Synthesis and Mesomorphic Behavior of New N-Heterotolane Liquid Crystals Containing a Naphthyl-Pyridyl Framework

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This article is dedicated to Professor Ted R. Taylor for his contribution to liquid crystals research in Brazil.

Abstract: A homologous series of the new N-heterotolane was synthesized using two cross-coupling reactions mediated by copper and palladium/copper. The final compounds present a naphthyl-pyridyl framework connected by an acetylene group. The evaluation of physico-chemical properties is described. All the compounds exhibit the smectic A mesophase.

Key words: liquid crystals, N-heterotolane, naphthyl-pyridyl framework, Buchwald protocol and Sonogashira coupling

Liquid crystals containing different heterocyclic rings constitute a fascinating branch of condensed matter due to their molecular and mesomorphic properties. The incorporation of heteroatoms into the ring cause considerable changes on molecular properties. Among the heterocyclic rings, the pyridine ring is a common template for LC chemistry because of the nitrogen atom, which is able to change many electronic and structural parameters.1

As pointed out by Hird2 et al., molecules, which contain groups with high polarizability and high electron density, such as 2,6-naphthalene, 2,5-pyrimidine, 2,5-pyridine, 1,4-phenylene rings and acetylene linking groups, are promising candidates for liquid crystal materials with high optical anisotropy.

Conjugated acetylene compounds are an especially valuable class of molecules that found application in organic synthesis from natural products3a,b to high tech materials.3c–g Compounds with diphenylacetylene (termed tolane) connectivity represent an important class of compounds showing a wide variety of phases, including the chiral twist grain boundary (TGB) and blue phases (BP).

An extensive and reliable method for the preparation of conjugated acetylene compounds is the palladium-catalyzed coupling of terminal alkynes with aryl or alkenyl halides, which was described for the first time by Sonogashira and co-workers in 1975.4 An inexpensive reagent, 2-methyl-3-butyn-2-ol (mebynol),5a or a rather expensive one, trimethylsilylacetylene,5b were used as excellent vehicles for synthesizing terminal acetylene.

Previously we showed that tolane6a and its N-hetero version6b (pyridylphenylacetylene) are suitable core structures for liquid-crystalline molecules. We extended the utility of this approach to the synthesis of new N-heterotolanes containing naphthyl and phenyl groups attached to the acetylene moieties.

In contrast to the Sonogashira reaction, the straightforward synthesis of aryl ethers under SNAr conditions has a limited substrate scope. The traditional copper-catalyzed Ullmann synthesis7 is an alternative to the nucleophilic aromatic substitution. However, this classical methodology has several drawbacks. Progress in the arylation of alcohols, thiols and amines mediated by copper was accomplished by the Buchwald group8 and others,9 who annotated that this new procedure is far superior to the SNAr or Ullmann reaction.

The O-arylation reaction using the Buchwald protocol occurs at milder temperatures and is of broad scope providing the opportunity to explore the efficacy of this protocol in the formation of aryl oxygen bonds at C-2 position of the pyridine ring. The incorporation of a pyridyl group into the tolanes allows the evaluation of the influence of the nitrogen atom on molecular mesomorphic and spectral properties.

Our synthetic strategy is based on the sequential coupling at C-2 and C-5 positions of 2,5-dibromopyridine (1) (Figure 1). The 2,5-dibromopyridine (1) is etherified at the C-2 position selectively with (S)-2-methyl-1-butanol under conditions according to the Buchwald protocol, Subsequent to the C-O bond formation, the C-5 position is exposed to the Sonogashira reaction. The O-arylation coupling of 2,5-dibromopyridine (1) yielded the key intermediate 3a (Figure 1) in acceptable yields.6b The halogen group located at C-5 position of 1 could be conveniently manipulated to attach a variety of other groups through transition metal mediated cross-coupling reaction.

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The Buchwald protocol opens the possibility of accessing a great variety of new products, which would be very difficult to be made by a non-copper-mediated nucleophilic aromatic substitution reaction. The protocol can be successfully applied to the alkyl aryl ethers from secondary substrates such as allylic and chiral sec-phenyl ethyl alcohol. To our expectation this protocol reaction condition could be extended to more sterically hindered substrate such as chiral ethyl lactate, which is recognized as an attractive precursor for synthesis of chiral liquid crystals.

We explored the O-arylation coupling to prepare the intermediate 3b (Figure 2) in 30% of yield, which is a special intermediate with potential polar conformational bias.

