Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Tailoring the physical properties of some high birefringence isothiocyanato-based liquid crystals

Carmen Otilia Catanescu[a]; Shin-Tson Wu[b]; Liang-Chy Chien Corresponding author[a]
[a] Liquid Crystal Institute, Kent State University, Kent, OH 44236, USA [b] School of Optics/CREOL, University of Central Florida, Orlando, FL 32816, USA

To cite this Article Catanescu, Carmen Otilia , Wu, Shin-Tson and Chien Corresponding author, Liang-Chy(2004) 'Tailoring the physical properties of some high birefringence isothiocyanato-based liquid crystals', Liquid Crystals, 31: 4, 541 — 555

To link to this Article: DOI: 10.1080/02678290410001662240

URL: http://dx.doi.org/10.1080/02678290410001662240

LIQUID CRYSTALS, VOL. 31, NO. 4, APRIL 2004, 541–555

Taylor & Francis
Taylor & Francis Group

Tailoring the physical properties of some high birefringence isothiocyanato-based liquid crystals

CARMEN OTILIA CATANESCU, SHIN-TSON WU† and
LIANG-CHY CHIEN

Liquid Crystal Institute, Kent State University, Kent, OH 44236, USA
†School of Optics/CREOL, University of Central Florida, Orlando, FL 32816,
USA

(*Received 2 September 2003; accepted 18 November 2003*)

This paper describes the synthesis and characterization of several liquid crystal compounds having a tolane or terphenyl core structure and a high polarizability, isothiocyanato (NCS), terminal group. The synthesized compounds have high optical birefringerce (0.35 and 0.52), the highest being exhibited by the olefin-tolanes. Several eutectic mixtures are formulated and show improved properties over the single compounds, such as a broad nematic range, low melting temperature and relatively high clearing point. The birefringence of these mixtures is in the range 0.35–0.37. UV, viscosity and electro-optical measurements of the synthesized compounds are also reported. Dipole moment and polarizability calculations were made using CS-MOPAC and Hyperchem software computational programmes.

1. Introduction

During the last two decades a large number of liquid crystal materials have been synthesized and their properties investigated because of their potential application in liquid crystal displays (LCDs) and other devices [1]. With so many compounds available, it might seem an easy task choosing the perfect one for applications such as (LCDs), infrared sensors and optical beam deflectors. But these devices require materials with good thermal and photochemical stability, wide nematic temperature range (at which the device is likely to be used), low viscosity, proper response to an electric field, good stability over a long period of time and many switching cycles, good viewing angle, low voltage holding ratio (VHR) and power consumption, etc. [2, 3]. These requirements are usually achieved in more or less degree by using mixtures of different liquid crystals, carefully designed for a specific application.

In this report we describe synthetic efforts toward tailoring the properties of materials to obtain high dielectric anisotropy and high birefringence liquid crystals. Three series of compounds were synthesized—tolanes, terphenyls, and olefin-tolanes—bearing a terminal isothiocyanato group and laterally substituted fluorine atoms, well suited for fast switching devices. The introduction of fluorine atoms can lead to a high dielectric anisotropy ($\Delta\varepsilon$) while an appropriate selection of their positions can lower the viscosity, reduce melting points, depress smectic phase formation and improve LC solubility and stability [2, 4, 5]. High birefringence (Δn), another important physical property, can be achieved by introducing permanent dipoles at one end of the rigid core, such as the isothiocyanato group (the introduction of the NCS group as an efficient electron-acceptor extends the conjugation length of the tolane and terphenyl compounds, and therefore, enhances their birefringence); but usually high Δn is closely associated with high viscosity [6, 7]. To achieve fast switching times a low viscosity is required, and in general shorter molecules are less viscous than longer molecules.

Tarumi *et al.* [8], studied the dynamic behaviour of a TN cell, finding that the switch-on (τ_{on}) and switch-off (τ_{off}) times can be described by the following equations:

$$\tau_{\mathrm{on}} \propto \left(\frac{d}{\pi}\right)^2 \frac{\gamma_1}{K_{\mathrm{eff}}} \left[\frac{1}{\left(\frac{V}{V_{\mathrm{th}}}\right)^2 - 1}\right] \tag{1}$$

$$\tau_{\mathrm{off}} \propto \left(\frac{d}{\pi}\right)^2 \frac{\gamma_1}{K_{\mathrm{eff}}} \tag{2}$$

$$V_{\mathrm{th}} = \pi \left\{\frac{[K_{11} + (K_{33} - 2K_{22})/4]}{\varepsilon_0 \Delta\varepsilon}\right\}^{\frac{1}{2}} = \pi \left(\frac{K_{\mathrm{eff}}}{\varepsilon_0 \Delta\varepsilon}\right)^{\frac{1}{2}} \tag{3}$$

where γ_1 and K_{eff} are the rotational viscosity and the elastic constant of the liquid crystal material, respectively,

Author for correspondence; e-mail: lcchien@lci.kent.edu

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2004 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290410001662240

V is the applied voltage, V_{th} is the threshold voltage, and d is the cell gap. From these equations, it is obvious that a reduction in the cell gap by using a higher birefringence LC to offer the same optical retardation is much more efficient than reducing the γ_1; still a low viscosity is highly desirable.

2. Experimental

2.1. *Characterization*

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 Merck Silicagel 60. 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 a Nikon polarizing optical microscope; 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 $2^\circ\mathrm{C\,min^{-1}}$ 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 several compounds was measured using a sodium lamp ($\lambda = 589$ nm) at $T = 295.9$ K, 10% of the compound being dissolved in a Merck LC host (ZLI-5100-100 with $\Delta n = 0.1716$). All Δn values were extrapolated to 100% concentration.

2.2. *Tolanes*

In the search for new materials with improved properties, several tolanes having laterally substituted fluorine atoms and a NCS terminal group were synthesized, because tolane substances have proved to have a better combination of physical properties than other materials [9]. The saturated alkyl chain was linked with the rigid core through an oxygen or sulphur atom. Only three of the compounds exhibit the nematic phase, the others have a crystalline structure.

Ten novel compounds were prepared according to the procedure detailed in scheme 1. All homologues were synthesized using the same method [10].

Alkyloxy/sulphanyl bromobenzenes **a** were synthesized using Williamson's etherification in near-quantitative yields. Compound **b** was converted into the alkyne **c** via compound **b** using the 2-methylbut-3-yn-2-ol method. A palladium-catalysed coupling reaction of the alkyne with 4-bromo-2,6-difluoro-aniline gave compound **d** in moderately low yields, but its conversion to the final compound **e** gave high yields. The first attempt to recrystallize the NCS-based compound from ethanol led to its interaction with the solvent, and a thiocarbamic acid ester was formed (analogous to the reaction of isocyanates with alcohols that give rise to *N*-carbamates). This side reaction was also reported by Seed *et al.* [11], thus further crystallizations of all NCS-based compounds were performed in hexane.

2.3. *Terphenyls*

The most common method used for the synthesis of terphenyl compounds is a cross-coupling reaction. There are several routes to carbon–carbon bond formation, but in the case of multiple ring compounds the following methods are usually employed:

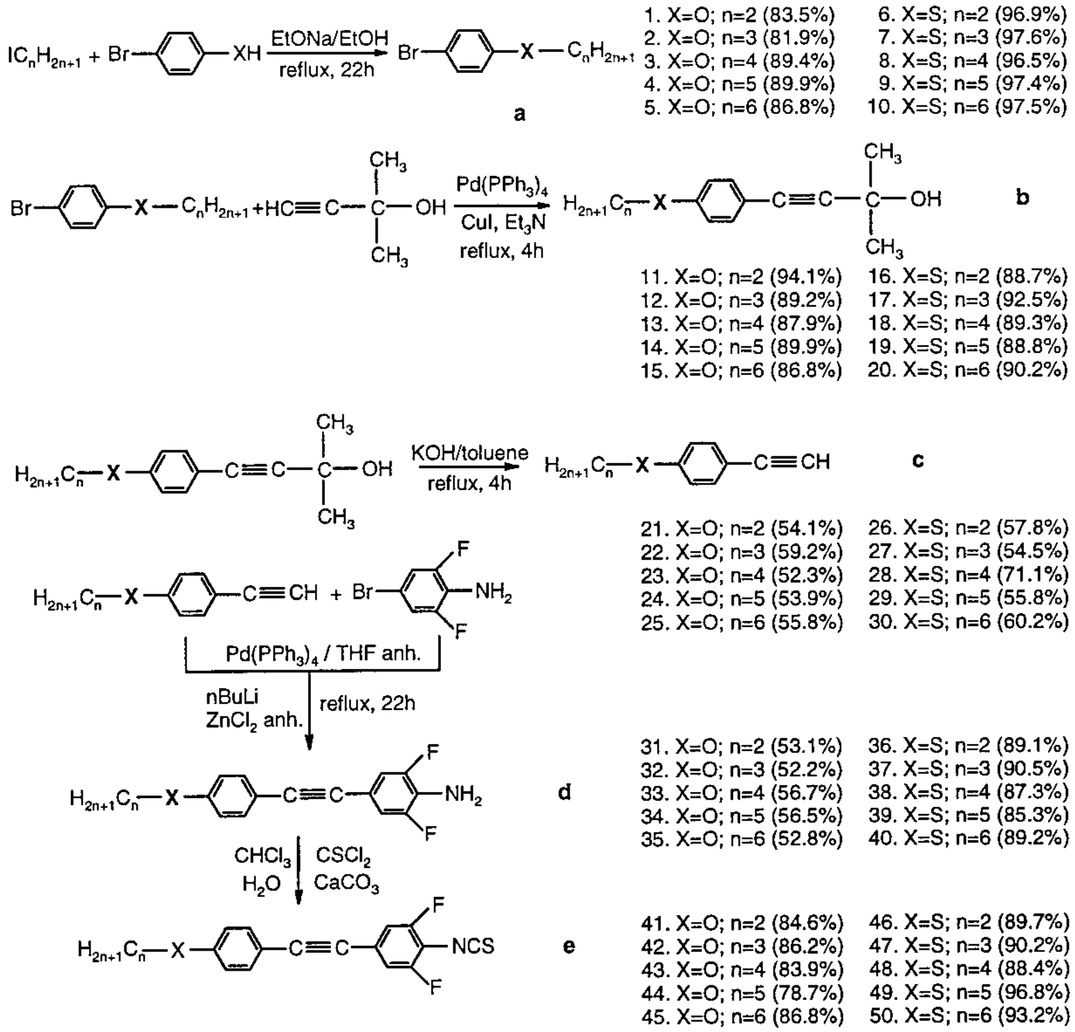
(a) Suzuki coupling of aryl boronic acids with aryl halides or aryl tosylates in the presence of a palladium catalyst [12–19];
(b) metal-mediated coupling of two aryl halides [20, 21].

