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High birefringence difluoroisothiocyanate biphenyl tolane liquid crystals

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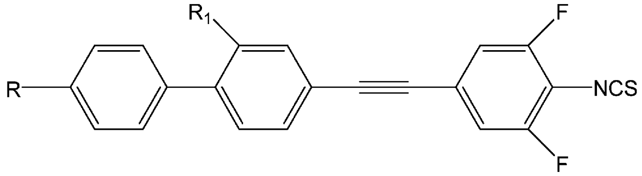
Several difluoroisothiocyanato-based biphenyl tolanes exhibiting high optical birefringence are presented and their representative molecular structure is shown below.



The optical birefringence of these liquid crystals lies between 0.44 to 0.48. Several eutectic mixtures of the biphenyltolanes with other compounds have been formulated and their properties investigated. The molecular simulations of polarizability and dipole moment of biphenyl tolanes are also presented.

1. Introduction

One of the most important properties of liquid crystals is their optical birefringence [1]. High birefringence and low viscosity polar liquid crystals are highly desirable for display and telecommunication applications because, for example, high birefringence enhances the display brightness for cholesteric displays [2] and improves the response time of a thinner cell gap that is used for laser beam steering at near infrared [3].

Most display devices operate in the visible spectral region. However, the sensitivity of some detectors is in the IR region. High resolution, wide dynamic range and fast response are needed to provide the capability for simulating complex targets and for real-time interaction with video formats and with computer image generation systems. High birefringence liquid crystals have small absorption (except at some localized vibrational bands) in the infrared region and therefore, they are good materials for this application [4].

But to design a high birefringence polar liquid crystal while maintaining a low viscosity is a challenging task [5]. The molecular dimension (shape and size), conjugation length, packing density and temperature, all make important contributions to the birefringence and these parameters are interrelated. For example, increasing the molecular conjugation would increase the birefringence, but would also increase its viscosity. However, the major concerns for highly conjugated LC compounds are high melting point, increased viscosity and low photo-stability. All these factors need to be taken into consideration while designing high birefringence LC compounds for practical applications.

Merck commercial nematic mixtures of biphenyls are still widely used in display devices after several decades of use since their discovery. Hence, many efforts are being made to find and develop new materials with improved properties. The complexity of modern liquid crystal (LC) mixtures is the consequence of the many and often contradictory material parameters that have to be taken into account for a LC material to meet the requirements of a LC display. Besides viscosity and dielectric anisotropy, one of the most important physical properties is the birefringence (Δn). The product of the birefringence and the cell gap (Δnd) is fixed for operation in the first or second transmission minimum [1]. Therefore, liquid crystal mixtures with high birefringence enable thin cells to be used and give a faster switching dynamics. High birefringence materials can be obtained by synthesizing highly conjugated molecules with polar end groups, such as difluoroisothiocyanate, to give high dielectric anisotropy.

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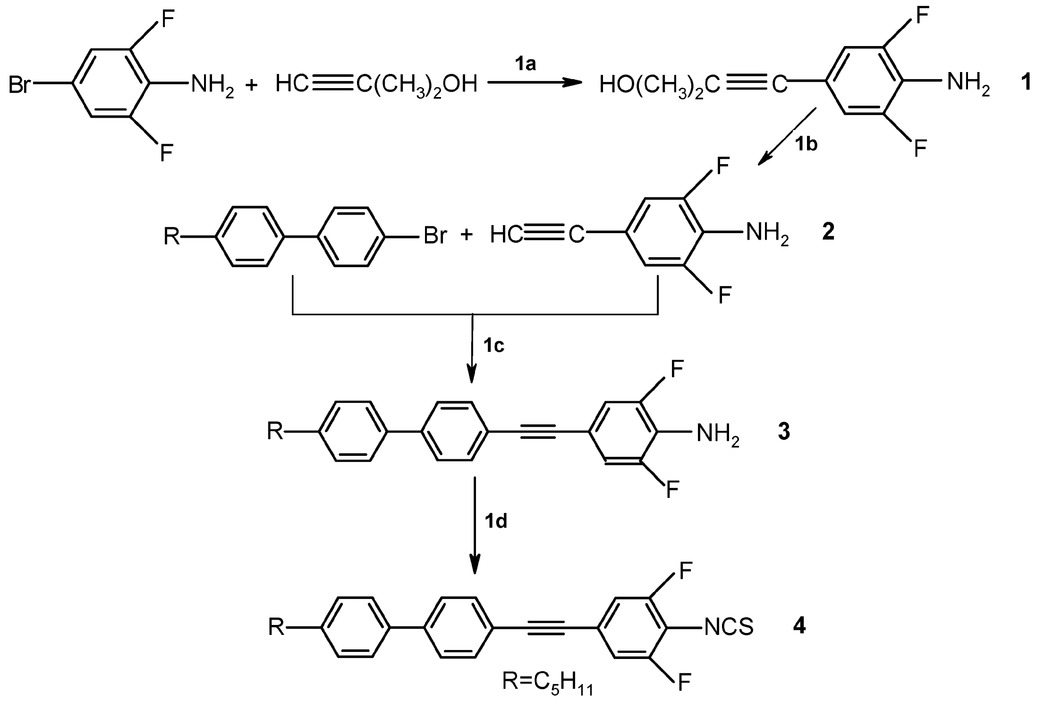
Previously we reported a series of difluoro-substituted and isothiocyanate end group for tolane, olefin tolane and terphenyl compounds that showed birefringence values ranging from 0.35 to 0.52 [6]. This paper presents the synthesis, characterization and optical properties of some difluoroisothiocyanate biphenyl tolanes.

