the nonyloxy and decyloxy homologues was observed by both DSC and polarizing microscopy. The latent heats for the S_A–S_A transition for the nonyloxy and decyloxy homologues of compound **2** are 0·08 and 0·36 kJ mol^{-1}, respectively. Sadashiva reported that the S_{Ad} phase for compound **11** commences from the dodecyloxy homologue [18].

The transition temperatures for compounds **1–11** are plotted against the carbon number (n) in figure 1.

In order to clarify the thermal properties of the S_A phases for compounds **1, 2, 7,** and **8**, some binary phase diagrams were examined, and the results are shown in figures 2 and 3.

The higher members of compounds **1** and **2** show two kinds of S_A phase, and exhibit the S_A–S_A transition. In an earlier paper [23], we reported that the layer spacings for the upper and lower S_A phases for the nonyloxy homologue of compound **2** are 1·3 and 1·2 times the fully extended molecular length, respectively; these facts indicate that both S_A phases have a partially bilayered arrangement. Figure 2 (*a*) shows the phase diagram for the mixture of 4-octyloxyphenyl 4-(4-octyloxybenzoyl-oxy)benzoate (OPOBB) and the nonyloxy homologue of compound **2**, for which it would be reasonable to assume that the S_A phase of OPOBB has a monolayer
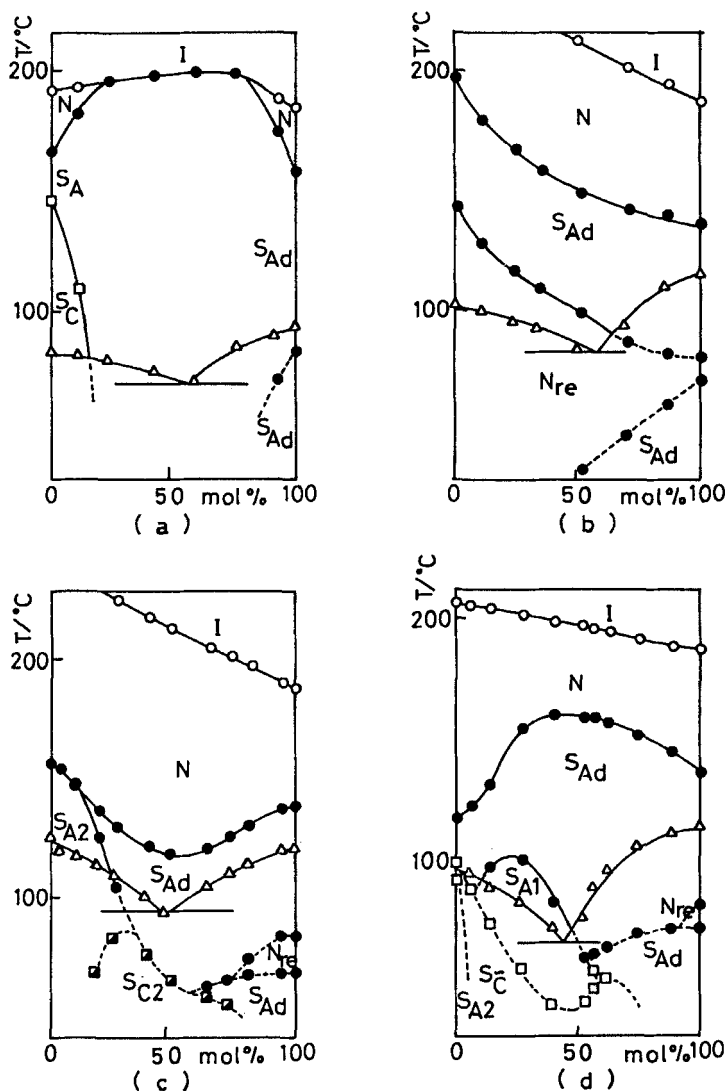
Figure 2.   Binary phase diagrams for the mixtures of: (*a*) OPOBB (on the left-hand side) and the nonyloxy homologue of compound **2** (on the right-hand side); (*b*) OBBCA and the octyloxy homologue of **2**; (*c*) HPCBB and the octyloxy homologue of **2**; (*d*) OPNBB and the octyloxy homologue of **2**.

arrangement. The S_A phase of OPOBB and the upper S_A phase are miscible, though $T_{S_A N}$ shows a non-linear behaviour when plotted against the molar concentration of each component. On the other hand, $T_{S_A-S_A}$ of the nonyloxy homologue decreases with an increase in the concentration of OPOBB.