We attempted to use method (b) since it involves only three steps. Unfortunately, this approach led to low yields (~10%) of product even after using more catalyst, butyllithium and zinc chloride, and increasing the reaction time to 5 days. We therefore reverted to the Suzuki coupling reaction (scheme 2).

The boronic acid can be prepared from an aryllithium or aryl Grignard reagent, obtained *in situ* from an aryl bromide or aryl iodide with BuLi or Mg in dry tetrahydrofurane by treatment with tri-isopropyl borate or trimethyl borate (at −78°C under dry nitrogen) followed by the hydrolysis of the borate ester (*in situ*) with 10% HCl). The boronic acids are stable in air and insensitive to moisture; they can be prepared in large quantities, stored and used when required [13].

The Suzuki coupling reaction for preparing unsymmetrical biaryl or multi-aryl systems is carried out in a two-phase medium of benzene/ethanol or 1,2-dimethoxyethane and aqueous 2 M sodium carbonate. The boronic acid is added in 10–20% excess and the reaction is catalysed by 3 mol% of tetrakis(triphenylphosphine)palladium(0). A nitrogen atmosphere is used to protect the catalyst and the stirred mixture is heated under reflux until tlc analysis reveals a complete reaction (usually ~3–4 h but often overnight for convenience) [13].

However, when using benzene/ethanol as a two-phase medium we obtained low yields (~15%) (and many by-products) due to the protodeboronation reaction that



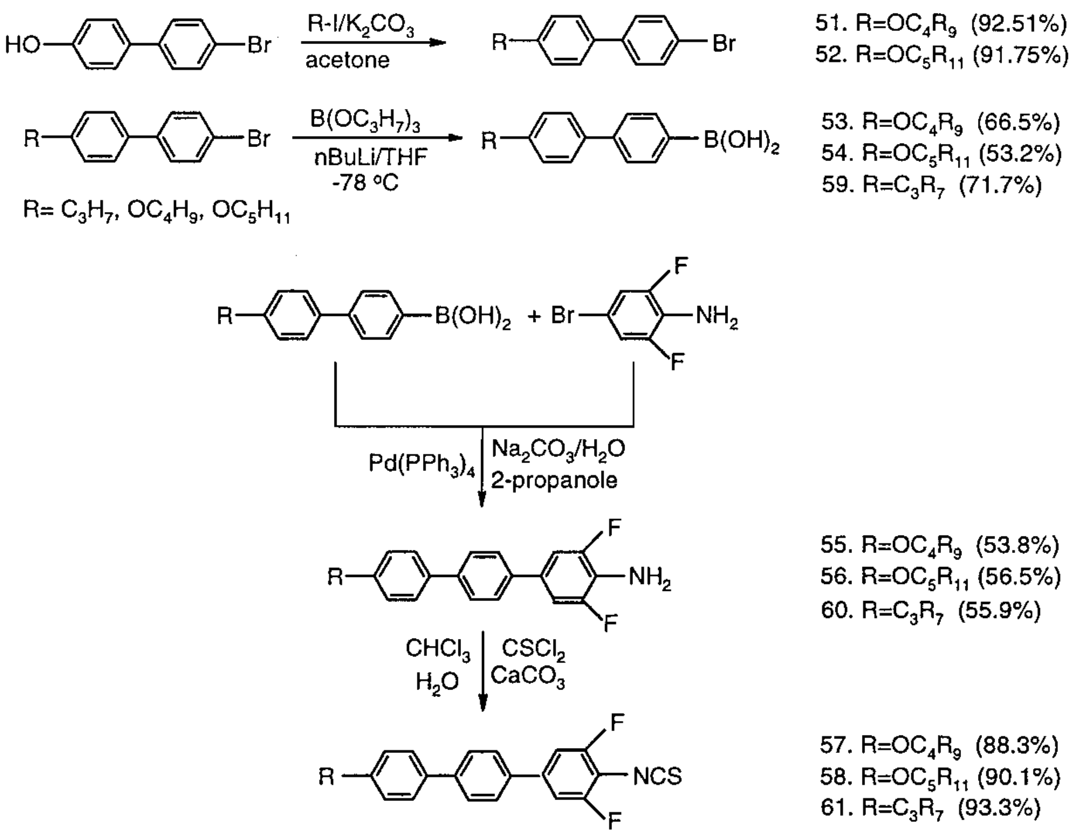
Scheme 1. The synthesis of alkoxy- and alkyl-sulfanil-PTP(3,5F)NCS compounds.

occurred during the coupling procedure. Changing the solvent to triethylamine [13] or protecting the amine group [22] was unsuccessful, but after switching to the 1,2-dimethoxyethane better yields were obtained (50–60%) and fewer by-products. One alkyl-terminated terphenyl was also synthesized using this procedure (scheme 2).

2.4. *Olefin tolanes*

The introduction of an alkenyl group next to the rigid core of a tolane compound will increase its conjugation length and, thus, its birefringence, with probably a similar contribution to the birefringence as a phenyl ring, but inducing a much lower viscosity. Three compounds were synthesized according to the reaction scheme 3 [23]. First attempts at synthesizing these compounds using the coupling reaction of 4-bromo-2,6-difluoroaniline with 1-alkenyl-4-ethynebenzene resulted in low yields and by-products that were difficult to remove. By connecting the acetylene group to 4-bromo-2,6-difluoroaniline, the coupling reaction with the olefin part gave the desired product in good yield and with no by-products (scheme 3). The final step, in which the amine group is converted to isothiocyanate, needed more thiophosgene and $CaCO_3$ than normally used for the synthesis of alkoxy/alkyl-sulphanyl or terphenyl compounds, and more reaction time.

The purification of the final product was difficult. Three or four purifications by column chromatography were needed to obtain a white compound. We also observed that with the increase in number of methylene units near the olefin group, the chemical stability of the product decreased (a yellowish colour appeared after removing the solvent); therefore the final olefin compounds must be stored under nitrogen in dark brown bottles. The yellow colour still appeared after a few



Scheme 2. The synthesis of alkyl- and alkoxy-PPP(3,5F)-NCS compounds using Suzuki coupling.

days, weeks or months (depending on the compound), suggesting that these olefin tolanes are chemically unstable, the olefin group being oxidized over time.

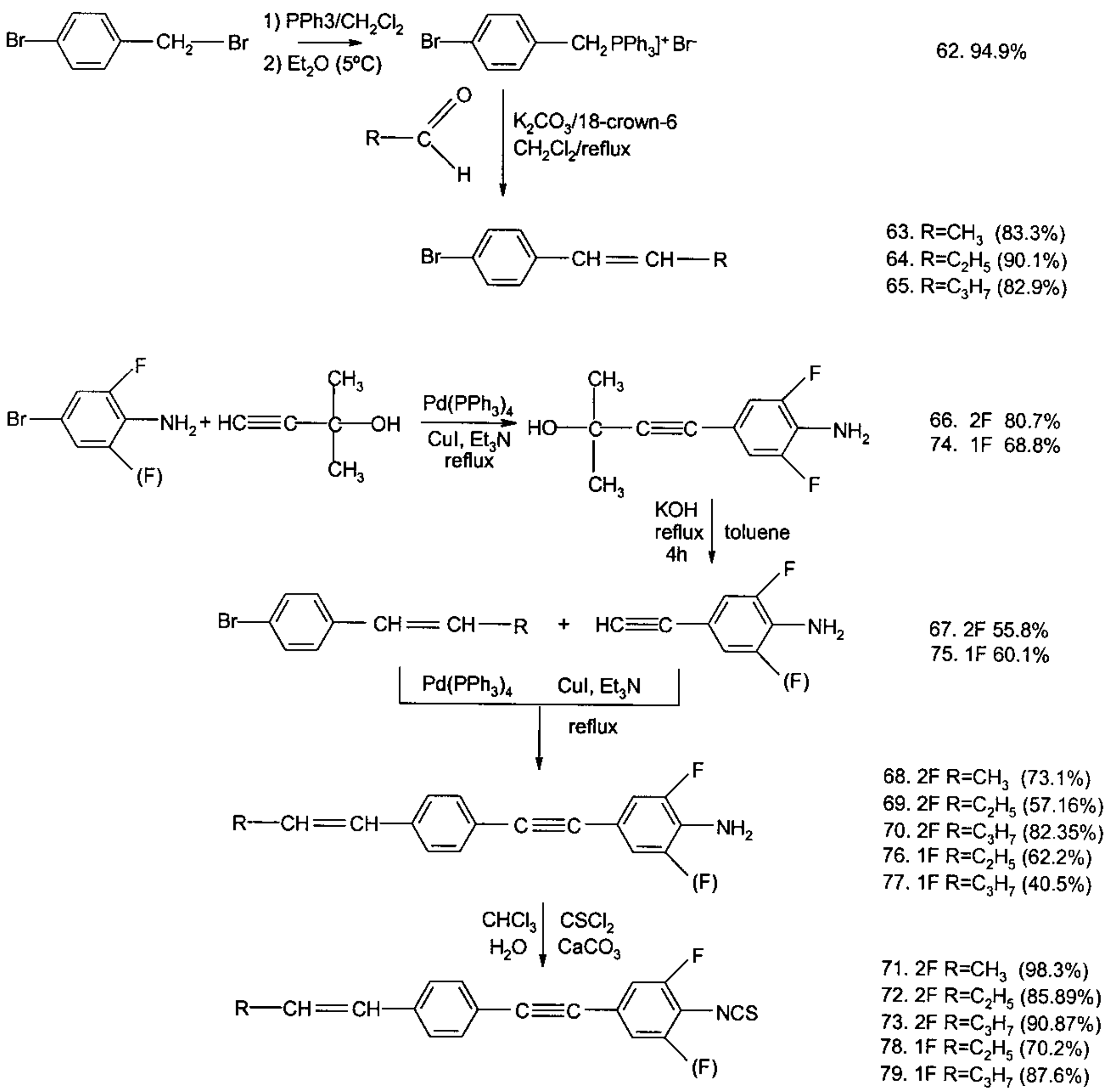
Another interesting observation was that for a limited time after removing the solvent from column chromatographed solutions, the compounds remained in the liquid state, even though their melting points are above room temperature. We also observed that, near the isotropic temperature, higher olefin tolane homologues were oriented in a homeotropic state (in the range 5–9°C), viewed through the polarizing optical microscope, with the mesophase being visible only under shearing. The DSC thermograms showed sharp crystallization peaks, but broad melting peaks, suggesting that either the samples contained small traces of impurities undetected by HPLC, or that solid–solid transitions (conformational changes in the solid phase) appeared while heating the samples.