2. Experimental

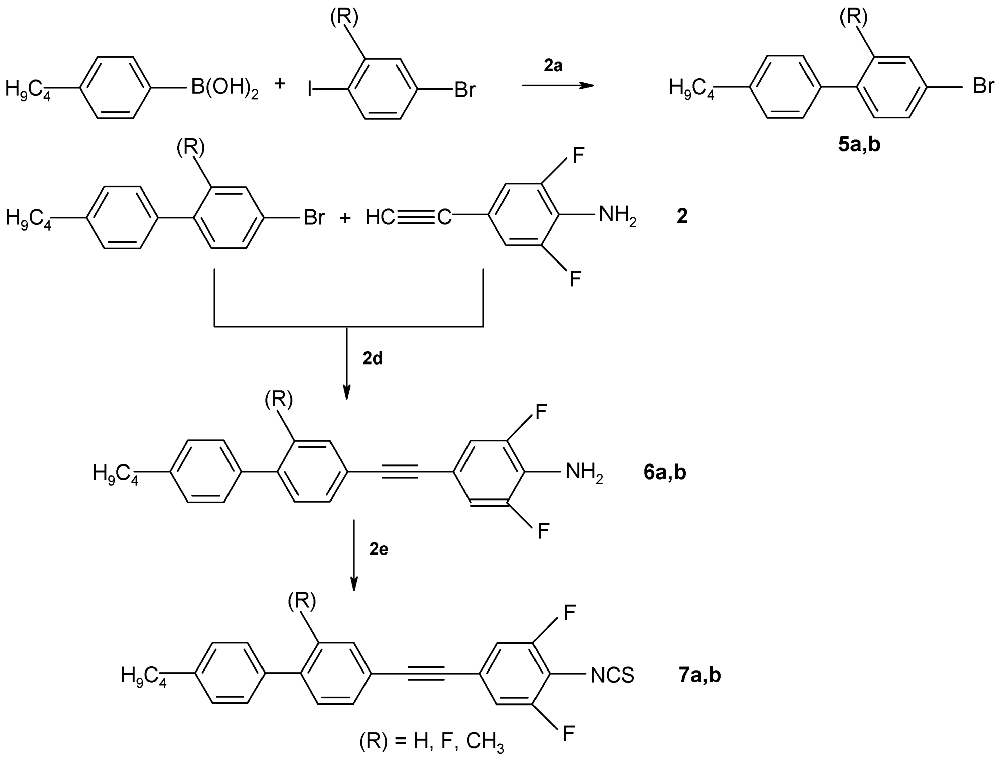
Confirmation of the structures of the intermediates and the final products was obtained by ^{1}H NMR spectroscopy using a Varian Gemini 200 MHz spectrometer with tetramethylsilane as internal standard. IR spectra were recorded using a Nicolet Magna 550 FTIR spectrometer (NaCl crystal window). Thin layer chromatography was performed using aluminium sheets with silica gel 60 F_{254} (Merck) which were examined under UV light (365 nm). Column chromatography was performed under gravity using Silicagel 60 (Merck). Melting points of the final products were determined using a Thomas-Hoover Capillary Melting Point Apparatus. Transition temperatures were determined using a Mettler FP52 heating stage and FP5 temperature control unit in conjunction with polarizing optical microscopy (POM) (Nikon), and the transitions were confirmed by DSC analysis (Perkin Elmer Pyris 1, Perkin Elmer TAC 7/DX, Perkin Elmer Intracooler 2P). Heating and cooling cycles were run at rates of 4°C min^{-1} under a nitrogen atmosphere with samples measured in closed lid aluminium pans. Mesophase type was assigned by visual comparison (under the microscope) with known phase standards. The birefringence ($\Delta n = n_e - n_o$) of the compounds was measured using a sodium lamp ($\lambda = 589$ nm) at $T = 296.35$ K, 15–25% of the compound being dissolved in a LC host (E44 with $\Delta n = 0.2578$ or BDH 13739 with $\Delta n = 0.1410$). All Δn values were extrapolated to 100% concentration.

