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New mesogenic compounds with unconventional molecular structures 1,2-Phenylene and 2,3-naphthylene bis[4-(4-alkoxyphenyliminomethyl)benzoates] and related compounds

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Invited Lecture

New mesogenic compounds with unconventional molecular structures

1,2-Phenylene and 2,3-naphthylene bis[4-(4-alkoxyphenyliminomethyl)benzoates] and related compounds

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DSC and X-ray studies on a series of 1,2-phenylene bis[4-(4-alkoxyphenyliminomethyl)benzoates] are presented. The phases were shown to be classical nematic and/or smectic by their continuous miscibilities with reference mesophases. The layer spacings in the smectic A phase measured as a function of the alkyl chain length revealed that the mean tilt angle of the linear three-ring part of the molecule to the layer normal is about 37° and that the molecular core is V-shaped with an angle of about 70° between the two out-stretched benzoate legs. This molecular model accounts for the effects of a methyl group introduced into the 3- or 4-position of the 1,2-phenylene moiety on the mesomorphic properties. Both the nematic and smectic A properties are markedly promoted by replacement of the 1,2-phenylene group by the 2,3-naphthylene group.

The phases exhibited by the less-elongated series of 2,3-naphthylene bis(4-alkoxybenzoates) are also nematic and/or smectic A, but are now monotropic. The formation of stable smectic A and metastable **B** phases by a series of 1,2,3-tris[4-(4-alkoxybenzylideneamino)benzoyloxy]benzenes is described.

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1. Introduction

Although classical thermotropic liquid crystals are commonly composed of rod-like molecules, there are many types of low molecular weight compounds with unconventional molecular structures which can form nematic and/or smectic phases [1]. However, mesogenic compounds with a bend in the middle of the molecule have not attracted much interest. As long ago as 1929, Vorländer described the liquid-crystalline properties of a number of compounds such as bis[4-(4-methoxyphenylazo)phenyl] isophthalate and 1,2-phenylene bis[4-(4-ethoxyphenylazoxy)benzoate) for which he supposed obtuse- and acute-angled configurations, respectively [2–4]. The latter compound was classified by Demus under fused twins, more particularly under the terminal–terminal parallel, rigid bound type and its mesophase was noted to be nematic [1]. Then, Wiegand studied the thermal behaviour of six isomeric bis(4-methoxybenzylideneamino)naphthalenes. Liquid crystals were given by the 1,4, 1,5-, and 2,6-compounds but not by the 1,6-, 1,7-, 2,7-compounds [5]. More recently, Jin *et al.* reported bis[4-(4-butylphenylazo)phenyl] isophthalate to show no mesophase and concluded that a linear molecular shape is a mesogenic prerequisite when a compound contains two mesogenic units [6]. Later, the same

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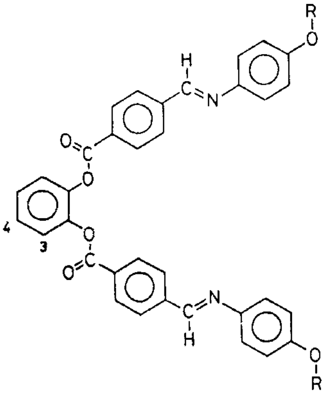
group observed a metastable nematic phase for a compound in which two mesogenic units were connected through flexible spacers to the 1- and 3-positions of the central benzene ring [7].

Interest in multi-ring systems with an acute-angled configuration led us to work on 1,2-phenylene bis[4-(4-alkoxyphenyliminomethyl)benzoates], the 2,3-naphthylene analogues, and some related compounds. The mesomorphic behaviour of a homologous series of 1,2-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates] was the subject of a previous investigation [8].

2. Results and discussion

2.1. *1,2-Phenylene bis[4-(4-alkoxyphenyliminomethyl)benzoates]*



2.2.1. *DSC studies*

The transition temperatures, the associated enthalpies, and the layer spacings for the smectic A phase are listed in table 1. The mesophases were classified on the basis of the textures, the nematic phase by a schlieren texture, the smectic A phase by a fan texture, and the smectic B phase by a mosaic texture. Figure 1 is a plot of the transition temperatures as a function of the alkyl chain length.

Compared with the thermodynamic data for 1,2-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates] published earlier [8], the melting points of the lower members in the present series are markedly depressed, while the N–I transition temperatures exhibited by the methoxy to octyloxy homologues are not much affected by inversion of the azomethine group. The metastable smectic B phase is promoted compared to that of the corresponding isomeric compound and is observable for the tetradecyloxy homologue, as well as for the pentyloxy to decyloxy homologues. The smectic A phase shows a strong tendency to be homeotropic. The enthalpies at the N–I transition, those at the S_A–N transition, and those at the S_A–I transition, are typical [9], but the enthalpies associated with the S_B–S_A transition are significantly larger than those found for the isomeric compounds. In other aspects, inversion of the linking group has no appreciable effect on thermal behaviour.

For comparative purposes the mesomorphic behaviour of phenyl 4-(4-alkoxyphenyliminomethyl)benzoates was studied, and the results are in table 2. All members from methoxy to decyloxy exhibit a stable nematic phase and their clearing points are surprisingly similar to those of the 1,2-phenylene bis[4-(4-alkoxyphenyliminomethyl)benzoates]. A smectic A phase appears in the propoxy to hexadecyloxy homologues and its thermal stability is generally lower relative to that of the twin system. No smectic B phase is observed with these conventional mesogens.