In order to compare their properties with those containing two fluorine atoms in the vicinity of the isothiocyanate group, the synthesis of single-fluoro olefin-tolanes was also performed (compounds **78**, **79**, scheme 3). As anticipated, their transition temperatures were somewhat higher than their two-fluorine counterparts. We also noticed that their nematic phase range was a little narrower than that of compounds **71**–**73**. The stability of the single-fluoro olefin-tolanes displays features similar to those of the difluorine-based olefin-tolanes.

3. Results and discussion

3.1. *Single compounds*

Some of the physical characteristics of the final compounds are presented in table 1. As can be seen, none of the alkylsulphanyltolanes (compounds **46**–**50**) exhibit a mesophase, because of the smaller molecular aspect ratio (length/breadth, *L*/*D*) compared with that of the alkoxytolanes. The similar alkoxytolanes with longer alkyl chains have monotropic or enantiotropic behaviour (compounds **43**–**45**). In the case of compounds **41** and **42**, the alkyl chain is probably too short to overcome the minimum value for the *L*/*D* ratio predicted by the Maier–Saupe theory and, therefore, the mesophase remains unrevealed. With compound **43**, the length of the molecule increases the *L*/*D* ratio and monotropic behaviour is observed, giving however a metastable phase. On increasing the length of the molecules and, hence, their molecular weight, the mesophase becomes stable and enantiotropic behaviour is exhibited by the higher tolane homologues, although the mesophase range is very narrow (only 7–10°C on heating).



Scheme 3. The synthesis of alkenyl-PTP-NCS compounds.

We can also see a decreasing trend in the clearing temperatures in both tolane series, the longer the chain the lower the temperatures, but the odd–even effect of the methylene units upon the clearing temperature appears only for longer chains (4–6 methylene units).

The lower values of the transition temperatures observed in the case of the alkylsulphanyltolanes, compared with those of the alkoxytolanes, suggests that the bulkier sulphur leads to a lesser degree of molecular chain packing (molecular order), which may also explain the absence of a mesophase.

When passing from a tolane system to a terphenyl system, the effect of the phenyl ring, compared with that of the triple bond, on the properties of the NCS compounds is quite significant (compounds **57**, **58**, **61**). Not only are the transition temperatures very high because the three-phenyl ring system is much more rigid (even though the terphenyl group is not coplanar due to steric hindrance), but also the mesophase range is much larger than for the tolanes and this indicates a better mesogenicity of the terphenyl compounds. One may also notice that the alkoxy terminal chain induces a higher ordering of the molecules (by increasing the polarizability of the molecules) and thus higher transition temperatures, an additional smectic phase being observed when compared with the alkylterphenyl homologue.

As for the two synthesized alkoxyterphenyls, an increase in the number of the methylene units (compound **58**) led to a larger smectic phase than for its

Table 1. Physical characteristics of the NCS-based compounds. M_w = molecular weight; ΔH_m = fusion enthalpy of the compound (melting), values obtained from the third heating curve (DSC measurements); Cr = crystallization temperature on cooling at 2°C min^{-1}; Sm = 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); Δn = birefringence, extrapolated values to 100% concentration (mixtures of EM_x + ZLI 5100-100 = 10:90).

Compound	M_w/g mol^{-1}	ΔH_m/kcal mol^{-1}	Cr/°C	Sm/°C	N/°C	I/°C	N range/°C	Δn
41	315	5.93	87.5			95.4		
42	329	7.79	78.5			86.8		
43	343	6.67	32.3		(59.7)	61.6	(27.4)	0.3787
44	357	7.07	25.7		49.5	56.6	7.1	0.3503
45	371	8.57	46.3		54.7	65.1	10.4	
46	331	7.91	61.7			89.6		
47	345	7.73	68.7			80.8		
48	359	6.95	47.1			58.4		0.3977
49	373	6.33	19.6			34.4		
50	387	9.04	48.1			55.5		
57	395	2.76	158.8	161.9	168.4	230.0	61.6	
58	409	2.66	154.0	157.5	179.6	219.3	39.7	0.3987
61	365	3.05	64.2		106.7	194.9	88.2	0.3827
71	311	6.0	101.2		111.8	129.9	18.1	0.5280
72	325	4.32	59.6		74.5	102.3	27.8	
73	339	3.39	33.1		54.6	87.6	33	
78	307	3.20	61.4		87.8	96.9	9.1	
79	321	4.47	61.3		84.2	110.8	26.6	

lower homologue, but it lowered the melting and clearing temperatures; therefore, one may say that for this conjugated system longer terminal alkoxy chains stabilize the smectic phase. It was also observed that all three terphenyl compounds align in a homeotropic state while in the nematic phase, and they react under pressure in the range 10–12°C above the clearing temperature, the mesophase being clearly visible under shearing. In the case of compound **58**, the homeotropic state persists in the smectic phase too; the uniformity of this behaviour leading to a very well ordered structure after crystallization.

The third series of compounds designed for obtaining high Δn materials comprises compounds **71**–**73**, **78** and **79**. We expected that the effect on the liquid crystalline and physical properties of a double bond attached directly to the tolanes would lead to an increase of the nematic range compared with the alkoxytolanes; it did so, but it also raised their transition temperatures. The most important feature of these materials is that they have the highest value of birefringence from all the synthesized compounds; yet they also have the lowest stability, which drastically diminishes their importance in LCDs.

3.2. *Eutectic mixtures*

The wide temperature range and high clearing temperatures of the alkoxy terphenyls are desirable properties in a LCD, but they also display a smectic phase and high melting temperatures. The higher homologues of the alkoxy- and alkyl-sulphanyl tolanes series have lower melting temperatures, but narrow range or even no mesophase, therefore we formulated nine eutectic mixtures (table 2) using some of the materials from the three series of synthesized compounds, in an attempt to obtain better liquid crystalline properties. The eutectic mixtures were formulated based on the Schroder–van Laar equations:

$$T_i = \frac{\Delta Hf_i}{\frac{\Delta Hf_i}{Tf_i} - R \ln x_i} \qquad (4)$$

$$x_i + x_j = 1 \qquad (5)$$

$$T_c = \sum_i x_i T_{ci} \qquad (6)$$

where T_i is the temperature at which the pure component i melts in the mixture, H_{fi} is the heat fusion enthalpy of the component i, T_{fi} is the melting point of the pure component i; $Tf_i = T_m$, R is the gas constant (1.98 cal mol^{-1} K^{-1}), x_i is the mole fraction of the component i, and T_c is the clearing point.

As one can see from table 2, in most cases experimental values of the transition temperatures are in good agreement with predicted values. Five of the eutectic mixtures (EM_2, EM_3, EM_6, EM_7 and EM_9) showed wide range nematic phases, EM_9 displaying the best properties in terms of transition temperatures and birefringence. We also observed that, even though the melting points of the last three mixtures are below room temperature, they crystallize after a few days. All

Table 2. Physical characteristics of the eutectic mixtures. T_i = the melting temperature of the pure component in the mixture, theoretical value; T_{ie} = the melting temperature of the mixture, experimental value (from DSC thermograms); T_c = the clearing temperature of the pure component in the mixture, theoretical value; T_{ce} = the clearing temperature of the mixture, experimental value (from DSC thermograms); ΔH = fusion enthalpy of the mixture (melting), values obtained from the third heating curve; Δn = birefringence, extrapolated values to 100% concentration (mixtures of EM_x + ZLI 5100-100 = 10:90); Cr = crystallization temperature on cooling at 2°C min^{-1}.