3. Results and discussion

Three novel biphenyl tolanes were synthesized following the synthetic paths shown in schemes 1 and 2. They are abbreviated as *n*PPTP, *n* being the number of methylene units within the alkyl chain. PPTP stands for phenyl-phenyl-tolane-phenyl. Thus, compound **4** is 5PPTP, **7a** is 4PPTP and **7b** is 4PPTP(3F). Some of their physical characteristics are presented in table 1. All three compounds are high birefringence liquid crystals ($\Delta n = 0.44$–0.48), with high clearing temperatures and wide mesophase ranges. The synthesis of the alkyl biphenyltolanes proceeded with no significant difficulty, except in the case of the methyl-substituted compound; the intermediates seemed to have low reactivity, and no final product was obtained.



Scheme 1. Synthetic route for the pentyl biphenyl tolane. 1a. $Pd(PPh_3)_4$, CuI, Et_3N; 1b. KOH, toluene; 1c. $Pd(PPh_3)_4$, CuI, Et_3N; 1d. $CSCl_2$, $CaCO_3$, $CHCl_3$, H_2O.



Scheme 2. Synthetic route for the butylbiphenyl tolanes. 2a. $Pd(PPh_3)_4$, CuI, Et_3N; 2b. KOH, toluene; 2c. $Pd(PPh_3)_4$, CuI, Et_3N; 2e. $CSCl_2$, $CaCO_3$, $CHCl_3$, H_2O.

As can be seen from table 1, compounds **4** and **7a** show smectic phases; see also DSC scans, figures 1 (*a*), and 1 (*b*), compound **7b** exhibits only the nematic phase, figure 1 (*c*). POM of the three compounds showed only schlieren textures, but DSC analysis indicated the presence of a smectic phase for samples **4** and **7a**.

