Nematogens for Matrix-Addressed Twisted Nematic Displays, II

Maged A. Osman and T. Huynh-Ba
Brown Boveri Research Center, CH-5405 Baden, Switzerland

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Nonpolar Aromatic Nematogens, Biphenyls and Phenyl Pyrimidines, Lateral Halo-Substituents, Mesophase Thermodynamic Stability, Application in Displays

Nonpolar aromatic nematogens useful in mixtures for high performance matrix-addressed twisted nematic displays were synthesized. Nematic phases were obtained by introducing lateral halo-substituents in purely smectic biphenyls and phenyl pyrimidines. Because of their chemical stability, low viscosity and negative dielectric anisotropy, the substituted biphenyls can also be used in mixtures of negative dielectric anisotropy which are needed for the homeotropic nematic and guest-host displays with positive contrast. The effect of lateral halo-substituents on the mesomorphic properties of rod-like molecules is discussed.

Introduction

The need for nematogens which possess low ratios of the dielectric anisotropy to the dielectric constant perpendicular to the optical axis ($\Delta e/e^*$), and of bend to splay elastic constants ($k_{33}/k_{11}$) in high performance matrix-addressed TN-displays was pointed out in part I of this work [1]. Nematic mixtures of polar (terminally cyano substituted) and nonpolar (dialkyl or alkyl alkoxy derivatives) liquid crystals (LC's) [2–5] were shown to be quite useful for this application, since the nonpolar compounds usually possess the required low $\Delta e$ and $k_{33}/k_{11}$ ratios [1, 6–8] beside their low viscosity. The polar components are incorporated in the mixtures to obtain the necessary large positive $\Delta e$ and to increase the optical anisotropy ($\Delta n$), since the todays ~8a TN-displays need a nematic phase with $\Delta n$ of at least 0.14. The dielectric and bend elastic constants of polar-nonpolar mixtures were found to show negative deviations from the additivity rule, which is also in favour of their use in matrix-addressed TN-displays [5, 9, 10]. The limitation on the application of these mixtures however, is given by the fact that most of the aromatic nonpolar LC's (relative large $\Delta e$) described in the literature are smectic. Many of the few known nematic nonpolar compounds also induce smectic phases in the polar nematic LC's [11–13]. Therefore, new nonpolar nematogens which don't suffer from these disadvantages are required.

Lateral substituents are generally known to depress the clearing point of mesogenic compounds [14]. However, the introduction of a fluoro sub-

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halo-substituents in such molecules on their mesomorphic behaviour. It was hoped that the lateral halo-substituents can disturb the layered structure packing of the smectic molecules without completely destabilizing their mesophase. Lateral halo-substituents are also known to increase $\varepsilon_1$, and a reduction of $\Delta\varepsilon/\varepsilon_1$ is to be expected [1].

**Results and Discussion**

The 1,4-bis-(4-trans-n-pentyl cyclohexyl) benzene [19], which shows only a smectic phase with high clearing point was chosen as a model compound for this study. The effect of lateral halo-substituents on its mesomorphic behaviour [20] is shown in Table I. Introduction of a lateral fluoro substituent in the aromatic nucleus of compound 1, depressed the smectic phase and favoured a nematic one. Bulkier halogen atoms such as chlorine and bromine completely eliminated the smectic phase, and a nematic one was obtained instead. Although it was possible to supercool the nematic phases of compounds 3 and 4 down to 0 °C, no smectic phase was observed. A lateral fluoro substituent decreased the clearing point of compound 1 by 53 °C only, while a chlorine lowered it by 100 °C and a bromine by 115 °C. In other words, the N-I transition decreased with increasing volume of the lateral substituent. However, lateral halo-substituents were able to eliminate or suppress the smectic phase and favour the nematic one.