Eutectic	Mixtures composition (w%)	Cr/°C	T_i/°C	T_{ie}/°C	T_c/°C	T_{ce}/°C	N range/°C	ΔH/J g^{-1}	Δn
EM_1	44:49 = 35.5:64.5	2.6	21.9	31.9	42.1	44.6	12.7	46.7	
EM_2	44:58 = 69.4:30.6	13.5	39.2	39.7	106.3	104.4	64.7	42.9	0.3537
EM_3	44:61 = 60.7:39.3	1.1	35.6	34.5	110.8	109.2	74.7	38.3	0.3567
EM_4	44:71 = 81.6:18.4	4.1	43.7	39.7	69.9	65.2	25.5	51.6	
EM_5	49:58 = 82.2:17.8	−2.5	28.7	31.7	67.2	41.1	9.4	60.4	
EM_6	49:61 = 68.0:32.0	−16.8	23.4	27.8	85.5	66.1	38.3	49.8	0.3644
EM_7	44:49:61 = 25.4:47.6:27.0	−24.2	14.0	13.2	83.1	68.9	55.7	37.4	0.3504
EM_8	44:49:71 = 32.4:59.3:8.3	−12.0	19.8	17.8	49.4	32.5	14.7	39.1	0.3594
EM_9	44:49:61:71 = 23.4:44.3:26.0:6.3	—	12.1	8.9	87.3	71.8	62.9	21.3	0.3724

mixtures show single melting and clearing peaks, although not sharp but rather broad (extended over 4–6°C), whilst on cooling multiple crystallization peaks were observed. This might be due to a poor solubility and miscibility of the compounds.

3.3. *Optical birefringence, polarizability and dipole moment*

An interesting and important property of liquid crystals is their optical birefringence. The refractive index for light propagating parallel to the axis of the fluid is different from the index for light propagating perpendicular to this direction, due to anisotropy in the dielectric response function. Orientational order, and hence birefringence, can be easily changed with the help of magnetic, electric or optical fields leading to large magneto-optical, electro-optical and opto-optical effects, which are important in all switching devices.

We measured the birefringence of several compounds and list the extrapolated values in table 1. As can be seen, Δn values lie between 0.35 and 0.53. The results for the extrapolated values of birefringence for the first series of compounds (**41**–**50**) show that they all exhibit high Δn, the sulphur-containing NCS tolanes presenting higher values of birefringence than the alkoxy types, because of the higher polarizability of the sulphur atom compared with oxygen.

Usually, an increase in the number of directly connected phenyl rings leads to an increase in birefringence. Δn measured for compounds **58** and **61** was 0.39 and 0.38, respectively, higher than for the alkoxytolanes because of better and longer molecular conjugation, but similar to the alkylsulphanyltolanes. This result again proves that the polarizability of the molecules plays a large role in enhancing the Δn of the materials, besides the length of the molecular conjugation.

Changing the aliphatic terminal group in the tolanes to an unsaturated alkenyl group led to the highest value for birefringence (compound **71**). In order to better understand structure–property relationships of the synthesized molecules, we calculated the polarizability tensor scalar (α) equation (7), and the anisotropy of the polarizability based on the Lorenz–Lorentz equation and Maier–Saupe theory [24], the results being presented in table 3.

$$\left[\frac{\left(n_e^2-1\right)}{\left(n_e^2+2\right)}+\frac{2\left(n_o^2-1\right)}{\left(n_o^2+2\right)}\right]\frac{3M}{4\pi d N_A}=\alpha_\parallel+2\alpha_\perp=\alpha_s \qquad (7)$$

where n_e and n_o are the extraordinary and ordinary refractive indices of the compounds (the extrapolated values), respectively, M is the molecular mass, d is the density (we assumed $d=1$), and N_A is the Avogadro number.

The electronic clouds of a molecule have different dimensions in different directions, therefore their elastic displacements in an electric field will vary in different directions; the polarizability of a molecule must therefore possess electric anisotropicity in space. In this case, the polarizability is described by a tensor which can be represented in the form of an ellipsoid of polarization. From this ellipsoid the polarizability of the molecule in space can be reduced to its polarizability in three mutually perpendicular directions α_x, α_y and α_z,

Table 3. Polarizability tensor scalar and molecular polarizability anisotropy.

Compound	n_e	n_o	$\alpha_s/10^{-23}\,\mathrm{cm}^3$	$\Delta\alpha/10^{-23}\,\mathrm{cm}^3$
43	1.9151	1.5364	14.88	2.16
44	1.9124	1.5621	15.83	2.06
48	1.9711	1.5734	16.36	2.29
58	1.9471	1.5484	18.12	2.66
61	1.9391	1.5564	16.24	2.28
71	2.0904	1.5624	14.52	2.58

corresponding to the three principal semiaxes of the ellipsoid. In anisotropic molecules, the polarizability along the direction of the valence bonds is always greater than in other directions. Also, it is always higher in conjugated molecules than in aliphatic molecules because the p-electrons, which possess a greater mobility than the s-electrons, are more subject to the action of an electric field. For molecules containing non-conjugated bonds, the polarizability can be regarded as the algebraic sum of the polarizabilities of the individual atoms or bonds. When conjugated bonds are present, the electronic polarizability exceeds the additive value, which is explained by the greater mobility of the π-electrons in conjugated systems. Thus the terphenyl compounds have the highest polarizability of all the compounds studied. One must also note that, with an increase in the volume of the electron charge cloud, the polarizability increases in magnitude. The greater the distance of the electron from the nucleus, the greater is its mobility and, hence, the higher the influence on it of an applied electric field. This is seen very well when comparing the alkylsulphanyltolanes with the alkoxytolanes, and also when comparing the alkoxyterphenyls with the alkylterphenyls. It is interesting to note that the polarizability of compound **61** is almost identical with that of compound **48**.

To obtain more information about the electronic structure of the synthesized compounds we performed molecular modelling and analysis using two application programs: CS MOPAC included in the Chem3D 8.0 package (product of CambridgeSoft) and Hyperchem 7.0 (product of Hypercube, Inc.). Our molecular modelling and computational analysis targeted the electronic properties of the NCS-based compounds, such as dipole moment and polarizability. Even though the total charge on a molecule is zero, the nature of chemical bonds is such that the positive and negative charges do not completely overlap in most molecules. Such molecules are said to be polar because they possess a permanent dipole moment. Therefore, the dipole moment expresses the degree of polarity of a molecule and studies of the dipole moment can sometimes provide information about the molecular structure.

The polarizability measures the extent to which a dipole moment is induced in a composite system exposed to external electric or magnetic fields. The induced dipole moment is proportional to the applied field, the constant of proportionality being the polarizability. The charge and magnetic moment characterize the first order response of the system to an external field, while the polarizability characterizes the second order response. More importantly, the polarizability represents the first order response of the internal structure of the composite system.

Computational methods calculate the potential energy surface of the molecule, which is a summation of analytical expressions representing the forces of interaction (bonded or non-bonded) among atoms in the molecule. The methods (MNDO, MNDO-d, MINDO/3, AM1, PM$_3$) differ in the way the surface is calculated and in the molecular properties derived from the energy surface. Since PM$_3$ (parameterized Model revision 3) is overall better than the other semi-empirical methods available in CS MOPAC, we used it to study the dipole moment and the polarizabilities of the synthesized NCS-based liquid crystals. Nevertheless, the online MOPAC manual notes that the various methods underestimate the polarizability (α) by about 50%, and at present this calculation only works for RHF (restricted Hartree–Fock) closed-shell systems.

Before performing these calculations we minimized the energy of the molecule (using the MM2 method). Finding the global minimum is difficult and challenging even for simple molecules. It requires a starting conformation that it is already in the valley of the global minimum and not in the local minimum valley. The process of conformation searching for the global minimum can be very time consuming, but some methods can be used for this, one of them being Monte Carlo simulations. The conformational analysis showed that none of the molecules are coplanar: the phenyl rings are twisted around the carbon–carbon σ-bond with a certain torsion angle, despite the fact that a better conjugation would be achieved by being flat. In the case of terphenyl compounds this is due to steric hindrance between adjacent hydrogen atoms, while for the tolanes the triple bond between the two phenyl rings is less rigid than a phenyl ring and hence the bonds are more flexible.

From table 4 one may see that the predicted values of the dipole moment for the alkoxytolanes (compounds **41**–**45**) are situated around 6 D, while those of the sulphur-containing tolanes (compounds **46**–**50**) are in

Table 4. Dipole moment and polarizabilities of NCS-based tolanes (MOPAC calculations). $\Delta\alpha = \alpha_x - (\alpha_y + \alpha_z)/2$.

Compound	L/Å	μ/D	α_{xx}/a.u.	α_{yy}/a.u.	α_{zz}/a.u.	$\Delta\alpha$/a.u.
41	17.01	5.94	501.9	120.7	98.9	392.1
42	18.02	5.97	514.5	128.7	105.9	397.2
43	19.44	5.99	525.9	136.3	113.4	401.05
44	20.47	6.01	535.6	144.1	121.5	402.8
45	21.87	6.02	545.6	151.9	129.0	405.15
46	17.38	5.10	538.8	122.6	110.5	422.25
47	18.16	5.13	549.6	130.4	118.6	425.1
48	19.64	5.16	560.4	138.6	126.6	427.8
49	20.47	5.17	568.1	145.6	137.5	426.55
50	21.97	5.19	577.7	151.6	147.3	428.25

the range 5.1–5.2 D. The lower values for the alkylsulphanyl series are in accord with the lower electronegativity of the sulphur atom compared with oxygen. The dipole moments of the two-fluorine-substituted olefin-tolanes (compounds **71**–**73**) have lower values than those of the corresponding alkoxytolanes, but higher than those of sulphur-containing tolanes, implying in this case that the oxygen atom contributes more to the dipole moment than the alkenyl group; hence, the situation is reversed when it comes to the polarizabilities. This result may suggest a poorly optimized structure because the dipole moment and polarizabilities are directly related one to another, so the trend should be the same. From tables 4 and 5 it can be seen that the longer the conjugation length (as in the olefin-tolanes and terphenyls compared with the corresponding alkoxytolanes), the higher the polarizabilities. In this case, the values of the polarizabilities obtained based on experimental refractive indices (table 3) are in agreement with the results from table 4. As expected, alkyl groups have a 'negative' impact on the dipole moments and polarizabilities compared with alkoxy groups (see the terphenyl compounds **57**, **58**, **61** of table 5).