After installing successfully the alkoxy group at C-2 position of the 2,5-dibromo-pyridine, we turned our attention to the next coupling reaction (Sonogashira coupling) at β-position of 6-bromo-2-naphthol (4). Before the coupling of the ethynyl group of 8a–d was accomplished we realized the alkylation reaction with alkyl bromides yielding the corresponding alkylated products 5 in yields of 80–90% (Scheme 1). As a consequence, the alkylated compounds were readily coupled with mebynol under the conditions of a copper/palladium-catalyzed cross-coupling reaction described by Melissaris and Litt. The treatment of the 2-hydroxypropyl group we used the procedure described by Melissaris and Litt. The treatment with alkali-metal hydroxides and toluene at more elevated temperatures following the classical deprotection method can cause some decomposition or some degree of polymerization of the starting material.

For the synthesis of 9a–d (Figure 3) a second Sonogashira coupling between 3a and homoarylalkyne 8a–d successfully completed the elaboration of the final N-heterotolanes 9a–d in a moderate yield. Thus, the homologous series were obtained in 60–70% yield as pale yellow solids after purification by column chromatography.

In order to explore the potential of the 2,5-pyridines as liquid crystal templates or dopants for liquid crystal mixtures, the synthesis of the chiral compound 10d was undertaken. We selected 8d to couple with 3b under Sonogashira conditions. Thus, treatment of homoarylalkyne 8d and pyridyllactate 3b in the presence of 0.3 mol% palladium catalyst at 90 °C for 20 h afforded the corresponding N-heterotolane derivative 10d (Figure 4) in 45% yield. All compounds were characterized by NMR and IR spectroscopy as well as elemental analysis.

 Thermal analysis of all N-heterotolanes 9a–d was characterized by differential scanning calorimetry (DSC) and is compiled in Table 1. The DSC thermograms of 9a–d showed that all samples are thermally stable. The transition temperatures and enthalpy values were collected from second heating scans. The texture of the mesophase was identified by microscopy studies. When the sample was cooled from its isotropic phase, the smectic A phase appeared, which exhibited focal–conic texture. The stable enantiotropic smectic A phase was found in all the samples 9a–d. For example, on heating the sample 9a, it entered the smectic A phase at 77 °C and finally melted to an isotropic liquid at 92 °C (Figure 5). The range of temperature for the mesophase is 15 °C. The two peaks observed at 77 °C and 92 °C were associated with K → S_A and S_A → I transitions, respectively, during the microscopy studies. For compound 9b, besides the S_A mesophase, on cooling, were observed continuous bands across the backs of the fans (Figure 6), which persisted for...
a long time. These changes are indicative of an E-smectic A phase transition. Compounds 9c and 9d show the arced focal–conic fan texture below their melting points. The DSC thermograms display only two endothermic peaks.

Figure 5  Smectic A focal–conic fan texture exhibited by 9a (90 °C, on cooling, 10×).

Figure 6  Arced focal–conic fan texture exhibited by 9b (69 °C, on cooling, 40×).

Figure 7 shows the dependence of the transition temperatures on the number of carbon atoms in the alkyl spacer for the 9a–d series. The usual even–odd alternations of temperature of the crystal smectic A phase and of the smectic A to isotropic phase transitions are observed. As n increases, the smectic A-phase range is increased. The melting points of the homologous series decrease following the even–odd effect, but the effect is less pronounced for the clearing temperatures. An exception is compound 9b, which has a crystal E phase. However, if we consider the mesophase range as a result of S A plus crystal E for 9b, then alternation even–odd is obeyed. The wider smectic A range (ΔT_{SMA–I} = 36 °C) is seen for 9d and the smaller smectic A range is seen for 9a (ΔT_{SMA–I} = 15 °C). The increase in stability of the smectic A phase of this series with increase of the chain length is related to a molecular recognition where two kinds of interactions may be envisaged. As n increases, the core–core and chain–chain interactions become more favorable. On a molecular level two domains are created with considerable differences in polar character.

Figure 7  Plot of transition temperatures against the number of carbon atoms (n) in the alkoxy chain of the compounds 9a–d.

For compound 10d, having a chiral lactate tail, the DSC and POM analyses reveal that the sample is stable under heating. The melting point temperatures and enthalpy values were collected from second heating scans. Their values for 10d are 32 °C and 5.7 kcal·mol–1, respectively. However, the new compound synthesized did not show mesomorphic behavior. The absence of liquid-crystalline properties makes it a good candidate for dopants for liquid-crystals-mixture studies. These studies are in progress and will be presented in due course.

