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Synthesis, mesomorphic and optical properties of isothiocyanatotolanes

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The synthesis, mesomorphic properties and UV absorption spectra of laterally fluorine substituted, and the corresponding unsubstituted, 4′-alkyl-, 4′-alkoxy-, 4′-alkylcyclohexyl-, 4′-alkylbicyclo[2,2,2]octyl- and 4′-alkylcyclohexylethyl-4-isothiocyanatotolanes are described. Multicomponent broad range nematic mixtures with birefringence values higher than 0.4 and moderate viscosities are developed.

1. Introduction

Polar nematic liquid crystal (LC) mixtures having high birefringence (Δn), low viscosity, and good photochemical stability are needed urgently for display, telecom light switching and laser beam steering applications [1, 2]. To achieve high values of Δn, linear conjugated molecules are the preferred candidates [3]. From a knowledge of structure–property relationships, it is quite unlikely simultaneously to achieve high values of Δn while maintaining low viscosity. Increasing birefringence is normally associated with an increased viscosity. However, a linear molecular structure is still a favoured choice from the viewpoint of obtaining a low viscosity [4]. As the conjugation length increases, the ultraviolet and thermal stability gradually decreases. A 'best' molecular structure will be found for these applications but there is no certainty that it will satisfy all the stated requirements.

Tolane-based liquid crystals exhibit reasonably high Δn, low viscosity, and good chemical, photo and thermal stability [4]. The same properties are also found for isothiocyanates [5]. Therefore, coupling the tolane and NCS groups could lead to high optical and large dielectric anisotropies while preserving a relatively low viscosity. To investigate this possibility, Seed et al. have prepared the 4′-alkylsulphanyl-4-isothiocyanatotolanes and their analogues containing a naphthalene ring [6–8]. These compounds indeed have impressive birefringences ($\Delta n = 0.5$ and 0.55). Unfortunately, the first series are

smectics and not suitable for nematic mixtures. Although the naphthalene series are nematics, their viscosities are relatively high.

In this paper, we report the synthesis procedures and physical properties of the compounds:
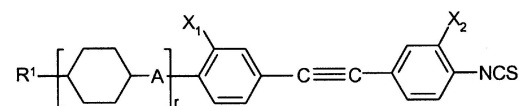
where, $r = 0$ or 1, A is a single bond or $-CH_2CH_2-$, and R^1 is an alkyl (C_nH_{2n+1}) or alkoxy group ($C_nH_{2n+1}O$). Recently, we presented preliminary results for a few of these compounds with $X_1 = X_2 = H$ (series **I**) and found that most of them exhibit the crystal E phase [9]. In order to convert smectic to nematic behaviour while preserving high birefringence values, we have added lateral fluoro-substituents: $X_1 = F$ and $X_2 = H$ (series **II**) and $X_1 = H$ and $X_2 = F$ (series **III**).

2. Synthesis

Members of series **II** and series **I** were prepared using the route shown in scheme 1. This procedure is similar to the one recently elaborated by us for the unsubstituted compounds **I** and described elsewhere [9]. The synthetic route used to obtain series **III** is shown in scheme 2. Both routes are described in the experimental section.