Bearing these facts in mind, and in order to obtain nematogens with small $\Delta\varepsilon/\varepsilon_1$, small $k_{33}/k_{11}$ and relatively large $\Delta n$ suitable for matrix-addressing, we studied the effect of lateral fluoro and chloro substituents on the mesomorphic properties of smectic aromatic nonpolar LC's of the biphenyl and phenyl pyrimidine series [21]. These two classes were chosen because of their high chemical stability, relative large $\Delta n$ and low viscosity compared to those of the nonpolar esters, which are commonly used today. The bromo derivatives were not investigated because of the strong depressing effect of the bulky bromo substituent on the clearing point. Table II shows the effect of these lateral substituents on the type, and thermodynamic stability of the mesophase. Substitution of the proton in position-3 of the 4-ethoxy-4'-n-pentyl biphenyl 5 by a fluorine atom lead to the disappearance of the smectic phase, but no nematic phase could be observed because of its relative high melting and freezing points. The supercooled melt of compound 6 didn’t show any mesophase down to 45 °C. The same observation was also made for the higher homologue 8. However, the low melting hexyloxy derivative 11 showed a short nematic phase on top of the smectic one with a clearing point which is 48 °C lower than that of the unsubstituted parent compound 10. From mixtures of the two homologues 6 and 11, an extrapolated clearing point of 26 °C can be assumed for compound 6, which is also 55 °C lower than that of the unsubstituted compound 5. A nematic equimolar mixture of both compounds 6 and 11 showed no smectic phase down to 20 °C (freezing point). No extrapolated value for the clearing point of compound 8 could be obtained, because of its tendency to crystallize. The introduction of a chlorine atom in the alkyl alkoxy biphenyl molecules instead of the fluorine lead to a stronger depression in the clearing point (70–80 °C), but the smectic phase was completely eliminated and a nematic one was obtained. Both compounds 9 and 12 didn’t show any smectic tendency down to —20 °C. Compound 12 has a remarkable low melting point, which renders it useful in developing eutectic mixtures with broad temperature ranges.

In the alkanoyloxy biphenyl derivatives (compounds 13 and 15), the fluoro substituent (compounds 14 and 16) was not able to eliminate the smectic phase but the chlorine gave a nematic compound 17. Again the clearing points were depressed by ~55 °C in the fluoro derivatives, and ~80 °C in the chloro compound. The introduction

<table>
<thead>
<tr>
<th>X</th>
<th>C</th>
<th>S</th>
<th>N</th>
<th>I</th>
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<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>· 50</td>
<td>196 [19]</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>F</td>
<td>· 61.0</td>
<td>79.2</td>
<td>· 142.8</td>
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<tr>
<td>3</td>
<td>Cl</td>
<td>· 46.1</td>
<td>—</td>
<td>· 96.1</td>
</tr>
<tr>
<td>4</td>
<td>Br</td>
<td>· 40.5</td>
<td>—</td>
<td>· 80.8</td>
</tr>
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</table>

(C = crystalline, S = smectic, N = nematic, I = isotropic, values given in brackets represent a monotropic phase and a dot shows the existence of a phase transition while a dash indicates that the corresponding phase is missing. All values are given in °C.)
Table II. Effect of lateral halo-substituents on the mesomorphic properties of some biphenyls and phenyl pyrimidines (for symbols see Table I).