Table 1  Transition Temperatures (°C) for the Series of N-Heterotolanes 9a–d and Enthalpy Values (ΔH, kcal·mol–1)

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>K</th>
<th>T</th>
<th>ΔH</th>
<th>E</th>
<th>T</th>
<th>S_A</th>
<th>T</th>
<th>ΔH</th>
<th>I</th>
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<tr>
<td>9a</td>
<td>C_7H_{15}</td>
<td>77</td>
<td>3.4</td>
<td>–</td>
<td>–</td>
<td>92</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9b</td>
<td>C_8H_{17}</td>
<td>66</td>
<td>2.3</td>
<td>71*</td>
<td>97</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9c</td>
<td>C_9H_{19}</td>
<td>67</td>
<td>4.1</td>
<td>93</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9d</td>
<td>C_{10}H_{21}</td>
<td>58</td>
<td>4.8</td>
<td>–</td>
<td>94</td>
<td>1.4</td>
<td></td>
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</tr>
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</table>

* Enthalpy value: 1.5 kcal·mol–1.
1H NMR and 13C NMR spectra in CDCl3 were obtained using Varian 200 and 300 MHz spectrometers and TMS as internal standard. IR Spectra were recorded in nujol on a 3000 Galaxy Series spectrometer. Optical rotations were recorded on a Perkin-Elmer 341 polarimeter at the sodium D line. The thermal transitions and the mesomorphic textures were determined using an Olympus BX43 polarizing microscope in conjunction with a Leitz Wetzlar 417 heating stage and a Perkin Elmer 141 differential scanning calorimeter. The rate of heating or cooling was 10 °C/min. Elemental Analyses (CHN) were obtained using a Elemental Perkin Elmer 2400. Purification by column chromatography was carried out on 70–230 mesh Merck silica gel 60. (CHN) were obtained using a Elemental Perkin Elmer 2400. Purification by column chromatography was carried out on 70–230 mesh Merck silica gel 60. (CHN) were obtained using a Elemental Perkin Elmer 2400. Purification by column chromatography was carried out on 70–230 mesh Merck silica gel 60.

6-Bromo-2-nonyloxy napthalene (5c)
Yield: 83%.
IR (nujol): 2924, 2853, 1601, 1463, 1390, 1024, 874, 849, 811, 720 cm⁻¹.
1H NMR (200 MHz, CDCl3): δ = 0.9 (t, 3 H, J = 8.4 Hz, CH3), 1.3 (m, 14 H, CH2), 1.6 (s, 6 H, CH3), 1.8 (m, 2 H, CH2), 4.0 (t, 2 H, J = 6.6 Hz, OCH2), 7.1 (d, 1 H, J = 2.2 Hz, Ar), 7.2 (dd, 1 H, J = 6.4, 2.6 Hz, Ar), 7.4 (dd, 1 H, J = 6.8, 2.0 Hz, Ar), 7.6 (d, 1 H, J = 9.4 Hz, Ar), 7.7 (s, 1 H, Ar), 7.8 (d, 1 H, J = 1.4 Hz, Ar).
13C NMR (50 MHz, CDCl3): δ = 157.4, 133.1, 129.9, 129.6, 129.5, 128.4, 128.3, 120.1, 116.9, 106.5, 68.1, 31.8, 29.6, 29.4, 29.3, 26.1, 22.7, 14.2.

6-Bromo-2-n-octyloxy napthalene (5b)
Yield: 88%.
IR (nujol): 2924, 2853, 1601, 1463, 1390, 1024, 874, 849, 811, 720 cm⁻¹.
1H NMR (200 MHz, CDCl3): δ = 0.9 (t, 3 H, J = 8.4 Hz, CH3), 1.3 (m, 10 H, CH2), 1.8 (m, 2 H, CH2), 4.0 (t, 2 H, J = 6.6 Hz, OCH2), 7.1 (d, 1 H, J = 2.2 Hz, Ar), 7.2 (dd, 1 H, J = 6.4, 2.6 Hz, Ar), 7.4 (dd, 1 H, J = 6.8, 2.0 Hz, Ar), 7.6 (d, 1 H, J = 9.4 Hz, Ar), 7.7 (s, 1 H, Ar), 7.8 (d, 1 H, J = 1.4 Hz, Ar).
13C NMR (50 MHz, CDCl3): δ = 157.4, 133.1, 129.9, 129.6, 129.5, 128.4, 128.3, 120.1, 116.9, 106.5, 68.1, 31.8, 29.6, 29.2, 26.1, 22.7, 14.2.

