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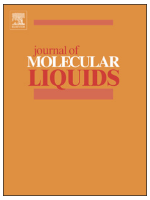

Synthesis and properties of chosen 4-butyl-phenyltolane derivatives – On the influence of core substitution on birefringence, mesomorphic and dielectric properties

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ABSTRACT

The synthesis and characterization of new liquid crystal (LC) compounds based on 4-[(4-butyl-2,6-difluorophenyl)ethynyl]biphenyl core are described. New family of dielectrically positive compounds presents alternative molecular approach to the conventional LC design. Correlations between molecular structure and mesomorphic properties for compounds being isothiocyanato, cyano, trifluoromethoxy, chloro and fluoro terminated analogues as well as other known from the literature have been drawn. Additionally, the experimentally determined physical properties (birefringence, dielectric anisotropy) for presented derivatives of phenyl tolane are compared with DFT calculation's results. Compounds are characterised by ^{1}H NMR spectroscopy and mass spectrometry (electron ionization) analysis. They show an enantiotropic nematic behavior in broad temperature range, confirmed by a polarizing thermomicroscopy, differential scanning calorimetry and dielectric spectroscopy. Detailed synthetic procedures are attached. Synthesized compounds stand as promising components of medium to highly birefringent liquid crystalline mixtures.

1. Introduction

Significant attention has been focused on the search of new medium to highly birefringent liquid crystals having wide mesogenic temperature range and high chemical stability. One of the most widely explored units is still phenyltolane molecular core. Here the synergy effect of combining three-phenyl ring system with orthogonal π electronic system of triple bond gives beneficial input to electron polarizability along the main molecular axis. Additionally, the shape anisotropy of the molecular core ensures reasonable melting point and wide mesophase temperature range above it [1]. Compounds with phentyltolane ring system in itself and in connection with other families of liquid crystals have been found to be promising materials that can achieve high efficiency for microwave devices such as switchable phase shifters [2], tuneable filters [3], antennas [4] and other applications [5]. Therefore, there is a huge interest in studying properties of medium to high birefringent liquid crystal in the microwave region up to terahertz frequencies [6].

Large number of liquid crystals based on 4-(phenylethynyl)biphenyl core, also known as phenyltolanes, have been prepared so far [1]. The majority of synthesized structures possess mainly fluorine or/and chlorine atoms as lateral substituents. That molecular approach enables controlling the values and signs of dielectric anisotropy, viscosity, and also other parameters responsible for molecular dynamics in an electric field. Common denominator of what we can find for known types of molecules (in particular those with positive dielectric anisotropy) is typical sequence of structural units building the molecule, which is biphenyl-acetylene-benzene, counting in the direction of the resultant dipole moment sense (See Fig. 1a) [7]. Even here many compounds show unwanted smectic phases, which significantly reduce its possible utilization in nematic mixtures. Therefore in this work we decided to apply different molecular approach (with a reverse sequence benzene-acetylene-biphenyl), based on 2,6-difluorophenyl-acetylene unit presented in Fig. 1b.

Lateral fluoro-substitution, in particular a 2,6-difluorophenyl-acetylene unit (Fig. 1b), brings unique and valuable nematic stability, leading to a strong application potential. Previously we reported alkyl-alkyl terminated analogues of liquid crystals with this structural unit [8]. Much earlier, this molecular core was also investigated by Buchecker [9] and Seils [10], leading to very useful mesogenic properties. In this article, we decided to widen that data with properties of analogues terminated by following polar groups (CN, NCS, F, Cl, OCF_3) – See General Structure below, which we believe enrich the knowledge of structural correlations and mesogenic properties. Due to comparison needs, we decided to fix the elastic alkyl chain on butyl homologues in particular, also