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Table 1. Transition temperatures (T/°C), enthalpies (ΔH/kJ mol^{-1})†, and layer spacings in the smectic A phase (d/nm) for 1,2-phenylene bis[4-(4-alkoxyphenyliminomethyl)benzoates].

n‡	C	S_B	S_A	N	I	d
1	● 149 (44)			● 187 (0·1)	●	
2	● 156 (54)			● 191 (0·2)	●	
3	● 150 (42)		[● 111 (2·2)]§	● 166 (0·2)	●	
4	● 151 (55)		[● 143 (3·4)]§	● 172 (0·2)	●	
5	● 145 (43)		● 155 (4·3)	● 166 (0·2)	●	2·36
6	● 116 (36)	[● 87 (12)]§	● 160 (3·5)	● 170 (0·3)	●	2·50
7	● 115 (25)	[● 87 (9·7)]§	● 164 (3·3)	● 167 (0·3)	●	2·61
8	● 115 (38)	[● 86 (12)]§	● 171 (4·0)	● 172 (1·5)	●	2·74
9	● 116 (37)	[● 85 (11)]§	● 173 (5·8)		●	2·88
10	● 121 (44)	[● 83 (10)]§	● 177 (5·7)		●	3·01
12	● 97 (87)	[● 79 (8·5)]§	● 177 (7·0)		●	3·29
14	● 101 (100)	[● 74 (—)]§	● 177 (7·7)		●	3·57
16	● 106 (120)		● 169 (8·3)		●	3·85

† Values in parentheses.
‡ The number of carbon atoms in the alkyl group.
§ Monotropic transitions.

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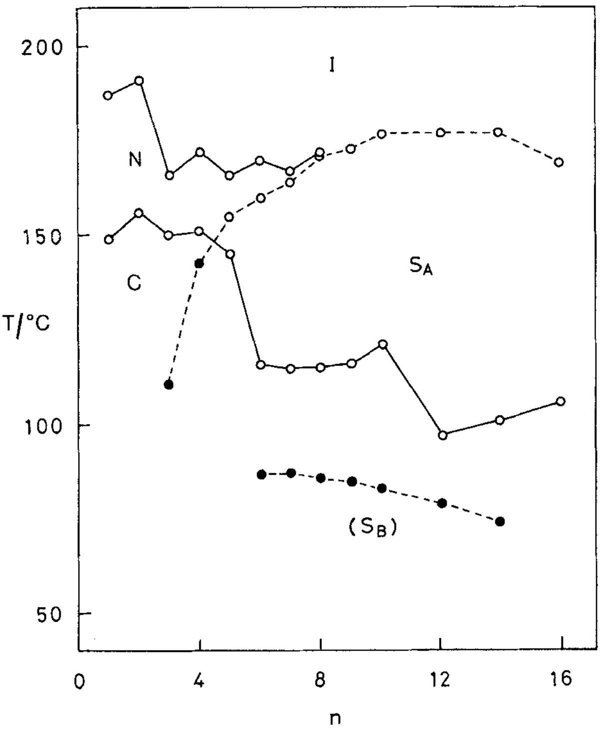

Figure 1. Plots of transition temperatures against the number carbon atoms in the alkyl group for 1,2-phenylene bis[4-(4-alkoxyphenyliminomethyl)benzoates]. The open and full circles are transitions observed in the processes of heating and cooling respectively.

Table 2. Transition temperatures (T/°C), enthalpies (ΔH/kJ mol^{-1})†, and layer spacings in the smectic A phase (d/nm) for phenyl 4-(4-alkoxyphenyliminomethyl)benzoates.

n†	C		S_A		N		I	d
1	●	142 (35)			●	184 (0·3)	●	
2	●	160 (40)			●	194 (0·4)	●	
3	●	145 (36)	[●	137 (1·2)]§	●	172 (0·3)	●	
4	●	137 (35)	●	148 (1·3)	●	178 (0·4)	●	2·45
5	●	120 (36)	●	146 (1·4)	●	167 (0·4)	●	2·57
6	●	116 (35)	●	150 (1·4)	●	166 (0·4)	●	2·70
7	●	120 (44)	●	151 (1·8)	●	161 (0·5)	●	2·83
8	●	109 (40)	●	154 (2·8)	●	163 (0·8)	●	2·93
9	●	120 (52)	●	154 (2·8)	●	158 (0·8)	●	3·07
10	●	108 (48)	●	156 (3·3)	●	157 (1·2)	●	3·17
12	●	115 (59)	●	154 (5·8)			●	3·45
14	●	116 (68)	●	152 (6·3)			●	3·67
16	●	119 (71)	●	149 (7·1)			●	3·92

† Values in parentheses.
‡ The number of carbon atoms in the alkyl group.
§ Monotropic transition.

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2.1.2. *Phase diagrams*

The identification of the mesophases detailed in 2.1.1. was confirmed by the uninterrupted miscibility with reference mesophases. The phase diagram for mixtures of the ethoxy homologue and 4,4′-azoxyanisole (hereafter abbreviated as PAA, C 117·5 N 135 I) is presented in figure 2. The N–I transition point curve is slightly convex upwards, whereas the dashed curve calculated by the equal G analysis, assuming an ideal mixture, is concave upwards [10]. As will be described below, the molecule under examination is probably V-shaped and the stabilization of the nematic phase by mixing with PAA may be attributed to the more efficient space-filling arising from the specific molecular shapes of the component molecules. Diele *et al.* have demonstrated the appearance of a smectic A phase in the phase diagram of a binary system of a nematogenic swallow-tailed compound and a nematogenic rod-like compound [11]. The incorporation of short rod-like molecules into the free space between the bulky swallow-tailed ends of the other molecules was considered to induce a more ordered mesophase, and the terms filled smectic A phase was proposed. Although no smectic phase is induced in the present binary system, similar space-filling may give stabilization of the nematic phase.

The phase diagram of the binary system composed of the octyloxy derivative and ethyl 4-(4-phenylbenzylideneamino)benzoate is shown in figure 3. The latter component displays a smectic A phase stable between 121·6 and 131°C [12], a monotropic S_A–S_B transition at 106°C and a *virtual* N–I transition just below the clearing point. The presence of the latter transition can be confirmed in the binary system. While the N–I transition point curve is convex upwards in this diagram too, both the S_A–N and S_B–S_A transition curves are pronouncedly concave upwards.