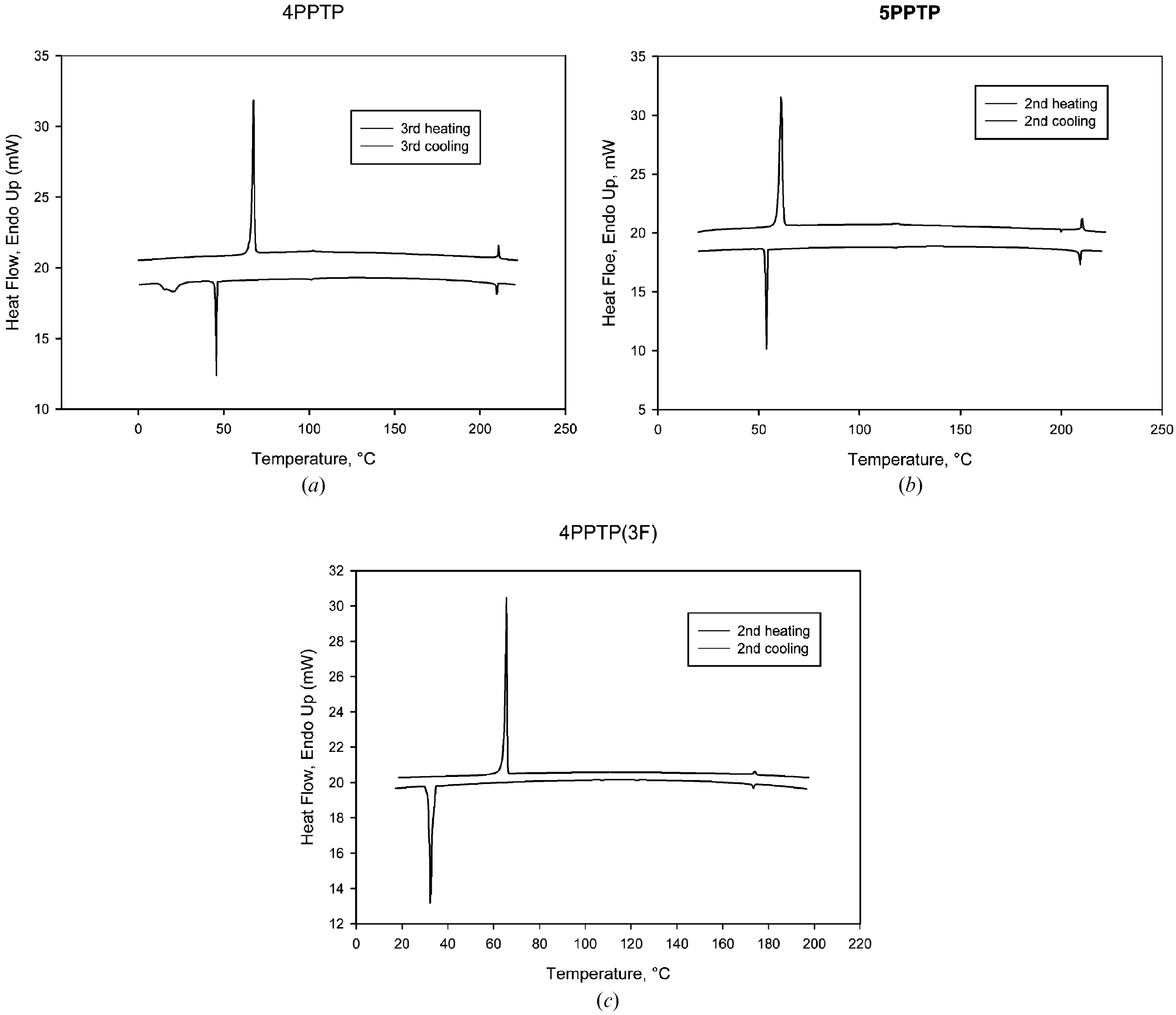
The introduction of a fluorine atom in the 3-position of the biphenyl core breaks the symmetry of the molecule and therefore, the smectic phase is suppressed. At the same time, it decreases the transition temperatures; less than 2°C in the case of the melting temperature, but almost 40°C in the case of the clearing temperature. The birefringence of compound **7b** is only 0.44 compared with 0.48 for **4**, because the fluorine atom at the 3-position of the biphenyl core points towards the alkyl end, in the opposite direction to the isothiocyanate and the other two fluorine groups. Several mixtures were formulated to test the miscibility of compound **4** in common liquid crystals (table 2). Two of the mixtures were analysed under POM (table 2), the data showing that 5PPTP leads to an increased mesophase range of the formulated mixtures compared with that of the liquid crystal host.

Several eutectic mixtures were also formulated based on compound **4** and some isothiocyanate tolanes (1-(4-pentyloxyphenyl)-2-(3,5-difluoro-4-isothiocyanatophenyl) ethyne) and terphenyls (4″-*n*-propyl-3,5-difluoroterphenyl-4-isothiocyanate) previously synthesized and reported [3]. The observed temperature range of these mixtures was quite large, but the melting temperatures

Table 1. Physical characteristics of the biphenyl tolanes[a].