6-Bromo-2-n-heptyloxy napthalene (5a)
Yield: 87%.
IR (nujol): 2924, 2853, 1601, 1463, 1390, 1024, 874, 849, 811, 720 cm⁻¹.
1H NMR (200 MHz, CDCl3): δ = 0.9 (t, 3 H, J = 8.4 Hz, CH3), 1.3 (m, 8 H, CH2), 1.8 (m, 2 H, CH2), 4.0 (t, 2 H, J = 6.6 Hz, OCH2), 7.1 (d, 1 H, J = 2.2 Hz, Ar), 7.2 (dd, 1 H, J = 6.4, 2.6 Hz, Ar), 7.4 (dd, 1 H, J = 6.8, 2.0 Hz, Ar), 7.6 (d, 1 H, J = 9.4 Hz, Ar), 7.7 (s, 1 H, Ar), 7.8 (d, 1 H, J = 1.4 Hz, Ar).
13C NMR (50 MHz, CDCl3): δ = 157.4, 133.1, 129.9, 129.6, 129.5, 128.4, 128.3, 120.1, 116.9, 106.5, 68.1, 31.8, 29.6, 29.2, 26.1, 22.7, 14.2.

4-(Decyloxy napthalen-2-yl)-2-methylbut-3-yn-2-ol (7d)
Typical Procedure
A one-neck round-bottom flask was charged with Et₃N (5 mL), mebylnol (6) (0.3 mL, 3.0 mmol) and 6-bromo-2-decyloxy napthalene (5d) (0.7 g, 2.0 mmol) under Ar. CuI (1.4 mg, 0.0074 mmol), PPh₃ (8.5 mg, 0.079 mmol) and PdCl₂(PPh₃)₂ (4.7 mg, 0.012 mmol) were then added to the stirred solution. The mixture was heated for 20 h at 90 °C. After cooling, the solid was filtered off. The remaining solid was purified by column chromatography. The yellow solid was obtained in 75% yield.
IR (nujol): 3330, 2921, 2851, 1600, 1462, 1376, 1252, 1172 cm⁻¹.
1H NMR (200 MHz, CDCl3): δ = 0.9 (t, 3 H, J = 8.4 Hz, CH3), 1.3 (m, 14 H, CH2), 1.6 (s, 6 H, CH3), 1.8 (m, 2 H, CH2), 2.2 (s, 1 H, CH3).
OH), 4.1 (t, 2 H, J = 6.6 Hz, OCH3), 7.1 (d, 1 H, J = 2.2 Hz, Ar), 7.2 (dd, 1 H, J = 6.4, 2.6 Hz, Ar), 7.4 (dd, 1 H, J = 6.8, 2.0 Hz, Ar), 7.6 (d, 1 H, J = 9.4 Hz, Ar), 7.7 (s, 1 H, Ar), 7.8 (d, 1 H, J = 1.4 Hz, Ar).
13C NMR (50 MHz, CDCl3): δ = 157.7, 134.1, 132.4, 129.1, 128.9, 128.2, 126.6, 119.6, 117.4, 106.4, 93.3, 82.6, 68.0, 65.6, 31.9, 31.6, 29.6, 29.4, 29.2, 26.1, 22.2, 14.1.

4-(6-Nonyloxyphenalen-2-yl)-2-methylbut-3-yn-2-ol (7c)

Yield: 60%.

IR (nujol): 3315, 2924, 2853, 2108, 1601, 1463, 1390, 1225, 1172, 874, 646 cm⁻¹.

1H NMR (200 MHz, CDCl3): δ = 0.9 (t, 3 H, J = 8.4 Hz, CH3), 1.3 (m, 10 H, CH2), 1.6 (s, 6 H, CH3), 1.8 (m, 2 H, CH2), 2.2 (s, 1 H, OH), 4.1 (t, 2 H, J = 6.6 Hz, OCH3), 7.1 (d, 1 H, J = 2.2 Hz, Ar), 7.2 (dd, 1 H, J = 6.4, 2.6 Hz, Ar), 7.4 (dd, 1 H, J = 6.8, 2.0 Hz, Ar), 7.6 (d, 1 H, J = 9.4 Hz, Ar), 7.7 (s, 1 H, Ar), 7.8 (d, 1 H, J = 1.4 Hz, Ar).

13C NMR (50 MHz, CDCl3): δ = 157.7, 134.1, 132.4, 129.1, 128.9, 128.2, 126.6, 119.6, 117.4, 106.4, 93.3, 82.6, 68.0, 65.6, 31.9, 31.6, 29.6, 29.4, 29.2, 26.1, 22.2, 14.1.

