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Chiral smectic C phases exhibited by biphenyl resorcylate and vanillate derivatives

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We report the synthesis and mesomorphic behaviour of alkoxybiphenyl resorcylate and vanillate derivatives with a chiral moiety obtained from chloro analogues of L-leucine, L-valine and L-isoleucine. The compounds have been characterized by NMR spectroscopy and the mesophases studied by DSC and optical microscopy. In the synthesized compounds, an enantiotropic chiral smectic C phase over a wide temperature range has been observed. Changes in the phase behaviour caused by structural variations in the core and the optically active alkyl chain are also discussed.

1. Introduction

A cursory survey of substituents present in aromatic mesogens indicates that hydroxy compounds are few in number when compared with halogen substituted analogues. In addition to the inductive and resonance effect, a hydroxyl group also influences the structural aggregations by formation of inter- and intra-molecular hydrogen bonding. A lateral hydroxyl group was initially incorporated in Schiff's bases to enhance the stability of the benzylideneamino linkage [1]. This group has been found to favour the chiral smectic C phase over other phases in some cases [2]. It has been demonstrated that the positioning of this group has a pronounced effect on the thermal stability of the chiral smectic C phase [3]. Examples of an increase in the spontaneous polarization value upon introduction of this group in a position favourable for intramolecular hydrogen bonding have also been reported [4–6]. Kaspar *et al.* have recently reported monotropic smectic C* phases observed in biphenyl vanillates with a derivatized lactate attached to the biphenyl ring [7]. In continuation of our earlier work [8], we report the synthesis and mesomorphic behaviour of three homologous series of alkoxybiphenyl resorcylate derivatives, and the decyl homologues of the vanillate derivatives, with a chiral moiety comprising the chloro analogues of amino acids L-leucine, L-valine, and L-isoleucine.

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2. Experimental

The target compounds were synthesized by the routes shown in scheme 1.

2.1. *Synthesis of 4-(4-decyloxyphenyl)phenol (**1**)*

To a stirred solution of sodium ethoxide, prepared by adding sodium (0.05 g atom) to absolute ethanol (200 ml), was added 4,4′-biphenol (0.05 mol) and the reaction mixture was heated under reflux for 1 h. The resulting dark solution was then cooled to room temperature and 1-bromodecane (0.055 mol) added to it. The reflux was continued with stirring for a period of 24 h. Ethanol was then removed *in vacuo* and the residual reaction mixture poured into ice-cold 10% aqueous HCl (50 ml). The organic layer was extracted with ethyl acetate (2 × 100 ml); an insoluble solid floating in the ethyl acetate layer was filtered off. The clear combined organic layer was then washed with water (3 × 100 ml), dried over anhydrous sodium sulphate, filtered and the solvent evaporated. The solid obtained was stirred with cold petroleum ether and the ether layer decanted off. The solid was then crystallized once from acetone and twice from ethanol to yield the desired pure product **1**. Yield 52%, m.p. 147°C [9].