Figure 2 (*b*) shows the phase diagram for the mixture of 4-*N*-[4-(4-octyloxy-benzoyloxy)benzylidene]-4′-cyanoaniline (OBBCA) and the octyloxy homologue of compound **2**, where OBBCA is known to show reentrant mesomorphism of the N_{re}–S_{Ad}–N–I type [20]. The S_A and N_{re} phases of the octyloxy homologue are miscible with those of OBBCA. However, the S_A–N_{re} transition temperature of the octyloxy homologue decreases with an increase in the concentration of OBBCA, and disappears
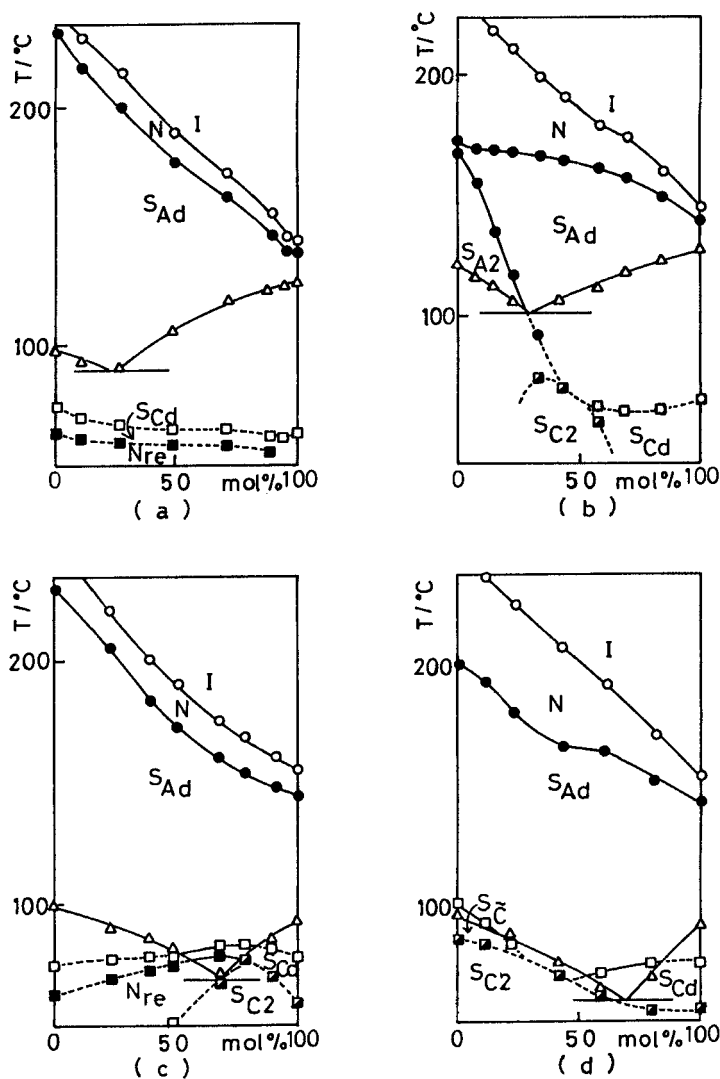
Figure 3. Binary phase diagrams for the mixtures of: (*a*) DBBCA (on the left-hand side) and the dodecyloxy homologue of compound **7** (on the right-hand side); (*b*) HPPCBB and the dodecyloxy homologue of **7**; (*c*) DBBCA and the decyloxy homologue of **8**; (*d*) OPCBCA and the decyloxy homologue of **8**.