Hyperchem simulations (table 6) showed a basically similar trend in polarizability results compared with experimental results (see table 3), and dipole moment values very close to those obtained by MOPAC calculations. Some differences appeared while computing the polarizability properties for the olefin-tolanes, which showed lower values than the alkoxytolanes, opposite that for data obtained by MOPAC or presented in table 3. This may again be the result of a poorly optimized conformation of the molecules (local minimum instead of a global minimum).

Table 6. Results of the geometry optimization and PM_3 calculations of the polarizability anisotropy and dipole moment (Hyperchem calculations). A = area; V = volume.

Compound	A/Å^2	V/Å^3	α/Å^3	μ/D
41	583.70	900.42	32.44	5.86
42	605.92	948.52	34.18	5.88
43	642.47	1001.97	36.01	5.92
44	679.64	1055.20	37.85	5.98
45	729.97	1115.58	39.78	6.01
46	589.11	920.59	34.71	4.93
47	627.45	974.27	36.54	4.95
48	663.60	1005.35	38.38	4.98
49	699.42	1081.50	40.21	5.05
50	749.54	1141.49	42.14	5.10
57	625.19	1107.88	43.11	5.79
58	677.23	1169.20	45.04	5.86
61	582.06	1014.13	40.08	5.54
71	591.16	903.06	32.99	5.69
72	637.16	964.32	34.83	5.74
73	669.80	1015.26	36.66	5.79
78	649.73	895.41	34.46	5.46
79	687.75	1001.89	36.30	5.53

3.4. *Electro-optic measurements*

In order to compare the electro-optical response of some of the synthesized compounds, we mixed 10 wt% of each compound with 90 wt% of a Merck LC mixture (ZLI 5100-100). Several EHC cells for homogeneous (anti-parallel) alignment, of thickness 4.6 μm, were filled with the mixtures by capillary action on a hot stage. The transmittance versus applied voltage and transmittance versus time curves were recorded using a set-up consisting of a He-Ne laser beam ($\lambda = 633$ nm), crossed polarizer and analyser, and a quarter-wave plate (Soleil-Babinet compensator with its optical axis parallel with the first polarizer). The LC cell was placed between the quarter-wave plate and the polarizer such that the optical axis (the rubbing direction) was at 45° with respect to the first polarizer.

Table 5. Dipole moment and polarizabilities of NCS-based olefin-tolanes, terphenyls and biphenyltolane (MOPAC calculations). $\Delta\alpha = \alpha_x - (\alpha_y + \alpha_z)/2$.

Compound	L/Å	μ/D	α_{xx}/a.u.	α_{yy}/a.u.	α_{zz}/a.u.	$\Delta\alpha$/a.u.
71	17.13	5.61	537.0	116.2	109.3	424.25
72	17.74	5.64	545.0	131.6	111.6	423.4
73	19.26	5.67	560.0	133.9	123.8	431.15
78	17.75	5.20	545.0	118.8	114.3	440.85
79	19.22	5.18	557.4	149.7	100.8	432.15
57	21.27	6.28	579.2	217.8	59.7	440.45
58	22.37	6.29	628.0	238.4	68.7	474.45
61	18.71	5.40	515.5	208.1	79.7	371.6

The results of the electro-optical measurements are shown in figures 1, 2 and 3 and presented in table 7. The switching times were measured by applying a square-wave a.c. voltage of 1 kHz from 1.4 to 10.0 V and 10.0 to 1.4 V for switching on and off, respectively.

From figures 1, 2 and 3 it can be seen that overall the new compounds led to significant improvement of the birefringence while maintaining all other parameters unchanged or slightly improved. Their higher Δn may make them useful for LC displays with a smaller cell gap.

3.5. *UV measurements*

Because chloroform is not UV transparent below 250 nm, the UV spectra recorded in this solvent show the absorption peaks only above 250 nm. Small differences are seen between the UV absorption spectra of the NCS-based compounds performed in chloroform figure 4 (*a*), and hexane, figure 4 (*b*). In hexane, alkoxytolanes, alkylsulphanyltolanes and the olefin-tolanes

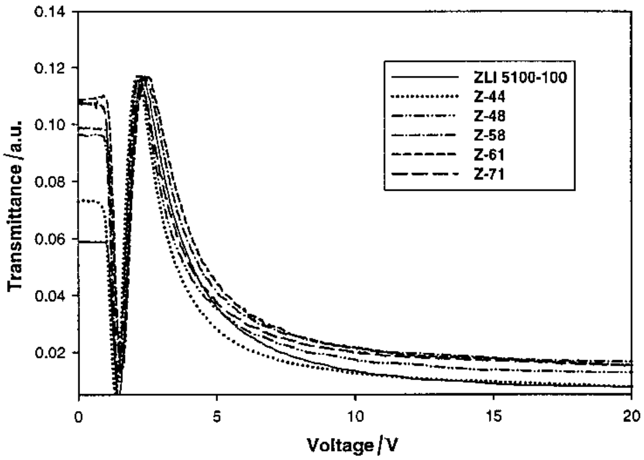


Figure 1. The effect of different NCS compounds on the transmission vs. voltage (normalized curves) of the Merck LC ZLI 5100-100 (10 wt% NCS compound dissolved in ZLI 5100-100).

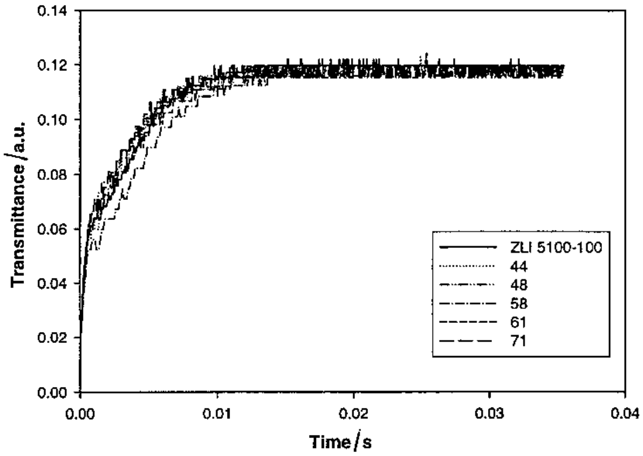


Figure 2. The effect of different NCS compounds on the transmission vs. turn-off time (normalized curves, switched from 10.0 to 1.4 V) of the Merck LC ZLI 5100-100 (10 wt% NCS compound dissolved in ZLI 5100-100).

exhibit three absorption peaks; first around 200 nm, second around 330 nm and the third around 350 nm.

The first peaks correspond to the E-bands (ethylenic bands) that are characteristic of aromatic structures. The second peaks are attributed to π→π* transitions resulting from the conjugated π-system (K-band). In this case a small bathochromic shift of the peaks recorded in chloroform is seen, accompanied by increasing intensity, as the polarity of the solvent is increased. The red shift presumably results from a reduction in the energy level of the exited state accompanying dipole–dipole interactions. The third peaks remain practically unchanged in the case of tolane compounds (with only a small red shift observed for the olefin-tolanes). These peaks correspond most probably to the R-bands (n→π* transitions) and/or B-bands. As for the terphenyl compounds, they present two UV absorption peaks in hexane, corresponding to the E and K bands, while the spectra recorded in chloroform show only one broad peak, around 320 nm. For these compounds, the K and B bands are submerged in one single peak. One may also note that the maximum absorption peak of the terphenyls is present at lower wavelengths than for the rest of the compounds, suggesting that molecular conjugation is higher within the tolanes because of the overlap of the π-orbitals of the phenyl ring with the p(n)-orbitals of the oxygen or sulphur atoms or the π-orbitals of the olefin group, respectively.

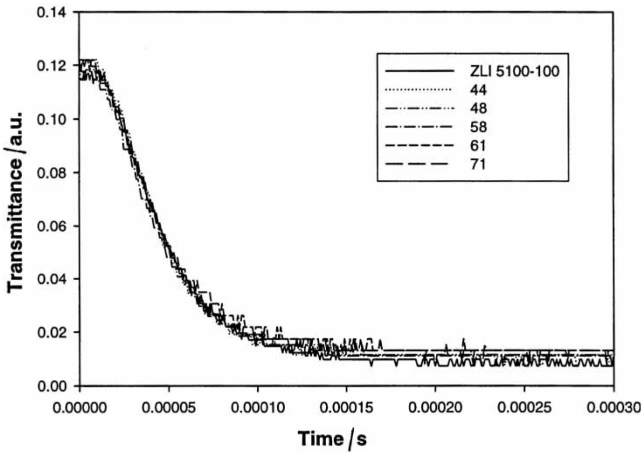


Figure 3. The effect of different NCS compounds on the transmission vs. turn-on time (normalized curves, switched from 1.4 to 10.0 V) of the Merck LC ZLI 5100-100 (10 wt% NCS compound dissolved in ZLI 5100-100).

Table 7. Results of the electro-optical measurements. **Z** = ZLI 5100-100 (Merck LC mixture used as host); V_{10} = voltage at 10% of the maximum transmittance; V_{90} = voltage at 90% of the maximum transmittance; V_{90}/V_{10} = sharpness, calculated as $\left(\frac{V_{90}}{V_{10}}-1\right)\times 100$; τ_{on} = switching time between 1.4 V and 10 V; τ_{off} = switching time between 10 V and 1.4 V.