<table>
<thead>
<tr>
<th></th>
<th>C</th>
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<td>5</td>
<td>( \text{C}_6 \text{C}_5 \text{O}_2 \text{H}_5 )</td>
<td>(72)</td>
<td>(81) [22]</td>
<td>(6)</td>
<td>(7)</td>
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<tr>
<td>6</td>
<td>( \text{C}_6 \text{C}_5 \text{O}_2 \text{H}_5 )</td>
<td>(57.8)</td>
<td>(-)</td>
<td>(26)*</td>
<td>(7)</td>
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<tr>
<td>7</td>
<td>( \text{C}_6 \text{C}_5 \text{O}_2 \text{H}_5 )</td>
<td>(37)</td>
<td>(80.1)</td>
<td>(88.1)</td>
<td>(7)</td>
</tr>
<tr>
<td>8</td>
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<td>(48.0)</td>
<td>(-)</td>
<td>(-)</td>
<td>(7)</td>
</tr>
<tr>
<td>9</td>
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<td>(38.1)</td>
<td>(-)</td>
<td>(7.5)</td>
<td>(7)</td>
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<tr>
<td>10</td>
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<td>(82)</td>
<td>(84) [22]</td>
<td>(7)</td>
<td>(7)</td>
</tr>
<tr>
<td>11</td>
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<td>(37.9)</td>
<td>(35.3)</td>
<td>(30.0)</td>
<td>(7)</td>
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<tr>
<td>12</td>
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<td>(1.7)</td>
<td>(-)</td>
<td>(11.1)</td>
<td>(7)</td>
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<tr>
<td>13</td>
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<td>(80)</td>
<td>(-)</td>
<td>(-)</td>
<td>(1)</td>
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<tr>
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<td>(46.3)</td>
<td>(24.2)</td>
<td>(7)</td>
<td>(7)</td>
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<tr>
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<td>(45.7)</td>
<td>(87.4)</td>
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<td>(30.9)</td>
<td>(-)</td>
<td>(1)</td>
</tr>
<tr>
<td>17</td>
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<td>(-)</td>
<td>(1)</td>
<td>(5)</td>
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<td>(47.7)</td>
<td>(-)</td>
<td>(1)</td>
</tr>
<tr>
<td>19</td>
<td>( \text{C}_6 \text{C}_5 \text{O}_2 \text{H}_5 )</td>
<td>(35.5)</td>
<td>(-)</td>
<td>(-)</td>
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<tr>
<td>20</td>
<td>( \text{C}_6 \text{C}_5 \text{O}_2 \text{H}_5 )</td>
<td>(106.4)</td>
<td>(185.2)</td>
<td>(-)</td>
<td>(1)</td>
</tr>
<tr>
<td>21</td>
<td>( \text{C}_6 \text{C}_5 \text{O}_2 \text{H}_5 )</td>
<td>(111.3)</td>
<td>(-)</td>
<td>(1)</td>
<td>(1)</td>
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</table>

* Extrapolated value from mixtures with compound 11.

of a lateral chloro substituent in the dialkyl phenyl pyrimidine 18 raised the melting point, and no mesophase could be observed in compound 19. However, the same substituent replaced the smectic phase in 5-(4-n-butylphenyl)-2-(4-n-pentylphenyl)pyrimidine 20 by a nematic one. The clearing point of the chloro derivative 21 is also 83 °C lower than that of the unsubstituted compound 20, which is in accordance with the results obtained in the biphenyl series.

From the above described results, it can be concluded that lateral halo-substituents lower the clearing points of mesogenic compounds, but they do favour the nematic phase. The steric effect of
the voluminous lateral substituent as well as the repulsion forces arising from the electronegativity of the halosubstituent probably increase the intermolecular separation. This decreases the intermolecular interactions [23], and offers an explanation for the depression in clearing point and suppression of the smectic phase, since the molecules will have less tendency to form a layered structure (correlated molecular centers). The increase in $k_{33}/k_{11}$ of fluoro substituted compounds [18] can also be interpreted in terms of the increased intermolecular separation and displacement of the molecular centers. The effect of lateral chloro substituents on the elastic constants has not been studied yet and could be somewhat different from that of the fluorine, since the width of the molecule is increased by this substituent more than by a fluorine. It is known that $k_{33}/k_{11}$ is influenced among other factors by the width to length ratio [24, 25].

The above described halogenated nematic biphenyls possess negative $\Delta \varepsilon$, beside their high chemical stability. This renders them useful as basic components of negative $\Delta \varepsilon$ mixtures, with laterally dicyano substituted compounds [26-28], which are needed for the HN- [29] and GH-displays with positive contrast [30].

The 3-fluoro-4-hydroxy-4'-n-pentyl biphenyl 22 (m. p. 99.8 °C), which was alkylated or esterified by standard methods to obtain the alkoxy and alkanoyloxy derivatives, was synthesized according to Scheme 1. The 2-fluoro-1,4-bis-(4-trans-n-pentyl cyclohexyl) benzene 2 was prepared from the corresponding amine, which was obtained by nitration of compound 1 followed by catalytic hydrogenation. The chloro and bromo derivatives were prepared by direct halogenation of the unsubstituted compounds.