Compound	*R*	R_1	M_w/g mol^{-1}	ΔH_m/kcal mol^{-1}	Sm/°C	N/°C	I/°C	N range/°C	Δn
4	C_5H_{11}	H	417	3.3	57.4	119.2	209.9	152.5	0.4838
7a	C_4H_9	H	403	2.95	67.2	102.3	210.9	143.7	
7b	C_4H_9	F	421	5.11	—	65.6	173.9	108.3	0.4417

[a] M_w=molecular weight; ΔH_m=the heat fusion enthalpy of the compound (melting), values obtained from the second or third heating curve (DSC measurements); *S*m=crystal to smectic phase transition; N=crystal to nematic phase transition or smectic to nematic; I=the clearing temperature of the pure compound (nematic to isotropic liquid transition); N range=nematic phase range at heating; Δn=birefringence, extrapolated values to 100% concentration (mixtures of 5PPTP:E44=10:90).



(*a*) (*b*) (*c*)

Figure 1. DSC thermographs of the biphenyl tolanes: (*a*) sample **7a**; (*b*) sample **4**; (*c*) sample **7b**.

were much higher than those calculated. The first hypothesis was that the miscibility of these compounds is poor. We also observed that the mixtures displayed a schlieren texture, but after two days a typical smectic texture was formed, which may explain the differences in the calculated and experimental transition temperatures.

Conformational analysis of the biphenyl tolanes showed a non-coplanar structure, with the NCS group forming an angle with the molecular axis. If the steric

Table 2. Miscibility study of compound **4** in E44 and 5CB.

	Composition/wt %[a]			Transition temp./°C
Mixture	80:20	75:25	70:30	75:25
E44:5PPTP	✓	✓	■	N 129.1 1
5CB:5PPTP	✓	■	✗	N 75.5 1

[a] ✓ Good miscibility; ■ low miscibility; ✗ no miscibility.

hindrances would permit a planar arrangement of the molecular structure, the rigid core would be fully conjugated, and the polarizability and hence the birefringence of these compounds much higher. The MOPAC calculations of the dipole moment and polarizabilities for the synthesized compounds (**4**, **7a** and **7b**) are presented in table 3.

The influence of the third fluorine atom introduced in compound **7b** is seen in both polarizability and dipole moment values, which also explains the lower birefringence, 0.44 compared with 0.48 of compound **4**.

4. Synthesis

4-Bromo-4′-*n*-pentylbiphenyl was purchased from TCI, 4′-*n*-butylbenzeneboronic acid was purchased form Lancaster Synthesis, Inc., while all other reagents and solvents were purchased form Aldrich and used without further purification. Compounds **4**, **7a** and **7b** were synthesized according to reaction schemes 1 and 2. The procedure was similar for all three compounds with an additional step in the case of **7a** and **7b**. The synthesis and ^{1}H NMR and IR characterization of **7a** are described below.

4.1. *4-Bromo-4′-n-butylbiphenyl, 5a*

In a three-neck round bottom flask equipped with a condenser, 4-*n*-butylphenyl boronic acid (1.5 g, 8.425 mmol), 1-bromo-4-iodobenzene (2.38 g, 8.425 mmol), tetrakis(triphenylphosphine)palladium(0) (0.389 g, 0.337 mmol) and sodium carbonate (3.57 g, 33.7 mmol) in 35 ml H_2O were suspended in 2-propanol (150 ml) and stirred under nitrogen at reflux for 7 h. A solution of HCl 2N was added to the reaction mixture with stirring. The organic layer was washed with water, then extracted into ether. The organic phase was washed with brine and water, then dried over sodium sulphate and concentrated *in vacuo*. The coupling product was purified by column chromatography on silica gel (hexane) to give an uncoloured liquid; yield 53.8%. ^{1}H NMR ($CDCl_3$) δ, ppm 0.74 (3H, t, alkyl CH_3), 1.18 (2H, sext, CH_2), 1.44 (2H, quint, CH_2), 2.45 (2H, t, CH_2), 7.1 (2H, d, ArH), 7.22–7.36 (6H, m, ArH). IR (film) ν_{max}/cm^{-1} 786, 845, 940, 1036, 1232, 1381, 1456, 1737, 2879, 2932, 2980, 3463.

4.2. *4-Ethyne-2,6-difluoroaniline, 2*

The synthesis and characterization of compound **2** has been described previously [5].