2.1.3. *X-ray studies*

The diffraction patterns recorded for the stable smectic phase of the reference compounds and the fused twins indicate the absence of in-plane order. The tendency of

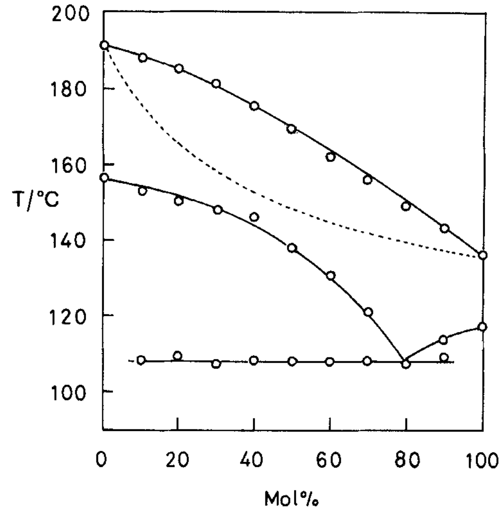

Figure 2. Phase diagram of the binary system: 1,2-phenylene bis[4-(4-ethoxyphenyliminomethyl) benzoate] and 4,4′-azoxyanisole (on the right hand side).

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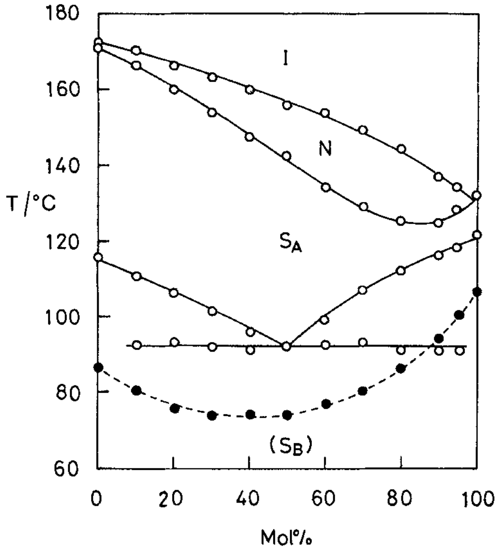

Figure 3. Phase diagram of the binary system: 1,2-phenylene bis[4-(4-octyloxyphenyliminomethyl)benzoate] and ethyl 4-(4-phenylbenzylideneamino)benzoate (on the right hand side). The open and full circles are transitions observed in the processes of heating and cooling respectively.

the mesophases to be homeotropic excludes the possibility of the smectic C type. Phenyl 4-(4-alkoxyphenyliminomethyl)benzoate molecules are regarded as terminal non-polar, and the smectic A phases given by such molecules have been considered to be of the monolayer type since the layer spacing is normally close to, but somewhat shorter than the molecular length in its most extended conformation [9]. As depicted in figure 4, using revised layer spacings [13], the Bragg spacings *d* represented by the open triangles (shaded ones for the phenyl 4-(4-alkoxybenzylideneamino)benzoates) are

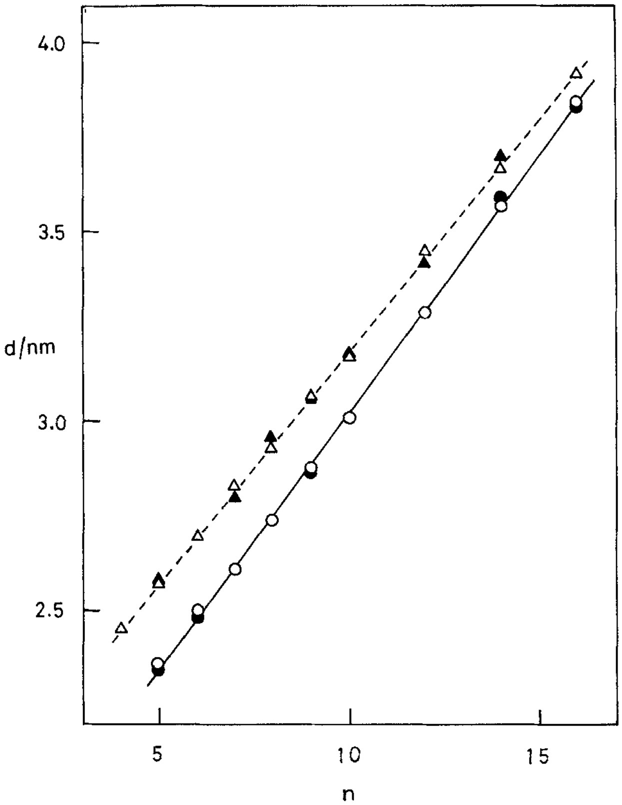

Figure 4. Bragg layer spacings for the smectic A phase of 1,2-phenylene bis[4-(4-alkoxyphenyliminomethyl)benzoates] (○) and bis[4-(4-alkoxybenzylideneamino) benzoates] (●) and those of phenyl 4-(4-alkoxyphenyliminomethyl)benzoates (△) and 4-(4-alkoxybenzylideneamino)benzoates (▲) plotted against the number of carbon atoms in the alkyl group. $d = 0{\cdot}122n + 1{\cdot}96$ (- - -) and $d = 0{\cdot}136n + 1{\cdot}67$ (——).

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approximated by $d = 0{\cdot}122n + 1{\cdot}96$, where n is the number of carbon atoms in the alkyl group. The increment per methylene group agrees well with those for alkylammonium alkanesulphonates and benzenesulphonates reported earlier [14, 15].