Mixture	V_{10} (V)	V_{90} (V)	V_{90}/V_{10} (%)	τ_{on} (ms)	τ_{off} (ms)
Z	1.50	2.18	45.33	0.20	13.8
Z-44	1.42	2.05	44.36	0.12	12.9
Z-48	1.52	2.12	39.47	0.14	11.2
Z-58	1.62	2.31	42.59	0.14	13.7
Z-61	1.66	2.42	45.78	0.14	11.1
Z-71	1.49	2.12	42.28	0.13	7.6

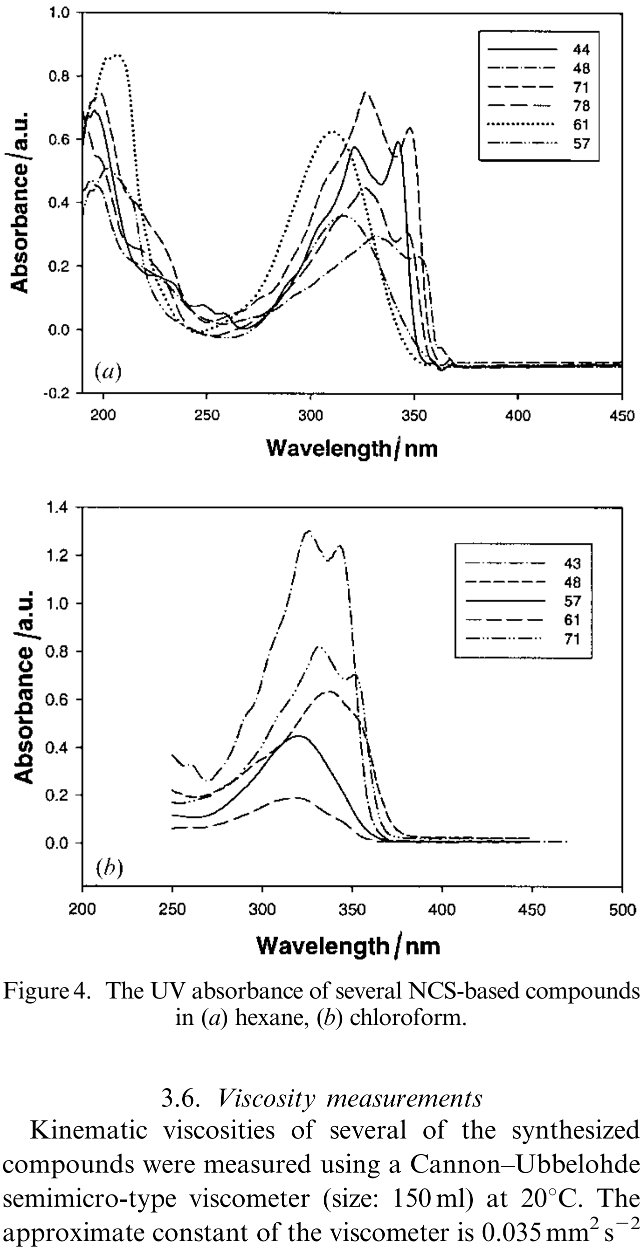


Figure 4. The UV absorbance of several NCS-based compounds in (*a*) hexane, (*b*) chloroform.

3.6. *Viscosity measurements*

Kinematic viscosities of several of the synthesized compounds were measured using a Cannon–Ubbelohde semimicro-type viscometer (size: 150 ml) at 20°C. The approximate constant of the viscometer is 0.035 mm^2 s^{-2} (cSt s^{-1}). A 10 wt% of each compound was dissolved in a Merck LC (E31). The kinematic viscosities of the samples (table 8) were calculated by multiplying the efflux time by the viscometer constant. As expected, alkoxy- and alkylsulphanyl-tolanes exhibited the lowest viscosities of all the compounds (having similar values), while the terphenyls showed the highest due to their increased molecular breadth. The viscosities of the olefin-tolanes were situated between them, the olefin group inducing a much lower viscosity than did a phenyl ring.

Table 8. The viscosities of some high birefringence liquid crystals.

Compound	Efflux time/s	Kinematic viscosity/mm^2 s^{-2}
E31	1474	51.59
44	1532	53.62
48	1540	53.90
58	1951	68.29
61	1590	55.65
71	1550	54.25

4. Synthesis details

4.1. *Tolanes*

4.1.1. *4-Butyloxy-1-bromobenzene **3***

4-Bromophenol (17.3 g, 0.1 mol) and potassium carbonate (21 g, 0.152 mol) were dissolved in 100 ml ethanol and 15 ml water. The reaction mixture was heated at reflux and stirred for 2 h. 1-Iodobutane (18.4 g, 0.1 mol) in 60 ml ethanol was added dropwise and stirred at reflux for 22 h. After cooling, the solution was poured into cold water (600 ml), extracted twice with dichloromethane, washed with saturated aqueous sodium hydrogen carbonate and then water, dried over Na_2SO_4 and filtered. Finally the solvent was evaporated *in vacuo* and the crude product purified by column chromatography (hexane/ethyl acetate = 4/1) to give a colourless liquid; yield 89.14%. ^{1}H NMR ($CDCl_3$) δ, ppm 0.98 (3H, t, $J=7.3$ Hz, alkyl CH_3), 1.55 (2H, sext., $J=6.9$ Hz, γCH_2), 1.77 (2H, quint., βCH_2), 3.93 (2H, t, $J=6.59$ Hz, CH_2O), 6.8 (2H, m, $J=8.79$ Hz, ArH *ortho* to OCH_2), 7.34 (2H, m, $J=9.15$ Hz, ArH *ortho* to Br). IR (film) ν_{max}/cm^{-1} 656, 814, 980, 1077, 1170, 1250, 1295, 1393, 1485, 1599, 1680, 2875, 2935, 2966.

4.1.2. *1-Butyloxy-4-(3-hydroxy-3-methylbut-1-ynyl) benzene **13***

Compound **3** was added dropwise to a suspension of 3-methylbut-1-yn-3-ol (10 g, 0.119 mol), tetrakis(triphenylphosphine)palladium(0) (3.08 g, 2.64 mmol), and copper(I) iodide (0.572 g, 2.64 mmol) in dry triethylamine (300 ml) at room temperature. The reaction mixture was then heated under reflux for 4 h. When cooled, the solution was filtered and the solvent removed *in vacuo*. Dichloromethane was added and the organic layer washed with saturated ammonium chloride solution (2 × 300 ml), then water (500 ml). The CH_2Cl_2 extracts were dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. The crude product was purified by column chromatography (hexane/ethyl acetate = 5/1) to give a yellowish-red viscous liquid; yield 70.8%. ^{1}H NMR ($CDCl_3$) δ, ppm 0.97 (3H, t, $J=7.32$ Hz alkyl CH_3), 1.49 (2H, m, $J=7.33$ Hz γCH_2), 1.72 (6H, s, 2 CH_3 Hz), 1.78 (2H, m, βCH_2), 2.1 (1H, s, OH), 3.95 Hz (2H, t, $J=6.59$ Hz, OCH_2), 6.83 (2H, m, $J=8.6$ Hz, ArH *ortho* to OCH_2), 7.31 (2H, m, $J=8.8$ Hz, ArH *ortho* to C≡C). IR (film) ν_{max}/cm^{-1} 840, 911, 970, 1050, 1173, 1264, 1376, 1508, 1599, 2226 (w, C≡C stretch), 2867, 2933, 2956, 3045, 3408 (s. OH).

4.1.3. *4-Butyloxyphenylethyne **23***

A mixture of compound **13** (9.6 g, 0.0413 mol) and potassium hydroxide (2.31 g, 0.0413 mol) in dry toluene (150 ml) was heated under reflux for 4 h. The acetone and toluene azeotrope was removed periodically using a Dean–Stark device and replaced with an equal volume of toluene. When cooled, the solvent was removed *in vacuo*. Diethyl ether was added and the organic phase washed with water (400 ml) and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the crude product purified by column chromatography (hexane) to give a slightly yellow liquid; yield 65.7%. ^{1}H NMR ($CDCl_3$) δ, ppm 0.97 (3H, t, $J = 7.32$ Hz, alkyl CH_3), 1.54 (2H, sext., $J = 6.95$ Hz, γCH_2), 1.78 (2H, quint., $J = 6.23$ Hz, βCH_2), 2.98 (1H, s, C≡CH), 3.95 (2H, t, $J = 6.59$ Hz, OCH_2), 6.84 (2H, m, $J = 8.79$ Hz, ArH *ortho* to OCH_2), 7.39 (2H, m, $J = 8.79$ Hz, ArH *ortho* to C≡C). IR (film) ν_{max}/cm^{-1} 830, 990, 1025, 1180, 1250, 1300, 1400, 1490, 1520, 1570, 1620, 2120 (w, C≡C stretch), 2881, 2933, 2966, 3045, 3295 (s, C≡CH stretch).

4.1.4. *1-(4-Amino-3,5-difluoro)-2-(4-butyloxyphenyl) ethyne **33***

n-Butyllithium (8 ml, 2.5 M in hexane) was added dropwise to a stirred, cooled (0°C) solution of compound **23** (2.821 g, 16.21 mmol) in dry THF (50 ml) under nitrogen. The reaction mixture was maintained under these conditions for 15 min, and a solution of anhydrous zinc chloride (3.2 g, 23.5 mmol) in dry THF (25 ml) was added dropwise at −5 to 0°C. The mixture was stirred at room temperature for 15 min and a solution of 4-bromo-2,6-difluoroaniline (3.372 g, 16.21 mmol) in dry THF (25 ml) was added dropwise at 0°C, followed by the addition of tetrakis(triphenylphosphine)palladium(0) (0.94 g, 0.814 mmol) in one portion. The mixture was heated and stirred under reflux overnight, then quenched with hydrochloric acid. The product was extracted into diethyl ether, washed with saturated sodium hydrogen carbonate solution (300 ml), and dried over Na_2SO_4. The solvent was removed *in vacuo* and the crude product purified by column chromatography (hexane/ethyl acetate = 6/1) It was recrystallized from hexane to give a light yellow solid; yield 50.61%. ^{1}H NMR ($CDCl_3$) δ, ppm 0.98 (3H, t, $J = 7.32$ Hz, alkyl CH_3), 1.50 (2H, sext., $J = 7.6$ Hz, γCH_2), 1.78 (2H, quint. $J = 6.95$ Hz, βCH_2), 3.86 (2H, s, NH_2), 3.97 (2H, t, $J = 6.59$ Hz, OCH_2), 6.87 (2H, dd, $J = 9.15$ Hz, ArH *ortho* to OCH_2), 6.96 (2H, dd, $J = 9.15$ Hz, ArH *ortho* to OCH_2), 7.39 (2H, dd, $J = 9.15$ Hz, ArH *ortho* to OCH_2). IR (film) ν_{max}/cm^{-1} 742, 834, 972, 1170, 1249, 1380, 1466, 1538, 1591, 1650, 2120 (w, C≡C stretch), 2854, 2920, 2953, 3183, 3315 (NH_2), 3440.