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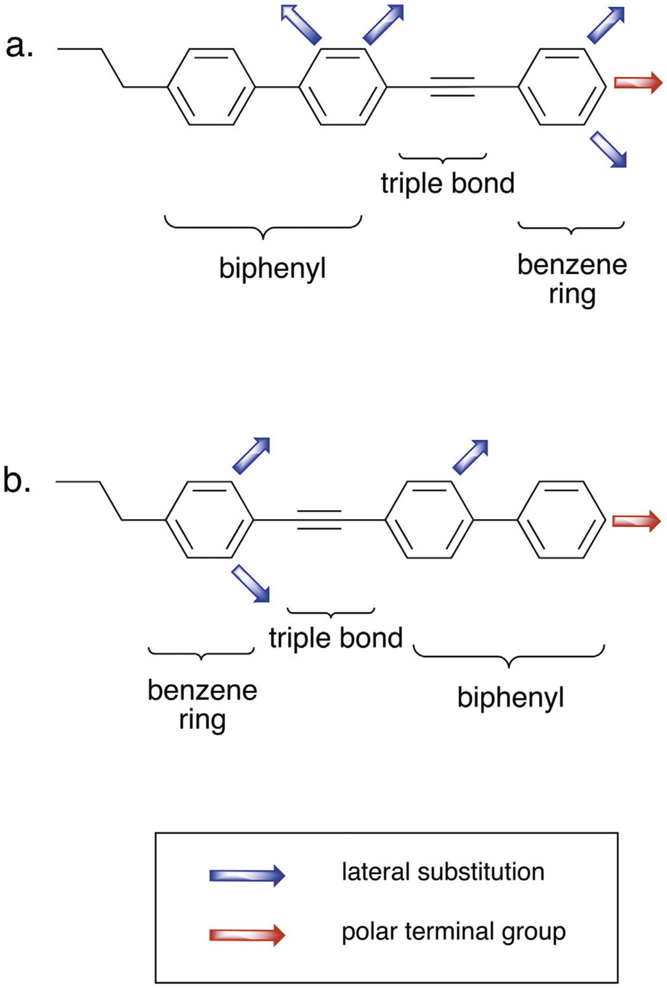
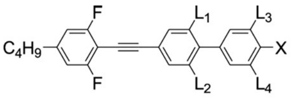


Fig. 1. (a) Conventional molecular approach to phenyltolane liquid crystal molecules, with a sequence of structural units: biphenyl-triple bond-benzene, and (b) modified molecular approach with a sequence: benzene-triple bond-biphenyl.

our previous studies of dialkylated compounds show the widest nematic range for this homologue [8]. However, there are also some structures, which possess other homologous members. We present detailed synthetic approaches with experimental procedures for all of investigated structures, together with their optical and dielectric properties.



where X = F, Cl, OCF_3, CN, NCS, C_4H_9;
L_n = F or H

General structure of investigated liquid crystals.

2. Experimental

2.1. Synthesis

Synthesis were started with the optimization of procedure for 4-alkyl-2,6-difluorophenyl-acetylene **4**. That was based on the copper catalysed coupling of aryl Grignard reagent with alkyl bromide, which we described previously in [11]. Then standard protocol for iodination and triple bond insertion allowed to obtain ready for further functionalization acetylene **4**, see Scheme 1.

Following the Sonogashira-Hagihara cross-coupling reaction of **4** with 1-bromo-3-fluorobenzene and 1-bromo-4-iodobenzene, we were able to obtain tolane structures **5** and **6** respectively. After that, compounds **5** and **6** were metalated into corresponding organo-magnesium and -lithium derivatives in order to obtain proper boronic esters **7** and **8**, which were ready for final Suzuki coupling reaction. Proposed strategy was used to synthesize final liquid crystals **10**–**14** and **17**–**21** (See Scheme 1). And isothiocyanate liquid crystals **15** and **22** were synthesized following the reaction of amine-structures **9** and **16** with thiophosgene $CSCl_2$.