The molecular core of the reference compounds, i.e. the limiting case of $n = 0$, is phenyl 4-(4-hydroxyphenyliminomethyl) benzoate or 4-(4-hydroxybenzylideneamino) benzoate is estimated to be about 2·1 nm long employing standard bond lengths, angles, and van der Waals radii. It has been proposed that the orientational disorder in smectic A phases causes most molecules to make fairly large angles with the normal to the smectic layer [16, 17]. For the present molecular core, a mean tilt angle of about 21° is given by $\cos^{-1}(1{\cdot}96/2{\cdot}1)$ and is within the range 0° to about 25° suggested by Leadbetter *et al.* [16].

The relation between the observed layer spacing and the number of carbon atoms in the alkyl group is well represented by $d = 0{\cdot}136n + 1{\cdot}67$ for both 1,2-phenylene bis[4-(4-alkoxyphenyliminomethyl)benzoates] and the isomeric compounds [13].

2.1.4. *Proposed model*

The length, 1·67 nm, is the projection along the layer normal of the linear three-ring system in the fused twin, which is identical with the molecular core of the related phenyl compounds. Assuming that the imaginary smectic A phase given by the fused twin molecules in the limit of $n=0$ is of the monolayer type, the mean tilt angle of the three-ring system would be $\cos^{-1}(1{\cdot}67/2{\cdot}1)=37°$. If one takes the angular distribution of the long axis of the three-ring system into consideration, an effective length shorter than 2·1 nm may be more suitable for the estimation. In any case, the mean angle between the two 4-(4-hydroxyphenyliminomethyl)benzoate or 4-(4-hydroxybenzylideneamino)benzoate moieties connected to the 1,2-phenylene ring would be about 70°, in reasonable agreement with the angle suggested by the structural formula.

As the molecules in a smectic A phase are in irregular up-and-down orientations, the alkyl groups extend outwards in both directions to the layer boundaries. Therefore, the actual fused twin molecules in the smectic A phase may form a partial-bilayer structure with overlapping V-shaped five-ring systems in the layer-centre. Such a model is most probable in terms of the smectic potential governed by the competition of the core–core attraction and the repulsion between the molten terminal alkyl chains [18]. The rather small increment per methylene group, 1·36 nm/2, may imply that the alkyl chains make a large tilt angle with the layer normal and are interdigitated and/or conformationally disordered.

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2.2. *3-Methyl and 4-methyl-1,2-phenylene bis[4-(4-alkoxyphenyliminomethyl)benzoates]*

Table 3 presents the thermodynamic and X-ray diffraction data for the 3-methyl derivatives. The crystalline and smectic B phases tend to be stabilized by the 3-methylation, whereas the nematic phase is completely eliminated. The stability of the smectic A phase is enhanced by the substitution in the lower homologous members, but is diminished in the higher members.

Table 3. Transition temperatures (T/°C), enthalpies (ΔH/kJ mol^{-1})†, and layer spacings in the smectic A phase (d/nm) for 3-methyl-1,2-phenylene bis[4-(4-alkoxyphenyliminomethyl)-benzoates.

n‡	C		S$_B$		S$_A$		N		I	*d*
1	●	179 (56)					[●	80]§	●	
2	●	184 (56)					[●	111]§	●	
3	●	162 (57)			[●	139 (6·5)]‖			●	
4	●	153 (43)			●	156 (8·3)			●	
5	●	133 (38)	[●	104 (3·0)]‖	●	160 (11)			●	2·40
6	●	137 (38)	[●	104 (4·1)]‖	●	158 (10)			●	2·52
7	●	142 (43)	[●	104 (4·8)]‖	●	161 (11)			●	2·63
8	●	142 (45)	[●	103 (4·6)]‖	●	162 (11)			●	2·77
9	●	139 (44)	[●	104 (4·3)]‖	●	164 (11)			●	2·90
10	●	136 (46)	[●	103 (3·8)]‖	●	165 (11)			●	3·01
12	●	135 (45)	[●	103 (2·6)]‖	●	164 (11)			●	3·25
14	●	126 (44)	[●	101 (4·8)]‖	●	161 (12)			●	3·52
16	●	129 (54)	[●	99 (—)]‖	●	160 (12)			●	3·75

† Values in parentheses.

‡ The number of carbon atoms in the alkyl group.

§ Virtual values estimated from binary phase diagrams with PAA.

‖ Monotropic transitions.

Table 4. Transition temperatures (T/°C), enthalpies (ΔH/kJ mol^{-1})†, and layer spacings in the smectic A phase (d/nm) for 4-methyl-1,2-phenylene bis[4-(4-alkoxyphenyliminomethyl)-benzoates.

n‡	C		S_B		S_A		N		I	d
1	●	170 (55)					●	213 (0·2)	●	
2	●	175 (54)					●	219 (0·2)	●	
3	●	159 (54)			[●	101 (0·6)]§	●	192 (0·2)	●	
4	●	147 (49)			●	150 (1·5)	●	194 (0·2)	●	
5	●	131 (37)	[●	86 (14)]§	●	169 (3·2)	●	183 (0·2)	●	2·44
6	●	130 (42)	[●	85 (12)]§	●	179 (3·4)	●	186 (0·4)	●	2·55
7	●	135 (43)	[●	90 (12)]§	●	186 (5·7)			●	2·70
8	●	134 (45)	[●	89 (12)]§	●	189 (6·4)			●	2·81
9	●	132 (45)	[●	90 (—)]§	●	191 (7·0)			●	2·92
10	●	130 (47)	[●	88 (3·2)]§	●	192 (7·6)			●	3·05
12	●	127 (51)	[●	85 (2·8)]§	●	191 (8·6)			●	3·35
14	●	125 (57)	[●	83 (—)]§	●	189 (9·4)			●	3·58
16	●	124 (60)			●	185 (9·8)			●	3·85

† Values in parentheses.
‡ The number of carbon atoms in the alkyl group.
§ Monotropic transitions.