4.1.5. *1-(4-Butylaxyphenyl)-2-(3,5-difluoro-4-isothiocyanatophenyl)ethyne **43***

A solution of compound **33** (2.4 g, 7.97 mmol) in chloroform (30 ml) was added dropwise at 0–5°C to a stirred, cooled (0°C) mixture of water (18 ml), chloroform (9 ml), calcium carbonate (1.25 g, 12.5 mmol) and thiophosgene (0.65 ml, 85 mmol). The mixture was then heated at reflux for 2 h and poured into water (100 ml). The separated organic layer was quenched with hydrochloric acid (45 ml, 1%) and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product purified by column chromatography (hexane) and recrystallization from hexane to give white crystals; yield 83.82%. ^{1}H NMR ($CDCL_3$) δ, ppm 0.98 (3H, t, $J = 7.32$ Hz, alkyl CH_3), 1.51 (2H, sext., $J = 6.59$ Hz, γCH_2), 1.78 (2H, quint, $J = 6.95$ Hz, βCH_2), 3.97 (2H, t, $J = 6.59$ Hz, OCH_2), 6.89 (2H, d, $J = 9.15$ Hz, ArH *ortho* to OCH_2), 7.05 (2H, d, $J = 8.1$ Hz, ArH *para* to NCS), 7.41 (2H, d, $J = 8.79$ Hz, ArH *ortho* to C≡C). IR (film in nujol) ν_{max}/cm^{-1} 722, 851, 1051, 1175, 1255, 1380, 1466, 1518, 1611, 2032 (NCS), 2098 (NCS, shoulder), 2216 (C≡C stretch), 2854, 2920, 2966.

4.2. *Terphenyls*

4.2.1. *4-(4-Butyloxyphenyl)phenylboronic acid **53***

A solution of *n*-butyllithium (10.5 ml, 2.5 M in hexane, 26.25 mmol) was added dropwise to a stirred, cooled (−78°C) solution of 4-(4-butyloxyphenyl)bromobenzene (compound **51**)(8 g, 26.2 mmol) in dry THF (46 ml) under nitrogen. The reaction mixture was stirred under these conditions for 2.5 h, then a previously cooled solution of tri-isopropyl borate (9.874 g, 52.5 mmol) in dry THF (35 ml) was added dropwise (at −78°C). The reaction mixture was allowed to warm to room temperature overnight. 10% HCl (25 ml) was added and the mixture stirred for 1 h at room temperature. The product was extracted into ether; the organic layer was washed with sodium hydrogen carbonate solution, water and brine, and dried over Na_2SO_4. The product was purified by column chromatography using hexane/ethyl acetate as eluent (6/1, then 2/1) (and then changing to ethyl acetate/ethanol = 4/1 because of the poor solubility in the previous eluent). A white powder resulted which was recrystallized from methanol; yield 66.5%. ^{1}H NMR ($CDCl_3$) δ, ppm 0.97 (3H, t, $J = 7.32$ Hz alkyl CH_3), 1.54 (2H, sext., $J = 6.9$ Hz, γCH_2), 1.81 (2H, quint., $J = 6.59$ Hz, βCH_2), 4.06 (2H, t, $J = 6.38$ Hz, OCH_2) 7.03 (2H, d, $J = 8.42$ Hz, ArH *ortho* to OCH_2), 7.5–7.8 (4H, m, $J=8.42$ Hz, ArH) 8.28 (2H, d, $J=8.1$ Hz, ArH *para* to $B(OH)_2$), no obvious OH absorption. IR (film) ν_{max}/cm^{-1} 670, 734, 790, 811, 1006, 1020, 1243, 1335, 1376, 1460, 1530, 1600, 2835, 2875, 2933, 3331 (OH), 3478.

4.2.2. *4″-n-Butyloxy-3,5-difluoroterphenyl-4-amine* **55**

4-(4-Butyloxyphenyl)phenylboronic acid (compound **53**) (4.71 g, 17.44 mmol), 4-bromo-2,6-difluoroaniline (3.628 g, 17.44 mmol), tetrakis(triphenylphosphine)palladium(0) (0.672 g, 0.58 mmol) and sodium carbonate (5.546 g, 52.35 mmol) in 15 ml H_2O were suspended in 2-propanol (250 ml) and the mixture was stirred under nitrogen at reflux for 7 h. A solution of HCl 2 N was added to the reaction mixture with stirring; the organic layer was washed with water and extracted into ether. The organic phase was washed with brine and water, dried over Na_2SO_4 and concentrated *in vacuo*. The coupling product was purified by column chromatography on silicagel (hexane/ethyl acetate = 6/1, then 4/1 and finally ethyl acetate) to give a pale brown solid; yield 53.8%. ^1H NMR ($CDCl_3$) δ, ppm 0.98 (3H, t, $J=6.95$ Hz, alkyl CH_3), 1.52 (2H, sext., $J=7.32$ Hz, γCH_2), 1.79 (2H, quint., $J=6.59$ Hz, βCH_2), 3.78 (2H, s), 3.77 (2H, s, NH_2), 4.01 (2H, t, $J=6.23$ Hz, OCH_2), 6.98 (2H, d, $J=9.15$ Hz, ArH *para* to NH_2), 7.1 (2H, d, $J=9.88$ Hz ArH *ortho* to OCH_2), 7.5–7.6 (6H, m, ArH). IR (film) ν_{max}/cm^{-1} 712, 818, 962, 1148, 1249, 1376, 1461, 1530, 1583, 1652, 2836, 2868, 2932, 2990, 3336 (NH_2), 3437.

4.2.3. *4″-n-Butyloxy-3,5-difluoroterphenyl-4-isothiocyanate* **57**

A solution of compound **55** (1.47 g; 4.16 mmol) in chloroform (18 ml) was added dropwise at 0–5°C to a stirred, cooled (0°C) mixture of water (8 ml), chloroform (4 ml), calcium carbonate (0.66 g, 6.65 mmol), and thiophosgene (0.638 g, 5.55 mmol). The mixture was heated at reflux for 2 h and poured into water (100 ml). The separated organic layer was quenched with hydrochloric acid (45 ml; 1%) and dried over Na_2SO_4; the solvent was removed *in vacuo*. The crude product was purified by column chromatography (hexane) and recrystallized from hexane to give white crystals; yield 88.3%. ^1H NMR ($CDCl_3$) δ, ppm 0.99 (3H, t, $J=7.2$ Hz alkyl CH_3), 1.5 (2H, sext., $J=6.6$ Hz, γCH_2), 1.77 (2H, quint., $J=6.6$ Hz, βCH_2), 4.02 (2H, t, $J=6.2$ Hz, OCH_2), 6.97 (2H, d, $J=8.79$ Hz, ArH *ortho* to OCH_2), 7.22 (2H, d, $J=9.8$ Hz, ArH *para* to NCS), 7.48–7.7 (4H, m, ArH). IR (film) ν_{max}/cm^{-1} 717, 760, 818, 866, 1031, 1254, 1286, 1371, 1397, 1461, 1547, 1578, 2003 (NCS), 2088 (NCS, shoulder), 2848, 2916, 2948.

4.3. *Olefin-tolanes*

4.3.1. *4-(Bromobenzyl)triphenylphosphonium bromide* ***62*** *[23]*

A mixture of 4-bromobenzyl bromide (24.994 g; 0.1 mol) and triphenylphosphine (26.228 g; 0.1 mol) in DMF (200 ml) was heated at reflux for 2.5 h, then cooled to room temperature and added dropwise to vigorously stirred, cooled (0°C) diethyl ether. The resulting white precipitate was collected by filtration and dried *in vacuo*; yield 94.9%. ^1H NMR ($CDCl_3$) δ, ppm 1.99 (2H, s, $ArCH_2$), 7.1 (2H, d, ArH *ortho* to CH_2), 7.48–7.65 (15H, m, $3C_6H_5$), 7.77 (2H, d, ArH *ortho* to Br). IR (film) ν_{max}/cm^{-1} 690, 720, 750, 840, 988, 1015, 1067, 1120, 1375, 1460, 1583, 2850, 2980.

4.3.2. *1-Bromo-4-(1-butenyl)benzene* ***64***

To a stirred solution of (4-bromobenzyl)triphenylphosphonium bromide (20.488 g, 0.04 mol), and potassium carbonate (5.528 g, 0.04 mol) in dry dichloromethane, 18-crown-6 was added at room temperature. The mixture was heated at reflux for 15 min, then propionaldehyde (2.323 g, 0.04 mol) was added in a dropwise fashion. The reaction mixture was heated at reflux overnight. When cooled, the solution was passed through a small column of silica gel and the solvent evaporated *in vacuo*. The crude product was purified by column chromatography using hexane as eluent to give a slightly yellow liquid; yield 90.1%. ^1H NMR ($CDCl_3$) δ, ppm 1.05 (3H, m, $J=6.96$ Hz, alkyl CH_3), 2.24 (2H, m, $J=6.59$ Hz, CH_2), 5.5–6.4 (2H, m, CH=CH), 7.18 (2H, m, $J=8.1$ Hz, ArH *ortho* to CH=CH), 7.42 (2H, m, $J=8.1$ Hz, ArH *ortho* to Br). IR (film) ν_{max}/cm^{-1} 690, 740, 790, 800, 842, 903, 958, 1012, 1074, 1176, 1313, 1395, 1456, 1476, 1586, 1647 (CH=CH), 1893, 2862, 2931, 2958, 3012.