2.1.1. Experimental procedures

The purity of the synthesized compounds was determined by thin-layer chromatography, SHIMADZU GCMS-QP2010S series gas chromatograph equipped with quadrupole mass analyser (MS), high-performance liquid chromatography (HPLC), HPLC-PDA-MS (APCI-ESI-dual source) Shimadzu LCMS 2010 EV equipped with polychromatic UV–VIS detector and MS (ESI/APCI) ionization source. Proton (1H) nuclear magnetic resonance (NMR) spectra in CDCl3 were collected using Bruker, model Avance III spectrometer.

1-butyl-3,5-difluorobenzene **2** - magnesium flakes (48.6 g; 2 mol) and THF (100 ml) were placed in a 4 dm^3 reactor and stirred under nitrogen. Small amount of THF solution of 1-bromo-3,5-difluorobenzene **1** (384 g; 2 mol) was added to initialize proper reaction. Then, the rest of solution was added dropwise. Temperature was controlled in a way to not exceed a 70 °C limit. After addition, the reaction mixture was stirred for 3 h. Next, *n*-bromobutane (272 g; 2 mol) was added dropwise to the reaction mixture reaction, solution was cooled to room temperature; then a 1 mol/dm^3 solution of catalyst Li_2CuCl_4 in anhydrous tetrahydrofuran was added (3%mol) to the reaction mixture. After that mixture was stirred in reflux for 5 h. The progress of the reaction was monitored by GC-MS, and when the reaction was finished, the mixture was poured into 1500 ml of water and 100 ml of 10% HCl. Crude product was extracted with pentane. Organic layer was washed three times with water, separated, dried with $MgSO_4$ and solvent evaporated. Product was distilled under reduced pressure. Boiling point 87 °C (27 mm Hg), yield 220 g (65%). MS(EI) *m/z*: 170 (M+); 141, 128, 101, 75.

5-butyl-1,3-difluoro-2-iodobenzene **3** - 1-butyl-3,5-difluorobenzene **2** (220 g; 1.3 mol) was mixed with anhydrous THF (1000 ml) under nitrogen and cooled to −78 °C in an acetone/dry ice bath. Solution of *n*-butyllithium dissolved in cyclohexane–hexane mixture (1.42 mol, 2.5 M) was added dropwise and temperature was kept below −70 °C. The reaction mixture was stirred for 2.5 h in −78 °C. Then a solution of iodine (360 g; 1.42 mol) in anhydrous THF was added dropwise and temperature was kept below −70 °C. The reaction mixture was allowed to reach room temperature. Saturated solution of Na_2SO_3 was added to the mixture to get rid of iodine excess. Then tetrahydrofuran was evaporated and crude product was treated with water and extracted with hexane. Organic layer was dried over $MgSO_4$ and concentrated on a rotary evaporator. Crude product was distilled at reduced pressure. Boiling point 127 °C (5 mm Hg), yield 350 g (91%), MS(EI) *m/z*: 296 (M+); 254; 140; 127.

5-butyl-2-ethynyl-1,3-difluorobenzene **4** - 5-butyl-1,3-difluoro-2-iodobenzene **3** (200 g; 0.68 mol), triethylamine TEA (93 ml; 0.67 mol), $PdCl_2(PPh_3)_2$ (0.3%mol), CuI (0.15%mol) and tetrahydrofuran (700 ml) were mixed and heated to 40 °C. Then 2-methylbut-3-yn-2-ol (62.4 g; 0.74 mol) was added dropwise and the reaction mixture was stirred at reflux for 1 h. When the reaction was finished, it was concentrated on rotary evaporator and the crude product was extracted with toluene, organic layer washed with water, dried over $MgSO_4$ and solvent evaporated. Crude was distilled at reduced pressure. Boiling point 95–100 °C (0.1 mm Hg), yield 143 g (85%), MS(EI) *m/z*: 252 (M+); 237; 209; 195; 151.

Protected acetylene from the previous step and anhydrous toluene (500 ml) were mixed and catalytic amount of sodium hydride (6% mol) was added. The mixture was stirred under reflux while

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