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We attempted to locate the virtual N–I transition temperatures in the methoxy and ethoxy homologues by studying the phase diagram of the binary system with PAA. In the ethoxy homologue–PAA system, the N–I transition curve is observable down to 30 mol% of PAA and is essentially straight, in contrast to the corresponding curve in figure 2, and extrapolation to 0 mol% yields the transition temperature 111°C. Similarly, the temperature for the methoxy homologue is located at 80°C. That is, the fall in N–I transition temperature is as large as 107°C in the case of the methoxy homologue and 80°C in the case of the ethoxy homologue.

The data for the 4-methyl derivatives are summarized in table 4. Contrary to the 3-methyl derivatives, both the nematic and smectic A phases are promoted over the whole series, with only one exception (the smectic A phase in the propoxy homologue), indicating that the substituent causes no appreciable steric effect.

A knowledge of the influence of a methyl group introduced into the related phenyl compounds on the nematic and smectic properties could be of assistance in interpreting the behaviour of the foregoing fused twins. The phenyl compounds are represented by the methoxy, butoxy, and octyloxy homologues (see table 5). The N–I transition temperature is decreased by a methyl group introduced into either the 2- or 3-position, but the influence of 3-methylation is much larger. The nematic properties of the butoxy and octyloxy homologues are completely lost upon the 3-methylation. The smectic thermal stability is also diminished by the substitution. For example, the smectic A phase of the butoxy homologue is eliminated by 2-methylation, whereas it survives 3-methylation. The similarity between the effects of methylation observed for the phenyl compounds and those for the 1,2-phenylene compounds may be taken as evidence that the 1,2-phenylene moiety is not in the middle of an elongate molecule, but at the apex of a V-shaped molecule. This conclusion is in good accordance with the model proposed in §2.1.4. The layer spacings in the smectic A phase are approximated by $d = 0{\cdot}123n + 1{\cdot}78$ for the 3-methyl derivatives and by $d = 0{\cdot}128n + 1{\cdot}79$ for the 4-methyl derivatives.

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Table 5. Transition temperatures (T/°C) and enthalpies (ΔH/kJ mol^{-1})† for methyl-substituted phenyl 4-(4-alkoxyphenyliminomethyl)benzoates.

n‡	Position§	C	$\mathrm{S_B}$	$\mathrm{S_A}$	N	I
1	2	● 134 (41)			● 139 (0·3)	●
1	3	● 130 (34)			[● 95 (0·1)]‖	●
1	4	● 128 (30)			● 275 (0·3)	●
4	2	● 95 (36)			● 142 (0·3)	●
4	3	● 105 (29)	[● 71 (1·7)]‖	● 128 (3·9)		●
4	4	● 139 (33)		● 142 (0·1)	● 254 (1·0)	●
8	2	● 61 (30)		● 101 (1·2)	● 115 (0·7)	●
8	3	● 85 (37)	[● 61 (1·4)]‖	● 127 (4·0)		●
8	4	● 111 (34)		● 180 (0·7)	● 220 (1·1)	●

† Values in parentheses.
‡ The number of carbon atoms in the alkyl group.
§ Position of the methyl group.
‖ Monotropic transitions.

Table 6. Transition temperatures (T/°C), enthalpies (ΔH/kJ mol^{-1})†, and layer spacings in the smectic A and B phases (d/nm) for 4-*tert*-butyl-1,2-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates].

n†	C	$\mathrm{S_B}$	$\mathrm{S_A}$	I	$d(\mathrm{S_B})$	$d(\mathrm{S_A})$
2	● 166 (48)			●		
3	● 133 (41)		[● 132 (3·1)]§	●		
4	● 123 (25)		● 176 (6·7)	●		
5	● 115 (34)		● 189 (9·1)	●		2·59
6	● 98 (31)	[● 72 (1·7)]§	● 194 (11)	●	2·77	2·70
7	● 77 (27)	● 79 (1·9)	● 195 (11)	●	2·89	2·81
8	● 80 (21)	[● 79 (1·1)]§	● 193 (9·2)	●	3·01	2·95
9	● 77 (24)	● 77 (2·7)	● 191 (13)	●	3·15	3·06
10	● 81 (20)	[● 76 (2·5)]§	● 189 (13)	●	3·29	3·17
12		● 73 (2·4)	● 184 (13)	●	3·48	3·38
14		● 71 (2·2)	● 180 (12)	●	3·79	3·62

† Values in parentheses.
‡ The number of carbon atoms in the alkyl group.
§ Monotropic transitions.

2.3. *4-tert-Butyl- and 4-phenyl-1,2-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates]*

2.3.1. *4-tert-Butyl derivatives*

Both the smectic A and B thermal stabilities are increased by the introduction of a *tert*-butyl group into the 4-position of the 1,2-phenylene moiety, but the nematic phase is completely lost (see table 6). Thus, the bulky *tert*-butyl group behaves as if it was a terminal substituent and also a lateral one. The $\mathrm{S_B}$–$\mathrm{S_A}$ transition temperature is close to the melting point in the hexyloxy to decyloxy homologues and the smectic B phase appearing in the dodecyloxy and tetradecyloxy homologues does not crystallize even at room temperature. Therefore, this series provides the opportunity of comparing the layer spacings of the two smectic phases. The smectic A phase gives $d=0{\cdot}114n+2{\cdot}01$ and the smectic B phase $d=0{\cdot}125n+2{\cdot}02$.

Table 7. Transition temperatures (T/°C), enthalpies (ΔH/kJ mol^{-1})†, and layer spacings in the smectic A phase (d/nm) for 4-phenyl-1,2-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates].

n‡	C		S_A		N		I	d
1	●	172 (31)			●	255 (0·1)	●	
2	●	147 (25)			●	258 (0·1)	●	
3	●	168 (25)			●	236 (0·2)	●	
4	●	169 (43)	[●	146 (1·1)]§	●	230 (0·5)	●	
5	●	147 (44)	●	166 (1·0)	●	213 (0·2)	●	2·60
6	●	133 (40)	●	181 (1·9)	●	207 (0·3)	●	2·70
7	●	116 (40)	●	197 (3·4)	●	207 (0·5)	●	2·86
8	●	101 (39)	●	201 (4·6)	●	206 (0·6)	●	2·96
9	●	102 (44)	●	203 (7·6)			●	3·11
10	●	102 (51)	●	205 (8·2)			●	3·23
12	●	99 (56)	●	206 (9·8)			●	3·50
14	●	91 (54)	●	204 (11)			●	3·77

† Values in parentheses.