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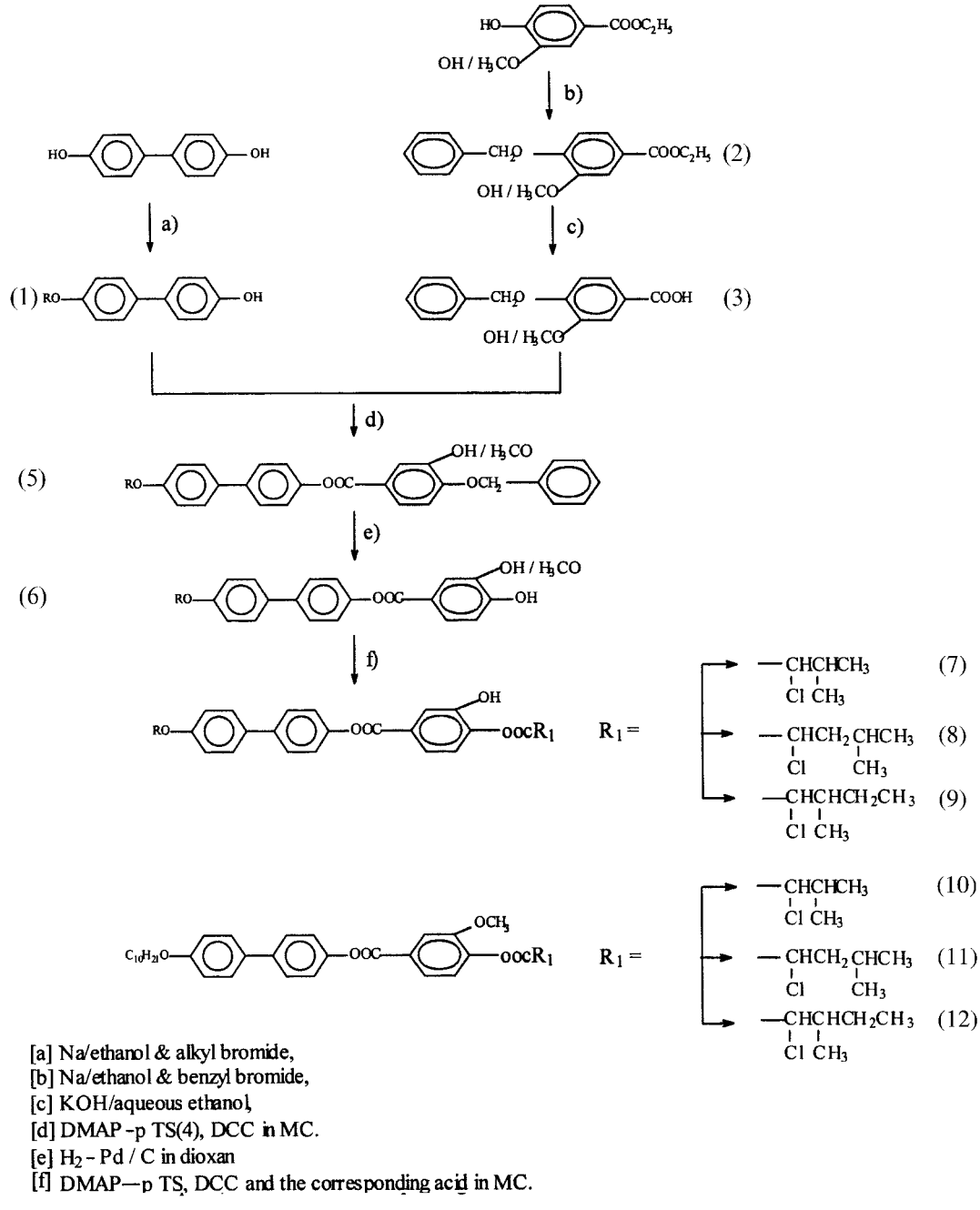


[a] Na/ethanol & alkyl bromide,
[b] Na/ethanol & benzyl bromide,
[c] KOH/aqueous ethanol,
[d] DMAP - p TS(4), DCC in MC.
[e] H_2 - Pd / C in dioxan
[f] DMAP—p TS, DCC and the corresponding acid in MC.

Scheme 1. Structures and synthesis scheme of target compounds.

2.2. *Synthesis of ethyl 4-benzyloxy-3-methoxybenzoate (**2**)*

To a stirred solution of sodium ethoxide, prepared by addition of sodium (0043 g atom) to absolute ethanol (150 ml), was added ethyl 4-hydroxy-3-methoxybenzoate (0.04 mol) and the reaction mixture was heated under reflux for 1 h. After cooling this clear solution to room temperature, benzyl bromide (0.044 mol) was added. The reaction mixture was then heated under reflux for 18 h. After completion of the reaction, ethanol was removed *in vacuo* and the residue poured into ice-cold water (60 ml). The organic portion was extracted twice with methylene chloride and the combined organic layer (200 ml) washed successively with 5% aqueous sodium hydroxide (5 × 60 ml), water (1 × 75 ml), dilute HCl (2 × 60 ml) and water (2 × 60 ml). The solution was then dried over anhydrous sodium sulphate and filtered. The solvent was removed *in vacuo* to yield a white solid, which was stirred with cold petroleum ether. The ether layer was decanted off and the obtained product **2** was crystallized from ethanol. Yield 83%, m.p. 80°C.

2.3. *Synthesis of 4-benzyloxy-3-methoxybenzoi c acid (**3**)*

A mixture of compound **2** (0.028 mol), potassium hydroxide (0.041 mol), water (4 ml) and ethanol (20 ml) was heated under reflux vigorously for 4 h. The reaction mixture was then poured into excess of water (200 ml) and acidified with cold dilute HCl to yield a white precipitate which was crystallized from acetone and then from ethanol to give the desired acid **3**. Yield 90%, m.p. 172°C.

2.4. *Synthesis of 4-N,N-dimethylaminopyridinium 4-toluenesulphonat e (**4**)*

A warm solution of 4-*N*,*N*-dimethylaminopyridine (0.1 mol) in dry benzene was added to a stirred hot solution of dehydrated *p*-toluenesulphonic acid (0.11 mol) in dry benzene, resulting in an immediate precipitation of a white powder. The reaction mixture was cooled, and the product **4** filtered and dried. Yield 95%, m.p. 168°C [10].