at around 50 mol% of OBBCA. Figure 2 (*c*) shows the phase diagram for the mixture of 4-hexylphenyl 4-(4-cyanobenzoyloxy)benzoate (HPCBB) and the octyloxy homologue of compound **2**, where HPCBB is known to show the S_{A2} phase [21]. In the figure, the S_{Ad}–N transition temperature shows a minimum of *c*. 45 mol% of HPCBB, and intersects the axis on the left-hand side at 166°C, indicating that HPCBB has a virtual S_{Ad}–N transition at this temperature. The $T_{S_{A2}S_{Ad}}$ value of HPCBB decreases steeply with an increase in the concentration of the octyloxy homologue, and a new titled phase (probably a S_{C2} phase) is formed in the 30–80 mol% range of HPCBB. On the other hand, the N_{re} and lower S_A phases of the octyloxy homologue disappear at concentrations of *c*. 70 and 60 mol% based on this compound respectively.

Figure 2 (*d*) shows the phase diagram for the mixture of 4-octylphenyl 4-(4-nitro-benzoyloxy)benzoate (OPNBB) and the octyloxy homologue of compound **2**, where OPNBB is known to show mesomorphism of the S_{A2}–$S_{\tilde{C}}$–S_{Ad}–N–I type [22]. In the diagram, the S_{Ad} phase of OPNBB is miscible with the S_A phase of the octyloxy homologue. The $S_{\tilde{C}}$–S_{Ad} transition temperature decreases steeply on increasing the concentration of the octyloxy homologue, and a new smectic phase is formed between 90 and 55 mol% of OPNBB (probably a S_{A1} phase). Conversely, the N_{re} and lower S_A phases of the octyloxy homologue are immiscible with any phase of the reference compound. The mixture of 42 mol% of OPNBB shows reentrant mesomorphism of the S_{A2}–S_{C1}–S_A–S_{Ad}–N–I type.

Figure 3 (*a*) shows the phase diagram for the mixture of 4-*N*-[4-(4-decyloxy-benzoyloxy)benzylidene]-4′-cyanoaniline (DBBCA) and the dodecyloxy homologue of compound **7**, where DBBCA is known to show mesomorphism of a N_{re}–S_{Cd}–S_{Ad}–N–I type [20]. Both the S_{Ad} and the S_{Cd} phases of DBBCA are miscible with the S_A and S_C phases of the dodecyloxy homologue, where the S_{Ad}–N and S_{Cd}–S_{Ad} transition temperatures show a linear correlation with the molar concentration. The N_{re}–S_{Cd} transition temperature also shows a linear correlation range between 100 and 10 mol% of DBBCA, indicating that the dodecyloxy homologue has a N_{re}–S_{Ad} transition at *c.* 55°C. Figure 3 (*b*) shows the phase diagram for the mixture of 4-heptylphenyl-4′-(4-cyanobenzoyloxy)benzoate (HPPCBB), where HPPCBB shows mesomorphism of a S_{A2}–S_{Ad}–N–I type [21]. Around the centre of the diagram the formation of a new tilted smectic phase (probably a S_{C2} phase) is shown, and a mixture of 42 mol% of HPPCBB shows mesomorphism of a S_{C2}–S_{Cd}–S_{Ad}–N–I type.

Figure 3 (*c*) shows the phase diagram for the mixture of DBBCA and the decyloxy homologue of compound **8**. The S_A and S_C phases of the decyloxy homologue are miscible with the S_{Ad} and S_{Cd} phases of DBBCA, respectively. However, the lower S_C phase disappears in the middle of the diagram. Figure 3 (*d*) shows the phase diagram for the mixture of *N*-[4-(4-octyloxyphenoxycarbonyl)benzylidene]-4′-cyanoaniline (OPCBCA) and the decyloxy homologue of compound **8**, where OPCBCA is known to show mesomorphism of a S_{C2}–$S_{\tilde{C}}$–S_{Ad}–N–I type [20]. In the diagram, the S_{C2}–$S_{\tilde{C}}(S_{Ad}, S_{Cd})$ transition temperature shows a linear correlation which the molar concentration, and the lower S_C phase of the decyloxy homologue is miscible with the S_{C2} phase of OPCBCA.