‡ The number of carbon atoms in the alkyl group.

§ Monotropic transition.

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2.3.2. *4-Phenyl derivatives*

A phenyl group introduced into the 4-position of the 1,2-phenylene moiety promotes both the nematic and smectic A phases (see table 7). Though the S_A–N transition temperature in the butoxy to hexyloxy homologues is lower than that of the corresponding *tert*-butyl derivative, the temperature is higher in the later members. It is noted that the compounds do exhibit a nematic phase even though phenyl is similar in size to *tert*-butyl, 45·84 versus 44·34 cm^3 mol^{-1} [19]. The layer spacings in the smectic A phase are represented by $d = 0{\cdot}131n + 1{\cdot}92$.

2.4. *2,3-Naphthylene bis[4-(4-alkoxyphenyliminomethyl)benzoates] and bis[4-(4-alkoxybenzylideneamino)benzoates]*

As substitution at the 4-position in the 1,2-phenylene compounds leads to considerable thermal stabilization of the nematic and smectic A phases, one can foresee that the 2,3-naphthylene analogues would be highly mesogenic. Indeed, the nematic phase is promoted by 85°C to 129°C and the smectic A phase by 60°C to 77°C by replacing 1,2-phenylene group with 2,3-naphthylene group (see table 8). No smectic B phase could be detected in the series.

The inversion of the azomethine group lowers the N–I transition temperature by 1 to 13°C and the S_A–N/I transition temperature by 11 to 26°C, resulting in the emergence of a nematic phase in the decyloxy homologue (see table 9). The melting point is also lowered with two exceptions (the hexyloxy and heptyloxy homologues). The temperature range for the smectic A phase is so broadened that the phase in the nonyloxy homologue has a range of the stable existence over 142°C.

As the melting points are higher in the first series and the compounds in the smectic A phase decompose gradually, the X-ray diffraction measurements were performed only on the second series. The increment per methylene group, 0·136 nm, agrees with that for the unsubstituted 1,2-phenylene compounds, but the spacing is invariably larger by 0·23 nm. This value agrees with the difference in the molecular width between

Table 8. Transition temperatures (T/°C) and enthalpies (ΔH/kJ mol^{-1})† for 2,3-naphthylene bis[4-(4-alkoxyphenyliminomethyl)benzoates].

n‡	C	S$_A$	N	I
3	● 205 (45)		● 295 (0·1)	●
4	● 163 (43)	● 203 (0·3)	● 286 (0·1)	●
5	● 155 (41)	● 221 (0·3)	● 276 (0·1)	●
6	● 148 (42)	● 232 (0·4)	● 269 (0·1)	●
7	● 143 (42)	● 241 (0·5)	● 263 (0·3)	●
8	● 140 (43)	● 245 (1·0)	● 257 (0·8)	●
9	● 138 (44)	● 249 (1·7)	● 254 (0·9)	●
10	● 135 (45)	● 250 (5·9)		●
12	● 144 (58)	● 249 (7·4)		●
14	● 127 (46)	● 244 (7·9)		●

† Values in parentheses.
‡ The number of carbon atoms in alkyl group.

Table 9. Transition temperatures (T/°C), enthalpies (ΔH/kJ mol^{-1}), and layer spacings in the smectic A phase (d/nm) for 2,3-naphthylene bis[4-(4-alkoxybenzylideneamino)benzoates].

n†	C	S$_A$	N	I	*d*
3	● 189 (51)	[● 134 (—)]§	● 294 (0·1)	●	
4	● 138 (41)	● 181 (—)	● 282 (0·2)	●	
5	● 138 (32)	● 198 (0·1)	● 263 (0·2)	●	2·59
6	● 156 (47)	● 215 (0·5)	● 260 (0·3)	●	2·69
7	● 151 (46)	● 225 (0·8)	● 252 (0·4)	●	2·83
8	● 100 (30)	● 231 (1·3)	● 248 (0·6)	●	2·98
9	● 93 (47)	● 235 (2·0)	● 244 (0·7)	●	3·13
10	● 99 (42)	● 234 (3·6)	● 238 (0·6)	●	3·25
12	● 117 (50)	● 237 (7·7)		●	3·53
14	● 111 (52)	● 233 (9·5)		●	3·79

† Values in parentheses.
‡ The number of carbon atoms in the alkyl group.
§ Monotropic transition.

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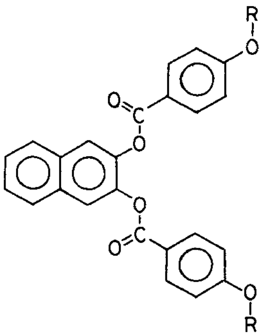
benzene and naphthalene nuclei, suggesting that the orientational distribution of the molecular symmetry axes relative to the layer normal is not much affected by the replacement.