2.5. *Synthesis of 4′-decyloxybiphenyl 4-benzyloxy-3-methoxybenzoat e (**5**)*

To a stirred mixture of compound **1** (0.015 mol), **3** (0.015 mol) and **4** (00076 mol) in methylene chloride (60 ml) was added *N*,*N*′-dicyclohexylcarbodiimide (0.225 mol) in methylene chloride (10 ml). The reaction mixture was stirred at room temperature for 36 h. It was then filtered, further diluted by addition of the solvent (50 ml) and washed successively with 5% aqueous sodium hydroxide (3 × 50 ml), water (1 × 50 ml), dilute HCl (1 × 50 ml), and water (2 × 50 ml). It was then dried over anhydrous sodium sulphate and the solid obtained after removal of the solvent was chromatographed on silica gel and eluted with a 30% mixture of chloroform in hexane. The pure solid obtained after evaporating the solvent was crystallized from acetone to yield ester **5**. Yield 78%, m.p. 132°C, Cr 132 N 146 I.

2.6. *Synthesis of 4′-decyloxybiphenyl 4-hydroxy-3-methoxybenzoat e (**6**)*

A solution of compound **5** (0.011 mol) in 1,4-dioxane (60 ml) containing 5% palladized charcoal (2 g) was stirred vigorously in an atmosphere of hydrogen for 20 h at room temperature. It was then filtered and the solvent distilled off *in vacuo*. The solid obtained was crystallized twice from ethanol to yield the product **6**. Yield 90%, m.p. 133.5°C.

2.7. *Synthesis of [S]-4′-decyloxybiphenyl 4-(2-chloro-3-methylbutanoyloxy)-3-methoxybenzoate (**7**), [S]-4′-decyloxybiphenyl 4-(2-chloro-4-methylpentanoyloxy)-3-methoxybenzoate (**8**), and [2S,3S]-4′-decyloxybiphenyl 4-(2-chloro-3-methylpentanoyloxy)-3-methoxybenzoate (**9**)*

Following a procedure similar to the one described for compound **5**, esterification of 4′-decyloxybiphenyl 4-hydroxy-3-methoxybenzoate with [*S*]-2-chloro-3-methylbutanoic acid yielded [*S*]-4′-decyloxybiphenyl 4-(2-chloro-3-methylbutanoyloxy)-3-methoxybenzoate (**7**), which was purified by column chromatography and recrystallized from ethanol. Yield 75%, m.p. 67.0°C, mesophase transition temperature (°C) and heats of transition (J g^{-1}) Cr 67.0 (40.3) SmC* 110.8 (0.3) SmA 133.8 (1.2) N* 139.1 (1.4) I.

By analogous reactions the following were obtained.

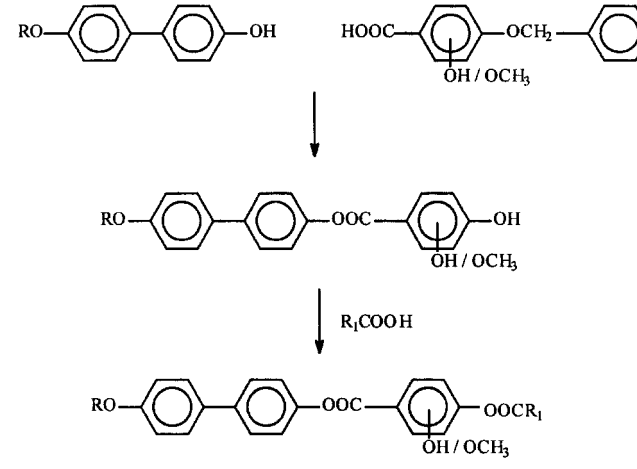
[*S*]-4′-Lecyloxybiphenyl 4-(2-chloro-4-methylpentanoyloxy)-3-methoxybenzoate (**8**). Yield, 78%, m.p. 69.5°C, mesophase transition temperatures (°C) and heats of transition (J g^{-1}) Cr 69.3 smC* 109.0 (1.1) SmA 117.8 (5.7) I.

[2*S*,3*S*]-4′-Decyloxybiphenyl-4-(2-chloro-3-methylpentanoyloxy)-3-methoxybenzoate (**9**). Yield 76%, m.p. 67.7°C, mesophase transition temperatures (°C) and heats of transition (J g^{-1}) Cr 67.7 SmC* 116.5 (0.3) SmA 129.5 (0.6) N* 133.07 (1.9) I.

3. Results and discussion

The structures and the synthetic scheme of the compounds under study are summarized in Scheme 2.

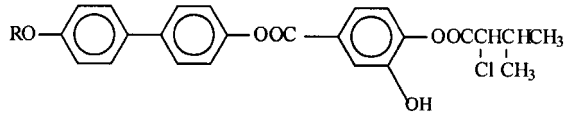
In the resorcylates, the hydroxyl group is inclined towards the bridging ester group in the core and is in a position favourable to form hydrogen bonding with the carboxylate group. In the vanillates, the methoxy group is inclined away from the core and is in a position to hinder the rotation of the ester carbonyl adjacent to the chiral carbon, thereby further hindering the already restricted rotation of the chiral centre.