4.3.3. *4-(3-Methylbut-1-yn-3-ol)-2,6-difluoroaniline* ***66***

4-Bromo-2,6-difluoroaniline (8.21 g, 39.469 mmol) in dry triethylamine was added dropwise to a suspension of 3-methyl-but-1-yn-3-ol (6.64 g, 78.938 mmol), tetrakis-(triphenylphosphine)palladium(0) (1.513 g, 1.31 mmol), and copper(I)iodide (0.249 g, 1.31 mmol) in dry triethylamine (300 ml) at room temperature. The solution was heated under reflux for 4 h; when cooled, it was filtered through celite and the solvent removed *in vacuo*. Dichloromethane was added and the organic layer washed with saturated ammonium chloride solution water, dried over Na_2SO_4 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 white solid; yield 80.7%. ^1H NMR ($CDCl_3$) δ, ppm 1.59 (6H, s, $2CH_3$), 2.05 (1H, s, OH), 3.87 (2H, s, NH_2), 6.9 (2H, dd, $J=9.8$ Hz, ArH ortho to C$\equiv$C). IR (film) ν_{max}/cm^{-1} 718, 786, 848, 940, 978, 1162, 1223, 1258, 1374, 1456, 1518, 1593, 1647, 2221 (w, C$\equiv$C stretch), 2860, 2920, 2980, 3210 (OH), 3368 (NH_2).

4.3.4. *4-Ethyne-2,6-difluoroaniline* **67**

A mixture of compound **66** (6.725 g, 31.87 mmol) and potassium hydroxide (2.68 g, 47.8 mmol) in dry toluene (250 ml) was heated under reflux for 4 h. The acetone and toluene azeotrope was removed periodically using a Dean–Stark device and replaced with an equal volume of toluene. When cooled, the solvent was removed *in vacuo*. Diethyl ether was added and the organic phase washed with water (400 ml), then dried over Na_2SO_4; the solvent was removed *in vacuo*. The crude product was purified by column chromatography (hexane) to give a white solid; yield 55.8%. ^{1}H NMR ($CDCl_3$) δ, ppm 2.98 (1H, s, C$\equiv$CH), 3.91 (2H, s, NH_2), 6.9 (2H, dd, $J=9.88$ Hz, ArH). IR (film) ν_{max}/cm^{-1} 717, 855, 962, 1158, 1320, 1370, 1435, 1457, 1520, 1578, 1642, 1727, 2108 w, C$\equiv$CH stretch), 2853, 2920, 2980, 3280, 3309, 3395, 3474.

4.3.5. *1-(3,5-Difluoro-4-aminophenyl)-2-[4-(1-butenyl)phenyl]ethyne* **69**

4-Bromo-4′-(1-butenyl)benzene (2.76 g, 13.07 mmol) in dry triethylamine (30 ml) was added dropwise to a suspension of 4-ethyne-2,6-difluoroaniline (2 g, 13.07 mmol), tetrakis(triphenylphosphine)palladium(0) (0.5034 g; 0.4356 mmol), and copper(I) iodide (0.0829 g, 0.4356 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 was washed with saturated ammonium chloride solution and water, dried over Na_2SO_4, 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 yellowish solid; yield 57.2%. ^{1}H NMR ($CDCl_3$) δ, ppm 1.075 (3H, m, $J=7.3$ Hz, alkyl CH_3), 2.28 (2H, m, $J=6.59$ Hz, CH_2), 3.8 (2H, s, NH_2), 5.6–6.4 (2H, m, CH=CH), 7.02 (2H, dd, $J=9.1$ Hz, ArH *para* to NH_2), 7.26 (2H, dd, $J=8.9$ Hz, ArH *ortho* to CH=CH), 7.42 (2H, dd, $J=9.2$, ArH *ortho* to C$\equiv$C). IR (film) ν_{max}/cm^{-1} 616, 685, 728, 813, 845, 957, 1153, 1227, 1264, 1360, 1435, 1450, 1520, 1578, 1636, 1902, 2190 (w, C$\equiv$C stretch), 2868, 2938, 3192, 3222, 3325, 3405, 3496.

4.3.6. *1-(3,5-Difluoro-4-isothiocyanatophenyl)-2-[4-(1-butenyl)phenyl]ethyne* **72**

A solution of compound **69** (2.12 g, 7.88 mmol) in chloroform (18 ml) was added dropwise at 0–5°C to a stirred, cooled (0°C) mixture of water (20 ml), chloroform (10 ml), calcium carbonate (2.366 g, 23.64 mmol), and thiophosgene (0.977 g, 23.64 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 Na_2SO_4; 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 85.9%. ^{1}H NMR ($CDCl_3$) δ, ppm 1.08 (3H, m, $J=7.2$ Hz, alkyl CH_3), 2.26 (2H, m, $J=6.9$ Hz, CH_2), 5.65–6.4 (2H, m, CH=CH), 7.14 (2H, dd, $J=9.6$ Hz, ArH *para* to NCS), 7.25–7.48 (4H, m, ArH). IR (film) ν_{max}/cm^{-1} 627, 706, 813, 860, 930, 960, 983, 1042, 1095, 1206, 1376, 1430, 1456, 1509, 1567, 1620, 2029 (s, NCS), 2104 (shoulder), 2204 (C$\equiv$C stretch), 2875, 2930.

5. Conclusions

Three series of isothiocyanato-based liquid crystals have been synthesized, with optical birefringence situated between 0.37 and 0.52. The olefin-tolanes show the highest optical birefringence amongst all the synthesized liquid crystals, because of a lengthened electronic conjugation. The terphenyl compounds display the highest viscosity because of a smaller molecular aspect ratio. Several eutectic mixtures show properties better than those of the single compounds, such as a broad nematic range, low melting temperature and relatively high clearing point. The optical birefringence of these mixtures lies between 0.35 and 0.37.

This work was supported in part by the DARPA STAB Program through Raytheon Lexington Laboratory and NSF ALCOM grants. The authors would like to acknowledge Liou Qiu, Karen Hullihen, Doug Bryant, Ivan Smalyukh and Anatoliy Glushchenko for their assistance in this study.

References

[1] De Gennes, P. G., and Prost, J., 1993, *The Physics of Liquid Crystals*, 2nd Edn, (Oxford: Oxford Science).
[2] Geelhaar, T., 1998, *Liq. Cryst.*, **24,** 91.
[3] Scheffer, T., and Nehring, J., 1995, *Liquid Crystals, Applications and Uses*, Vol. 1, edited by B. Bahadur (World Scientific) p. 231.
[4] Tarumi, K., Bartmann, E., Geelhaar, T., Schuler, B., Ichinose, H., and Numata, H., 1995, *Asia Display '95*, p. 559.
[5] Nakajima, S., Sugiyama, Y., Ichinose, H., Numata, H., and Naemura, S., 2000, *SID'00 Dig.*, p. 242.
[6] Spadlo, A., Darbrowski, R., Filipowicz, M., Stolarz, Z., Przedmojski, J., Gauza, S., Clarie, Y. H. FAN., and Wu, S. T., 2003, *Liq. Cryst.*, **30,** 191.
[7] Gauza, S., Clarie, Y. H., Wu, S. T., Seed, A. J., and Dabrowski, R., 2003, *Jpn. J. appl. Phys.*, **42,** 3463.

[8] Tarumi, K., Heckmeier, M., and Klasen, M., 2001, *SID 2001 Dig.* pp. 950–953.

[9] Ichinose, H., Nakajima, S., Sugiyama, Y., Numata, H., Naemura, S., and Manabe, A., 2000, *IDW'00 Dig.*, p. 77.

[10] Cross, G. J., Seed, A. J., Toyne, K. J., Goodby, J. W., Hird, M., and Artal, M. C., 2000, *J. mater. Chem.*, **10,** 1555.

[11] Seed, A. J., Cross, G. J., Toyne, K. J., and Goodby, J. W., 2003, *Liq. Cryst.*, **30,** 1089.

[12] Gray, G. W., Hird, M., Lacey, D., and Toyne, K. J., 1989, *J. chem. Soc. Perkin Trans. II.*, 2041.

[13] Hird, M., Gray, G. W., and Toyne, K. J., 1991, *Mol. Cryst. liq. Cryst.*, **206,** 187.

[14] Hird, M., Gray, G. W., and Toyne, K. J., 1991, *Mol. Cryst. liq. Cryst.*, **206,** 205.

[15] Gray, G. W., Hird, M., and Toyne, K. J., 1991, *Mol. Cryst. liq. Cryst.*, **204,** 43.

[16] Hird, M., Toyne, K. J., Gray, G. W., Day, S. E., and McDonnell, D. G., 1993, *Liq. Cryst.*, **2,** 123.

[17] Morgan, J., and Pinhey, J. T., 1990, *J. chem. Soc. Perkin Trans I*, 715.

[18] Chaumeil, H., Signorella, S., and Le Drian, C., 2000, *Tetrahedron*, **56,** 9655.

[19] Albrecht, M., and Schneider, M., 2000, *Synthesis*, **11,** 1557.

[20] Rajca, A., Wang, H., Bolshov, P., and Rajca, S., 2001, *Tetrahedron*, **57,** 3725.

[21] Collins, S. K., Yap, G. P. A., and Fallis, A. G., 2000, *Angew. Chem. int. Ed.*, **39,** 385.

[22] Mellisaris, A. P., and Litt, M. H., 1994, *J. org. Chem.*, **59,** 5818.

[23] Wu, S. T., and Neubert, M. E., 2001, US Patent 6 312 618 B1.

[24] Adamski, P., 1989, *Mol. Cryst. liq. Cryst.*, **177,** 1.