4. Discussion

The effect of the substituent on the mesomorphic properties has been frequently discussed in terms of the effective change in, for example, the nematic–isotropic and smectic A–nematic transition temperatures [1, 3]. Strictly speaking, however, such an argument is not sufficient for the qualitative analysis of polar liquid crystals, since both transition temperature and molecular arrangement in the mesophases change simultaneously. In this paper, polar liquid crystals indicate molecules having polar groups such as cyano, nitro, *N*-oxide, and sometimes aldehyde (group dipole moment > *c.* 3 D) [24] at the terminal position. Typical mesomorphism involving N and S_A phases for polar liquid crystals may be roughly represented by figure 4. In the figure, both vertical and horizontal axes indicate the arbitrary transition temperature and the carbon number in an alkyloxy or an alkyl chain incorporated in the molecule, respectively.

In general, T_{NI} decreases on ascending the series, due to an increase in the flexibility of the molecule and a decrease in the anisotropy of polarizability [3]. The
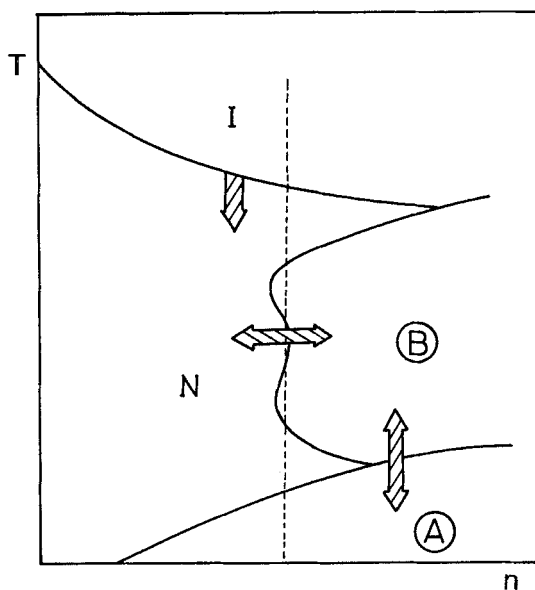
Figure 4. A plot of the transition temperature against the carbon number (*n*).

lateral substituents are known to decrease T_{NI} since an increase in the molecular breadth results [3]. For the nonyloxy homologues of the present compounds, chlorine, bromine, methoxy, and nitro groups at position X decrease T_{NI} by 43, 48, 70, and 72°C, respectively. Similarly, bromine, methoxy, and nitro groups at position Y decrease T_{NI} by 65, 76, and 73°C, respectively. For compounds **1–4** and **6–8** the reduction of T_{NI} due to the lateral substituent can be interpreted in terms of an increase in the molecular breadth around the core. For compound **9**, on the other hand, the methoxy group at position Z steeply decreases T_{NI} (139°C). The terminal meta-methoxy group may cause a bending of the molecular structure.

In order to understand the smectic properties of the present compounds, the mesomorphic properties of the phenyl 4-(4-alkyloxybenzoyloxy)benzoates, the fundamental materials for the present compounds, and some related compounds [10] are shown in table 4.