4-(6-Octyloxyphenalen-2-yl)-2-methylbut-3-yn-2-ol (7b)

Yield: 70%.

IR (nujol): 3315, 2924, 2853, 1600, 1462, 1376, 1252, 1172 cm⁻¹.

1H NMR (200 MHz, CDCl3): δ = 0.9 (t, 3 H, J = 8.4 Hz, CH3), 1.3 (m, 10 H, CH2), 1.6 (s, 6 H, CH3), 1.8 (m, 2 H, CH2), 2.2 (s, 1 H, OH), 4.1 (t, 2 H, J = 6.4 Hz, OCH3), 7.1 (d, 1 H, J = 2.2 Hz, Ar), 7.2 (dd, 1 H, J = 6.4, 2.6 Hz, Ar), 7.4 (dd, 1 H, J = 6.8, 2.0 Hz, Ar), 7.6 (d, 1 H, J = 9.4 Hz, Ar), 7.7 (s, 1 H, Ar), 7.8 (d, 1 H, J = 1.4 Hz, Ar).

13C NMR (50 MHz, CDCl3): δ = 157.7, 134.1, 132.4, 129.1, 128.9, 128.2, 126.6, 119.6, 117.4, 106.4, 93.3, 82.6, 68.0, 65.6, 31.9, 31.6, 29.6, 29.4, 29.2, 26.1, 22.2, 14.1.

2-Decyloxy-6-ethynylphenalene (8d)

Typical Procedure

KOH (0.3 g, 6.0 mmol) and i-PrOH (5 mL) were added and heated at 50 °C for 10 min. Then, a solution of 7d (0.7 g, 2.0 mmol) in i-PrOH (5 mL) was added in one portion. The mixture was heated under reflux for 2 h. The solvent was evaporated and the residue was dissolved in Et2O (25 mL) and was washed with H2O (3 × 25 mL). The organic phase was dried over Na2SO4. The solvent was evaporated and a yellow oil was obtained in 75% yield.

IR (nujol): 3315, 2924, 2853, 2108, 1601, 1463, 1390, 1225, 1172, 874, 646 cm⁻¹.

1H NMR (200 MHz, CDCl3): δ = 0.9 (t, 3 H, J = 8.4 Hz, CH3), 1.3 (m, 14 H, CH2), 1.8 (m, 2 H, CH2), 3.1 (s, 1 H, CH), 4.1 (t, 2 H, J = 6.6 Hz, OCH3), 7.1 (d, 1 H, J = 2.2 Hz, Ar), 7.2 (dd, 1 H, J = 6.4, 2.6 Hz, Ar), 7.4 (dd, 1 H, J = 6.8, 2.0 Hz, Ar), 7.6 (d, 1 H, J = 9.4 Hz, Ar), 7.7 (s, 1 H, Ar), 7.8 (d, 1 H, J = 1.4 Hz, Ar).

13C NMR (50 MHz, CDCl3): δ = 158.3, 134.8, 132.4, 129.6, 129.4, 128.5, 127.1, 120.2, 117.1, 106.8, 84.6, 78.0, 76.8, 68.5, 32.3, 30.0, 29.8, 29.7, 29.6, 26.5, 23.1, 14.6.
7.5 (d, 2 H, J = 8.4 Hz, Ar), 7.6 (dd, 1 H, J = 6.3, 2.7 Hz, Ar), 7.7 (s, 1 H, Ar), 7.9 (d, 1 H, J = 1.4 Hz, Ar), 8.4 (d, 1 H, J = 2.1 Hz, Ar).

1°C NMR (75 MHz, CDCl3): δ = 163.3, 157.8, 149.9, 141.0, 134.1, 131.0, 129.2, 129.0, 128.7, 128.3, 126.8, 119.7, 117.7, 113.0, 110.7, 106.4, 91.2, 85.9, 71.1, 68.0, 34.4, 31.9, 29.6, 29.4, 29.3, 29.2, 26.1, 22.7, 16.5, 14.2, 11.3.

Anal. Calcd for C30H35NO2: C, 81.38; H, 8.21; N, 2.54.

(5)-[6-(Nonyloxy)naphthalen-2-yl)ethynyl]-2-(2-methylbutyltyloxy)pyridine (9c)

Yield: 45%; [α]D25 –34 (c 1, CHCl3).

(5)-Ethyl 2-[[5-(6-Decyloxy)naphthalen-2-yl)ethynyl]pyridin-2-yl]oxypropionate (10a)

Yield: 68%; [α]D25 +6 (c 1, CHCl3).

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References