R_1 = $-CH(Cl)CH(CH_3)_2$
$-CH(Cl)CH_2CH(CH_3)_2$
$-CH(Cl)CH(CH_3)CH_2CH_3$

Scheme 2. Synthesis scheme of target compounds, summary.

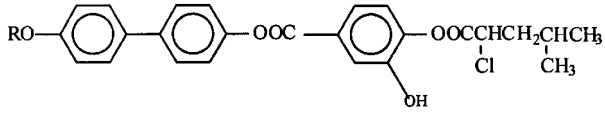
Table 1. Phase transition temperature (°C) of compounds **7**.



n^a	Cr		SmC*		SmA		N*		I
9	•	80.5	•	113.0	•	152.0	•	152.5	•
10	•	79.5	•	113.5	•	151.0	–		•
11	•	80.0	•	112.5	•	148.5	–		•
12	•	80.5	•	112.0	•	147.5	–		•

[a] Number of C atoms in alkyl chain *R*.

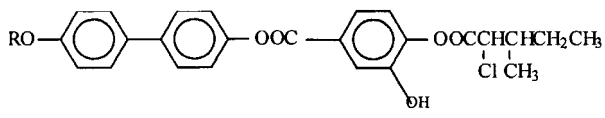
Table 2. Phase transition temperature (°C) of compounds **8**.



n^a	Cr		SmC*		SmA		I
9	•	79.5	•	95.5	•	140.0	•
10	•	88.5	•	112.0	•	142.0	•
11	•	87.5	•	113.0	•	139.0	•
12	•	93.5	•	114.0	•	138.0	•

[a] Number of C atoms in alkyl chain *R*.

Table 3. Phase transition temperature (°C) of compounds **9**.



n^a	Cr		SmC*		SmA		I
9	•	59.0	•	107.0	•	138.5	•
10	•	63.5	•	114.5	•	141.0	•
11	•	65.5	•	113.0	•	139.0	•
12	•	67.5	•	114.0	•	137.5	•

[a] Number of C atoms in alkyl chain *R*.

Table 4 gives the phase transition temperatures for compounds **7**. The thermal range of the smectic C* phase is 30–35°C and that of smectic A is 35–40°C. The latter shows a gradual decrease upon ascending the series.

The introduction of a methylene unit between the chiral carbon and the terminal isopropyl group lowers the thermal stabilities of smectic A phase but not that of smectic C* phase. The range of this phase is also reduced due to the enhanced melting points, see table 2 for data on compounds **8**.

Compounds **9** are isomeric to the compounds **8**, but with an additional chiral centre. A considerable lowering of melting points enhances the range of smectic C* phase which is about 45–50°C, see table 3.

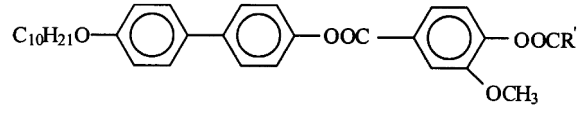
Table 4 gives data for compounds **10**, **11** and **12**. The chiral nematic phase which is absent in compound **11**, continues to persist in the decyl homologues of the other two compounds **10** and **12**. The change from resorcylate to the vanillate ring in the core lowers the thermal stabilities as well as the range of smectic A phase, whereas the thermal stabilities of the smectic C* phase are not much affected.

A lowering of the melting points in compounds **10** and **11** enhances the range of the smectic C* phase, but no such effect is seen in compound **12**. When compound **10** was observed under a polarizing microscope, it showed a banded focal conic texture; in the other two compounds a schlieren texture was observed by cooling the homeotropic smectic A phase. This smectic C*–smectic A transition is seen in the heating as well as the cooling cycles in the DSC plots and the smectic C* phase upon cooling (10°C min^{-1}) is seen to supercool to more than 40°C below the melting points, thereby providing a total phase range more than 75°C in case of compounds **10** and **11** and about 95°C for compound **12**.

4. Conclusions

We have synthesized the alkoxybiphenyl resorcylate and vanillate derivatives with a chiral moiety obtained from chloro analogues of L-leucine, L-valine, and L-isoleucine. In all the synthesized compounds, the smectic A phase is preceded by an enantiotropic smectic C* phase over

Table 4. Phase transition temperature (°C) of compounds **10**, **11** and **12**.



Compound	Cr		SmC*		SmA		N*		I
10	•	63.5	•	113.0	•	132.5	•	138.0	•
11	•	55.0	•	107.5	•	116.0	–		•
12	•	60.0	•	108.0	•	127.0	•	132.5	•

a wide temperature range, and in case of compounds with lateral methoxy group this ferroelectric phase is the predominant phase.

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