Table 4. The mesomorphic properties of the phenyl 4-(4-alkyloxybenzoyloxy)benzoates and related compounds.

$$C_nH_{2n+1}O-\bigcirc-COO-\bigcirc-COO-\bigcirc-R_1$$
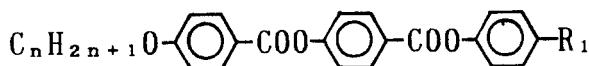
Compound	*n*	R_1	C		S_A		N		I	R†	μ/D^2‡
12	6	H	●	127°C	(●	115°C)	●	143°C	●	0·95	0
	8	H	●	118°C	●	129°C	●	140°C	●	0·97	
	12	H	●	114°C	●	135°C	●	135°C	●	1·0	
13	8	OCH₃	●	107°C	●	122°C	●	226°C	●	0·79	1·36
14	8	Cl	●	123°C	●	200°C	●	209°C	●	0·98	1·70
15	8	CHO	●	99°C	●	158°C	●	220°C	●	0·87	2·85
10	8	CN	●	123°C		158°C	●	233°C	●	< 0·76	4·40

† R = the ratio of the S_A–N and N–I transition temperatures [25].
‡ Dipole moment for the mono-substituted benzene [26].

For compound **12**, the fundamental material for the present compounds, the S_A phase commences from the hexyloxy homologue, and T_{S_A-N} and R gradually increase in ascending the series [9]. The formation of the S_A phase occurs in the A region, where the molecules form a monolayer arrangement. In an earlier paper [9], we showed that earlier members of the phenyl 4-(4-alkyloxybenzoyloxy)benzoate series form the S_A phase, and that this was probably due to the close packing effect of the bent molecules. Compound **14** shows the S_A phase, and $T_{S_A N}$ and R are higher than those of the octyloxy homologue of compound **12**. The formyl compound (**15**) also shows the S_A phase, but R is smaller compared to compounds **12** and **14**. The cyano compound (**10**) does not show the S_A phase, and R is less than 0·76. Therefore, the R values decrease in the compound order **14** > **15** > **10**. The order agrees with the inverse order of the dipole moment, as shown in table 4 [10]. Compound **13** having a methoxy group has a low R value since the dipole moment of the methoxy group is not so high. As mentioned in an earlier paper [10], the methoxy group increases the polarity around the ester group due to electronic interactions.

In the present compounds, the substituent is located at the lateral position of the molecule. Compounds **1** and **2** show the S_A phase in the A region. Interestingly, the smectic phase is neither S_{A1} nor S_{A2}, but is the S_{Ad} phase since the layer spacing is 1·2 times the fully extended molecular length. In fact, the S_{Ad} phase is immiscible with the other S_A phases such as S_{A1}, S_{A2}, and S_{Ad}. As we can see from figure 3, however, the S_{Ad} phase is located below the upper S_{Ad} and N_{re} phases and above the S_{A2}, S_{C2}, and S_{C1} phases. From the thermal point of view, therefore, this corresponds to the S_{A1} phase. The laterally positioned halogens may prevent the monolayer arrangement due to steric hindrance. On the other hand, compounds **3** and **4** do not show any S_A phase in the A region. The increased molecular breadth around the substituents might be unfavourable towards the formation of the S_A phase.

Compounds **1–4** show the S_{Ad} phase in the B region. The layer spacing for the nonyloxy homologue of compound **2** is 1·3 times the fully extended molecular length. Interestingly, the S_{Ad} phase commences from the octyloxy homologue for compound **2** as compared to the nonyloxy homologue for compound **10**, indicating that these lateral substituents facilitate the formation of this mesophase. In compounds **1** and **2**, the S_A phases in both the A and B regions are located close together such that the higher members undergo the S_{Ad}–S_{Ad} transition.

Compounds **6** and **7** having a substituent at position Y show no S_A phase in the A region, and the S_{Ad} phase in the B region commences from the dodecyloxy and undecyloxy homologues, respectively. Compound **7** shows the S_C phase in the low temperature area of the B region. On the other hand, compound **8** shows the S_C phase in the A region, where the phase commences from the nonyloxy homologue, and the S_A and S_C phases in the B region, where these phases commence from the decyloxy homologue. As we can see from figure 3, the lower S_C phase has the bilayer arrangement, and the upper S_C and S_A phases have the partially bilayered arrangement. The beginning of the S_{Ad} phase is lower than that for compound **7**, but is higher than that for compound **10**. These facts show that substituents at position Y are unfavourable towards the layer arrangement of these types of phase, which is probably due to steric hindrance. The polar interactions around the nitro group at position Y may play a role in the formation of the S_A and S_C phases.