**Scheme 1. Synthesis of 3-fluoro-4-hydroxy-4'-n-pentyl biphenyl.**

**Experimental**

The mesomorphic properties were investigated by DSC and polarizing microscopy using a PE-DSC2 and a Leitz Orthoplan equipped with a modified Mettler FP5/52 heating stage. The hot-stage was cooled by means of a cold nitrogen gas stream and the transition temperatures were measured at 0.2 °C/min heating rate. The differential thermal analysis was carried out at a rate of 5 °C/min. The GLC purity of all investigated products was 99.7% or better as determined on a 1 m 3% OV 25 open tubular column.

**General method of halogenation**

A solution of the necessary amount of halogen (Cl₂ or Br₂) in CCl₄ was added dropwise to a stirred suspension of the catalyst (Fe or AlCl₃) in a solution of the unsubstituted product in CCl₄ at 0 °C. The conversion degree was checked by GLC and kept below 70%.

2-Chloro-1,4-bis-(4-trans-n-pentyl cyclohexyl)- benzene (3)

Compound 1 was chlorinated according to the above described general method using iron powder as a catalyst. The raw product was purified by chromatography on silica gel using n-hexane as an eluent.

2-Bromo-1,4-bis-(4-trans-n-pentyl-cyclohexyl)- benzene (4)

The bromination of compound 1 was catalyzed by iron powder, and the product was purified by chromatography as described above, followed by crystallization from ethanol. $^1$H NMR (CDCl₃): 0.87 (t, $J = 6$ Hz, 6H, 2 CH₃); 1-2.1 (m, 34H, 16 CH); 2.4 and 2.8 (br. t, $J = 10$ Hz, 2H, CH next to arom. moiety); 7.1 (m, 2H, arom. CH); and 7.3 (br., 1H, arom. CH).

3-Chloro-4-hydroxy-4'-n-pentyl biphenyl (25)

The 4-hydroxy-4'-pentyl biphenyl was chlorinated to completion using iron powder as a catalyst, and the product was purified by chromatography (silica gel/toluene).

5-n-Heptyl-2-(4-n-pentyl phenyl)-pyrimidine (18)

Butyl iodide 17.5 mM was added dropwise to a stirred suspension of Mg 20 mM in dry ether, and the reaction mixture was then refluxed for 30 min. A solution of 15 mM 2-(4-cyano phenyl)-2-n-heptyl pyrimidine in dry ether was added dropwise to the Grignard reagent. The reaction came to an end after refluxing the mixture for 1 h, and was then worked up. The resulting ketone was crystallized from ethanol (C 66.5 S 94.1 I), and was reduced by heating with hydrazin hydrat 40 mM and KOH 40 mM in diethylene glycol at 135 °C for 2 h. Water
was then distilled off until the temperature increased to 195 °C, and the mixture was kept at this temperature for another 4 h. The cooled reaction mixture was diluted with water, and extracted with ether. Compound 18 was obtained by evaporating the dry neutral ethereal solution. The raw product was filtered through a short silica gel column using toluene as an eluent, and crystallized from ethanol.

5-n-Heptyl-2-(3-chloro-4-n-pentyl phenyl)-pyrimidine (19)

It was prepared by chlorination of compound 18 with AlCl₃ as a catalyst, and purified by chromatography using toluene as an eluent. Further crystallization from ethanol gave the pure product. ¹H NMR (CDCl₃): 0.9 (m, 6H, 2 CH₃); 1.1-2.0 (m, 16H, 8 CH₂); 2.7 (m, 4H, 2 CH₂ next to arom. moieties); 7.30 (d, 1H), 8.2 (br., d, 1H) and 8.4 (br., 1H) arom. CH; 8.6 (S, 2H, heterocyclic CH).

The position of the chloro substituent was assigned ortho to the n-pentyl group, since two of the three aromatic (phenyl) protons are strongly shielded by the nitrogens of the heterocyclic ring.

5-(4-n-Butyl phenyl)-2-(4-n-pentyl phenyl)-pyrimidine (20)

This compound was prepared by the same method described for compound 18, and the product was crystallized from ethyl acetate.