4.3. *1-(3,5-difluoro-4-aminophenyl)-2-[4-(1-butyl) biphenyl]ethyne, 6a*

4-Bromo-4′-*n*-butylbenzene (0.675 g, 2.34 mmol) in dry triethylamine (30 ml) was added dropwise to a suspension of 4-ethyne-2,6-difluoroaniline (0.5 g, 3.27 mmol), tetrakis(triphenylphosphine)palladium(0) (0.5034 g, 0.4356 mmol) and copper(I) iodide (0.151 g, 0.131 mmol) in dry triethylamine (100 ml) at room temperature. The solution was then heated under reflux for 4 h. When cooled, the mixture was filtered through celite and the solvent removed *in vacuo*. Dichloromethane was added and the organic layer washed with saturated ammonium chloride solution, water, then dried over sodium sulphate and the solvent evaporated *in vacuo*. The crude product was purified by column chromatography using hexane/ethyl acetate=6/1 as eluent to give a pale yellow solid; yield 54.2%. ^{1}H NMR ($CDCl_3$) δ, ppm 0.99 (3H, t, alkyl CH_3), 1.43 (2H, sext, CH_2), 1.68 (2H, quint, CH_2), 2.70 (2H, t, CH_2), 3.95 (2H, s, NH_2), 7.08 (2H, d, ArH *para* to NH_2), 7.28–7.36 (6H, m, ArH), 7.61 (2H, m, ArH *ortho* to $C{\equiv}C$). IR (film) ν_{max}/cm^{-1} 755, 860, 957, 1153, 1227, 1264, 1360, 1450, 1520, 1578, 1636, 1902, 2190 (w, $C{\equiv}C$ stretch), 2868, 2938, 3192, 3405, 3496.

4.4. *1-(3,5-Difluoro-4-isothiocyanatophenyl)-2-[4-(1-butyl)biphenyl]ethyne, 7a*

A solution of compound **6a** (0.36 g, 0.99 mmol) in chloroform (25 mL) was added dropwise at 0–5°C to a stirred, cooled (0°C) mixture of water (10 ml), chloroform (5 ml), calcium carbonate (0.5 g, 5 mmol) and thiophosgene (0.172 g, 1.5 mmol). The mixture was heated at reflux for 5 h and poured into water (100 ml); the separated organic layer was quenched with hydrochloric acid (45 ml, 1%), and dried over

Table 3. MOPAC calculations of dipole moment and polarizabilities of the biphenyl tolanes.

	Polarizability			Dipole moment/D				
Compound	α_{xx}	α_{yy}	α_{zz}				total	Length/Å
4PPTP	641.9	165.9	165.8	−3.947	−0.066	0.922	4.054	21.623
5PPTP	648.7	174.9	173.1	−3.965	−0.060	0.921	4.071	23.584
4PPTP(3F)	684.8	242.4	82.9	−3.279	−1.231	1.129	3.680	21.924

sodium sulphate. The solvent was removed *in vacuo*. The product was purified (three times) by column chromatography (hexane) and recrystallized from hexane to give white crystals; yield 86.7%. ^{1}H NMR ($CDCl_3$) δ, ppm 0.98 (3H, t, alkyl CH_3), 1.44 (2H, sext, CH_2), 1.66 (2H, quint, CH_2), 2.70 (2H, t, CH_2), 7.14 (2H, d, ArH), 7.55 (2H, d, ArH), 7.59–7.63 (6H, m, ArH). ^{13}C NMR ($CDCl_3$) δ, ppm 11.67, 20.055, 31.26, 32.976, 84.83, 90.86, 112.7, 118.07, 124.6, 126.7, 129.84, 135.0, 139.6, 140.55, 143.2. ^{19}F NMR ($CDCl_3$) δ, ppm -117.884, -117.867. IR (film) $\nu_{\max}/\mathrm{cm}^{-1}$ 747, 853, 1032, 1195, 1256, 1376, 1460, 1567, 2020 (s, NCS), 2100 (NCS, shoulder), 2210 (C≡C stretch), 2880, 2930, 3006.

5. Conclusions

The fluorinated isothiocyanate-based biphenyl tolane liquid crystals exhibit a nematic phase range exceeding 100°C. In spite of the reduction in clearing temperature and optical birefringence, the laterally attached fluoro group within the biphenyl core effectively eliminates the smectic phase which is seen in the other two compounds. The biphenyltolane liquid crysals exhibit high optical birefringences in the range 0.44–0.48, and show moderate solubility in commercially available liquid crystal mixtures.

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