Compounds **9** and **11** do not show any smectic phases in the A region and the S_{Ad} phase in the B region commences from the higher homologues of these compounds. The methoxy group at position Z is especially unfavourable towards mesomorphic phenomena.

The model in figure 4 may be expanded to include more general polar liquid crystals. The formation of the S_A phase in both the A and B regions is very common in polar liquid crystals. The S_A phase in the A region has a monolayer (S_{A1}) and/or a bilayer (S_{A2}) arrangement, and the molecules sometimes tilt with respect to the surface of the layer, giving the S_{C1} and S_{C2} phases in the lower temperature region, when the terminal alkyl chain is suitably long. The S_A phase commences from the lower homologues of the series, but $T_{S_A N}$ and R are not so high compared with those values for the corresponding less polar liquid crystals (for example compounds **12-15** and **10**).

The S_A phase in the B region, generally, commences from the higher homologues of the series, and has a partially bilayered arrangement; the molecules tilt in the low temperature region giving the S_{Cd} phase. The layer spacing in the S_{Ad} phase is usually 1·0-1·6 times the fully extended molecular length [27].

Since 4-(4-nonyloxyphenoxycarbonyl)phenyl 4-nitrobenzoate exhibits a complicated phase transition sequence involving reentrant nematic phases [28], the boundary between the S_{Ad} and N phases appears to be an uneven parabola, as shown in figure 4. If we assume the dotted line in the figure to be, for example, just an integer, we can expect the homologue to show mesomorphism of a $S_{A1}-N_{re}-S_{Ad}-N_{re}-S_{Ad}-N-I$ type. As is evident from the figure, separation of the smectic areas in both A and B regions gives a reentrant phenomenon. On ascending the series, both smectic areas merge, and eventually the reentrant nematic area disappears giving a S_A-S_A transition. When both S_A phases overlap, the homologues show only a S_A-S_A transition, this is typified by the 4-(4-alkylphenoxycarbonyl)phenyl 4-cyanobenzoates [21], and 4-(4-alkyloxyphenoxycarbonyl)phenyl 5-cyanofuran-2-carboxylate [29].

It is well known that some polar liquid crystals and mixtures show the antiphase of the S_A and S_C phases ($S_{\tilde{A}}$ and $S_{\tilde{C}}$, respectively) [2, 27]; these phases are usually formed in the boundary between the A and B regions.

The model in figure 4 may also be expanded into 'less polar' liquid crystals. The formation of the S_A phase in the A region is very common in these liquid crystals. The $T_{S_A N}$ values and the ratio (R) of $T_{S_A N}$ to T_{NI} are strongly dependent on the structural and electronic properties of the core. The $T_{S_A N}$ values gradually increase on ascending the series, and frequently the N phase is diminished by the S_A phase and disappears altogether in higher members of the series ($R = 1$). Generally, the molecules form a monolayer arrangement (S_{A1}), that is the ratio of the layer spacing to the molecular length is approximately equal to one. Interestingly, some liquid crystals such as cyclohexane [30] and perfluoroalkyl [31] derivatives show the S_A phase, the formation of which occurs probably in the A region, and the ratio of the layer spacing to the molecular length is greater than one similar to the S_{Ad} phase. Up to now, the formation of the S_A phase in the B region has not been found in non-polar liquid crystals.

5. Conclusion

The substituents at position X facilitate the formation of the S_{Ad} phase. Bromine and chlorine at position X induce the S_{Ad} phase in the low temperature region as well. The substituents at position Y are unfavourable towards the formation of S_{Ad} and S_{A1} phases, which is probably due to steric repulsion, except for the case of the nitro group. The substituents at position Z are also unfavourable towards the layer arrangement of the molecules.

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