5-(4-n-Butyl-3-chloro phenyl)-2-(4-n-pentyl phenyl)-pyrimidine (21)

Compound 20 was chlorinated in presence of AlCl₃, and the product was purified by chromatography (silica gel/toluene), followed by crystallization from ethanol. ¹H NMR (CDCl₃): 0.9 (m, 6H, 2 CH₃); 1.1-1.9 (m, 10H, 5 CH₂); 2.7 (m, 4H, 2 CH₂ next to arom. moieties); 7.3 (m, 4H), 7.56 (d, J = 2 Hz, 1H) and 8.35 (m, 2H) arom. CH; 8.90 (S, 2H, heterocyclic CH). The chloro substituent was assigned to the butyl substituted phenyl group, since two protons of the other phenyl group are part of the AA’ BB’ spin system which appears at 8.35 ppm. Their strong deshielding is caused by the two neighbouring nitrogen atoms of the pyrimidinyl group. Since the only proton which has a meta coupling (J = 2 Hz) appears at 7.56 ppm, the chloro substituent was assigned ortho to the butyl group.

2-Fluoro-1,4-bis-(4-trans-n-pentyl-cyclohexyl)-benzene (2)

A mixture of 2 ml conc. nitric acid, 6 ml conc. sulfuric acid and 20 ml glacial acetic acid was added dropwise to a stirred suspension of 10 mM compound 1 in an acetic acid-acetic anhydride mixture at —10 °C. The reaction mixture was stirred for one hour, and then worked up. The resulting nitro compound was purified by chromatography (C 51.2 N 57.0 I) and then catalytically hydrogenated to give rise to the corresponding amine (C 67.5 106.1). Equimolar amounts of conc. HCl and NaNO₂ were added to a cooled (0-5 °C) solution of the amine in THF under stirring. An excess of fluoroboric acid was then added dropwise to the diazonium chloride solution. The precipitated diazofluoroborate was filtered off, washed with cold fluoroboric acid and cold methanol. The well dried diazofluoroborate was then mixed with dry sea sand, and decomposed by heating at 250 °C under reduced pressure. The fluoro compound 2 was directly distilled, and crystallized from ethanol. Beside the phase transitions given in Table I, this compound showed a crystal-crystal transition at 41 °C.

3-Fluoro-4-hydroxy-4′-n-pentyl biphenyl (22)

A solution of 4-bromo-2-fluoro-anisole 20 mM in dry ether was added dropwise to a stirred suspension of 30 mM Mg in 20 ml dry ether and the mixture was stirred for 1 h. 4-n-Pentyl cyclohexanone 20 mM dissolved in dry ether was then added dropwise to the Grignard reagent, and the reaction mixture was refluxed for 1 h. After working up the reaction mixture in the usual way, the organic phase was evaporated and the product distilled under partial pressure. To a solution of the resulting 1-(3-fluoro-4-methoxy phenyl)-4-n-pentyl-1-cyclohexene (m.p. 64.2 °C) in ethylbenzene, 1 g Pd/C 10% and 5 g benzoquinone were added and the reaction mixture was refluxed overnight. The catalyst was then filtered off, and the organic phase washed with NaOH. The raw product was filtered through a short silica gel column (toluene), and crystallized from ethanol. The so obtained 3-fluoro-4-methoxy-4′-n-pentyl biphenyl was dissolved in acetonitrile, and refluxed together with trimethylsilylchlorid 4 g and NaI 25 g for 24 h. The raw product obtained by working up the reaction mixture was purified by chromatography over silica gel using toluene as an eluent followed by crystallization from ethanol (C 99.8 I).

**Compounds 5–12**

The desired alkyl iodide (11 mM) was added to a stirred solution of the corresponding hydroxy compound (10 mM) in alcoholic KOH, and the mixture was refluxed for 4 h. The alkoxy derivative was extracted in ether after distilling off the alcohol. The products were crystallized from ethanol.

**Compounds 13–17**

The desired acid chloride (11 mM) was added dropwise to a stirred solution of the corresponding hydroxy compound (10 mM) in pyridine, and the mixture was heated at 70 °C for 30 min. The reaction mixture was worked up in the usual way, and the products were crystallized from ethanol.
[29] H. Schad, SID Digest 1982, 244.