2.5. *2,3-Naphthylene bis(4-alkoxybenzoates)*



Further striking examples are provided by 2,3-naphthylene bis(4-alkoxybenzoates) (see table 10). The compounds show only monotropic liquid crystalline properties. Both the nematic and smectic A phases are promoted as the series is ascended. The enthalpies at some mesomorphic transitions could not be measured due to solidification of melts. Nevertheless, the transition temperatures could be determined by a change in the microscopic textures. The nematic phase adopts a schlieren texture and the smectic A phase a fan texture. The assignment of the nematic phase is supported by the phase diagram of the binary system comprising the octyloxy homologue and PAA shown in figure 5, in which the continuous N–I transition point curve is slightly

Table 10. Transition temperatures (T/°C) and enthalpies (ΔH/kJ mol^{-1})† for 2,3-naphthylene bis(4-alkoxybenzoates).

n‡	C		S_A		N		I
4	●	127 (46)			[●	19 (0·1)]§	●
5	●	102 (44)			[●	17 (0·1)]§	●
6	●	93 (42)			[●	35]§‖	●
7	●	105 (54)			[●	43 (0·2)]§	●
8	●	90 (47)			[●	55]§‖	●
9	●	85 (39)			[●	59]§‖	●
10	●	85 (40)			[●	65]§‖	●
12	●	84 (41)	[●	66]§‖	[●	70]§‖	●
14	●	84 (55)	[●	73 (4·1)]§			●
16	●	87 (70)	[●	76 (6·2)]§			●
18	●	91 (80)	[●	79]§‖			●

† Values in parentheses.

‡ The number of carbon atoms in the alkyl group.

§ Monotropic transitions.

‖ Determined by optical microscopy.

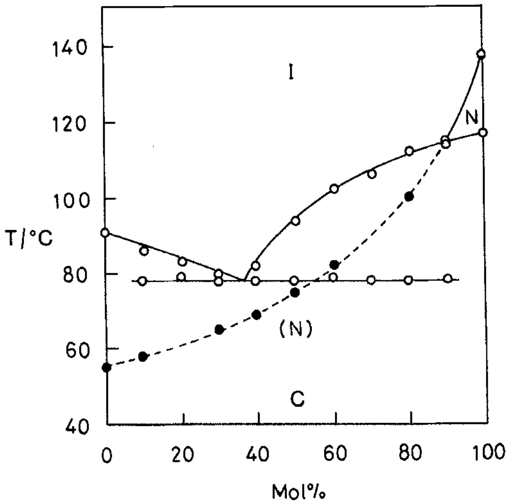


Figure 5. Phase diagram of the binary system: 2,3-naphthylene bis(4-octyloxybenzoate) and 4,4′-azoxyanisole (on the right hand side). The open and full circles are transitions observed in the processes of heating and cooling respectively.

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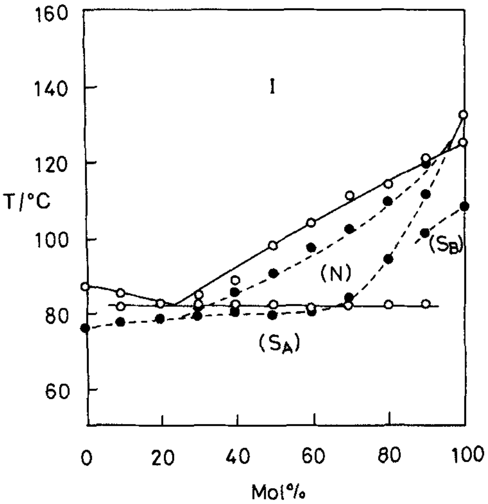

Figure 6. Phase diagram of the binary system: 2,3-naphthylene bis(4-hexadecyloxybenzoate) and ethyl 4-(4-phenylbenzylideamino) benzoate (on the right hand side). The open and full circles are transitions observed in the processes of heating and cooling respectively.

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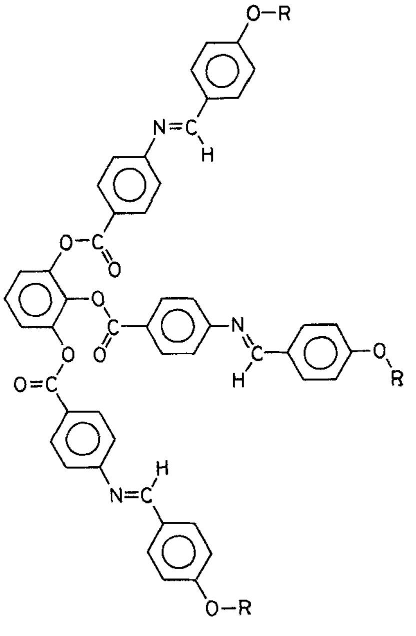
concave upwards. Figure 6 presents the diagram for mixtures of the hexadecyloxy homologue and ethyl 4-(4-phenylbenzylideneamino)benzoate. This shows that the virtual N–I transition in the hexadecyloxy homologue is located around 70°C. The emergence of a nematic phase in the present system may be rationalized in terms of the different molecular shapes of the components. Even a large difference in molecular length in mixtures of two homologues is enough to destabilize the smectic A phase [20].

2.6. *1,2,3-Tris[4-(4-alkoxybenzylideneamino)benzoyloxy]benzenes*



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In 1935, Schadendorff and Verdino reported that 1,2,3-tris(cholesteryloxycarbonyloxy)benzene yields a metastable mesophase which has not been characterized yet [21]. Accordingly, it seemed worthwhile to examine 1,2,3-tris[4-(4-alkoxybenzylideneamino)benzoyloxy]benzenes. We found a stable smectic A phase for the hexyloxy to tetradecyloxy homologues and an additional metastable smectic B phase for the hexyloxy to decyloxy homologues (see table 11). The former phase shows a fan texture and the latter a paramorphic fan texture. The S_A–I transitions are found within a range as narrow as 4°C and the S_B–S_A transitions within 5°C. The enthalpies at the clearing point are in the range 16–20 kJ mol^{-1} and are much larger than typical values compiled by Demus *et al.* [9]. Binary mixtures composed of the octyloxy homologue and phenyl 4-(4-octyloxybenzylideneamino)benzoate give the diagram shown in figure 7. The nematic phase is observable only above 70 mol% of the reference compound. It is certain that the smectic phases are of the A and B types respectively, as

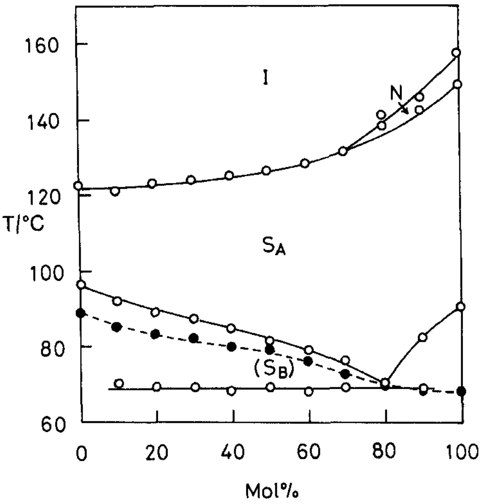

Figure 7. Phase diagram of the binary system: 1,2,3-tris[4-(4-octyloxybenzylideneamino)-benzoyloxy]benzene and phenyl 4-(4-octyloxybenzylideneamino)benzoate (on the right hand side). The open and full circles are transitions observed in the processes of heating and cooling respectively.

Table 11. Transition temperatures (*T*/°C), enthalpies (ΔH/kJ mol^{-1})†, and layer spacings in the smectic A phase (*d*/nm) for 1,2,3-tris[4-(4-alkoxybenzyleneamino)benzoyloxy)benzoates.

n‡	C		S_B		S_A		I	*d*
6	●	89 (89)	[●	87 (6·1)]§	●	119 (16)	●	2·48
7	●	96 (112)	[●	87 (6·3)]§	●	119 (18)	●	2·59
8	●	96 (113)	[●	88 (6·2)]§	●	122 (18)	●	2·71
9	●	101 (137)	[●	85 (5·7)]§	●	121 (19)	●	2·82
10	●	100 (131)	[●	83 (—)]§	●	122 (20)	●	2·92
12	●	104 (150)			●	119 (20)	●	3·22
14	●	106 (170)			●	118 (19)	●	3·47

† Values in parentheses.

‡ The number of carbon atoms in the alkyl group.

§ Monotropic transitions.

demonstrated by the uninterrupted S_A–I/N and S_B–S_A transition curves. Measurement of the layer spacing in the smectic A phase is hampered by gradual thermal decomposition; therefore, the values given in table 11 are not as precise as those obtained for other compounds. The important point is that they are shorter by about 0·2 nm than those for phenyl 4-(4-alkoxyphenyliminomethyl)benzoates and 4-(4-alkoxybenzylideneamino)benzoates. Apparently, the excessive steric crowding in the vicinity of the ester groups forces the three 4-(4-alkoxybenzylideneamino)benzoate moieties away from the coplanar configuration. Then, one may infer that the layer normal is not in a direction parallel to the extended central benzoate moiety. Such a molecular geometry may account for the low smectic thermal stabilities in this series.

3. Conclusions

In spite of the acute-angled molecular configuration, all the compounds reported in this paper exhibit classical nematic and/or smectic phases. Moreover, the behaviour of the 1,2-phenylene compounds resembles closely that of the related phenyl compounds.

Takenaka *et al.* have discussed the boundary between the rod-like and discotic liquid crystals in terms of molecular structure [22]. From the geometrical point of view, the discotic properties of molecules may be enhanced when the molecular length and breadth increase simultaneously, whereas the rod-like properties are enhanced when the molecule becomes longer. 1,2-Phenylene and 1,3-phenylene bis(4-octyloxybenzoates), which have acute- and obtuse-angled configurations respectively, can be classified neither as rod-like nor discotic; therefore, Takenaka *et al.* predicted poor mesomorphic properties for these compounds. As a matter of fact, both compounds are non-mesomorphic. However, our present study indicates clearly that their conclusion would have been different if sufficiently long-stretched groups had been employed in place of 4-octyloxybenzoate.

In order to predict mesomorphic properties, there is another feature to be considered. The anisotropic intermolecular forces maintaining order in liquid crystals are significantly influenced by the functional groups; that is, terminal and linking groups. If the linking group is asymmetric, one has to pay attention to the direction in which it points. As described above, inversion of the azomethine group affects noticeably the thermal behaviour of our compounds, though the mesophases remain mostly stable. The sense of the ester group is however more crucial, and its inversion is very unfavourable to the occurrence of mesophases, at least, in the present series of compounds.

1,3-Phenylene bis[4-(4-alkoxyphenyliminomethyl)benzoates] and their related compounds also exhibit classical mesophases and will be the subject of a forthcoming paper [23].

4. Experimental

4-Alkoxyanilines were obtained from 4-nitrophenol and the appropriate 1-bromoalkane, followed by reduction with zinc dust in 75 per cent aqueous ethanol [24]. 4-Alkoxybenzaldehydes were commercial products or were prepared by the alkylation of 4-hydroxybenzaldehyde following the method of Gray and Jones [25]. 4-(4-Alkoxyphenyliminomethyl)benzoic acids and 4-(4-alkoxybenzylideneamino)benzoic acids were obtained by the condensation of 4-alkoxyanilines with 4-formylbenzoic acid and of 4-alkoxybenzaldehydes with 4-aminobenzoic acid, respectively. The esterification of phenol, catechol naphthalene-2,3-diol, and pyrogallol with the 4-(4-alkoxyphenyliminomethyl)benzoic acids or 4-(4-alkoxybenzylideneamino)benzoic acids by the procedure of Hassner and Alexanian led to the desired compounds [26].

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The mesophases were identified by examination of their textures using a polarizing microscope in conjunction with a heated stage. The transition temperatures and enthalpies were recorded on a Rigaku Thermoflex differential scanning calorimeter at heating and cooling rates of 5 K min^{-1}. The phase diagrams were determined by calorimetry using 10 mol% incremental mixtures. X-ray powder diffraction measurements were made with a Rigaku autodiffractometer, Model RAD I VB, using filtered copper radiation. The temperature of the sample holder was regulated with the aid of a Chino temperature indicating controller, Model E 500.

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