3. Mesomorphic properties

The phase transition temperatures and associated enthalpy changes of compounds **I.7**, **II.7** and **III.7** are listed in tables 1 and 2, respectively. Tables 3 and 4
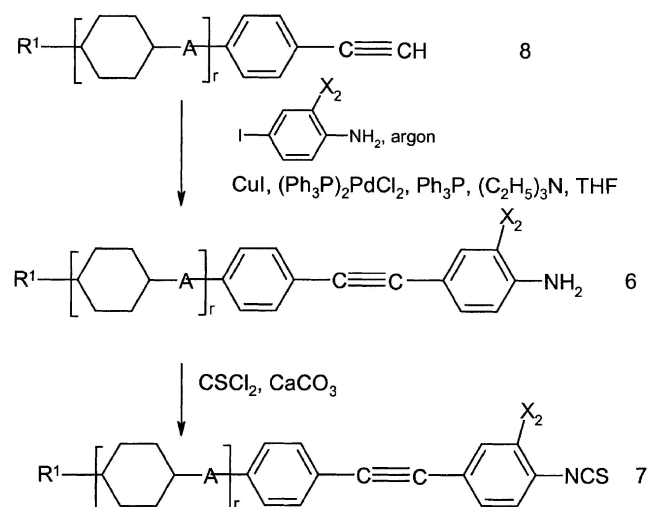
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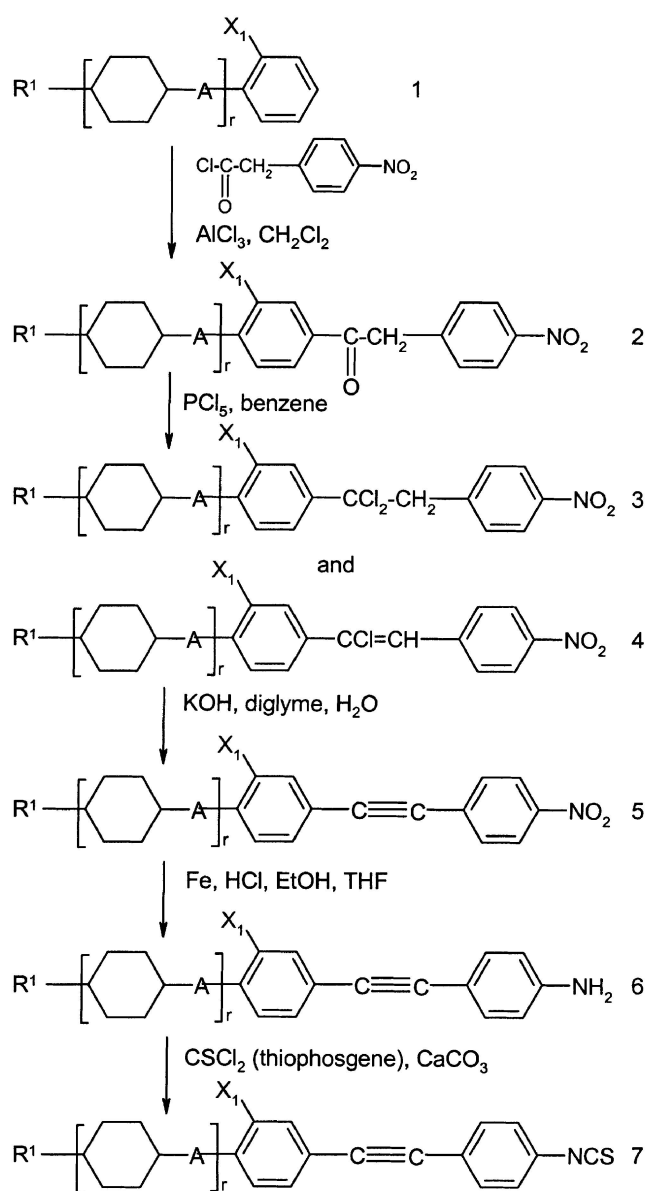
Scheme 1. Synthetic route for isothiocyanatotolanes; series **I** ($X_1 = H$) and series **II** ($X_1 = F$); $r = 0$ or 1, $A = a$ single bond or $-CH_2CH_2-$, $R^1 = $ alkyl (C_nH_{2n+1}) or alkyloxy ($C_nH_{2n+1}O$).

Scheme 2. Synthetic route for isothiocyanatotolanes; series **III** ($X_2 = F$); $r = 0$ or 1; $A = a$ single bond; $R^1 = $ alkyl (C_nH_{2n+1}) or alkyloxy ($C_nH_{2n+1}O$).

same was observed for the 4′-alkyl-4-isothiocyanato-tolanes (**nBT**) [10] for which only the crystal E phase was seen. Compound **I.7c** shows excellent reversibility of the phase transitions during heating and cooling cycles, see DSC traces shown in figure 1 (*a*), which con-firms the smectic-like character of both the observed phases. The crystal E phase assignment, was confirmed by miscibility studies with **4BT** and by the observation
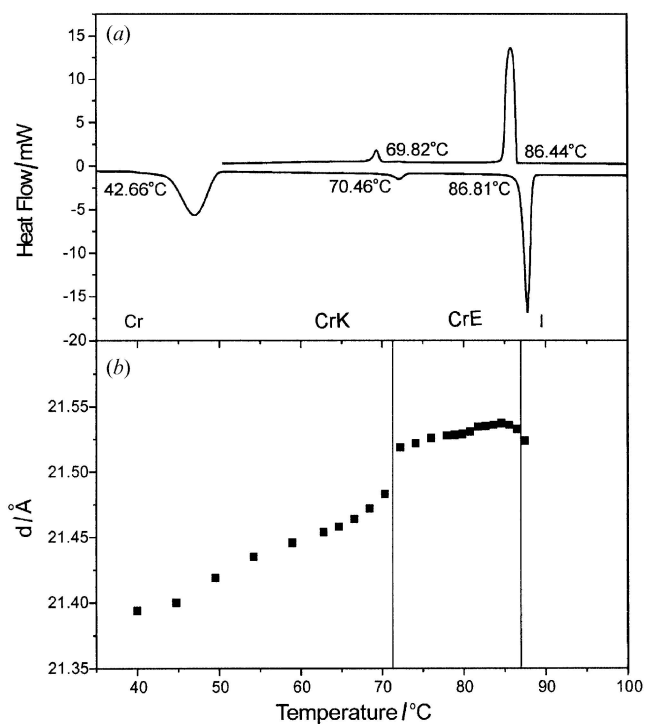
Figure 1. (*a*) The DSC trace of **I.7c**, and (*b*) the temperature dependence of the layer spacing *d*.

summarize the corresponding data for the intermediate nitroketones (**II.2**) and nitrotolanes (**II.5**). The phases were identified from their textures observed using polar-izing optical microscopy (POM) and by miscibility with standard compounds.

Two-ring 4′-alkyl-4-isothiocyanatotolanes exhibit only two crystal-like smectic phases (the members containing ethyl to pentyl chains were investigated). The phases are monotropic for the ethyl, propyl, and pentyl members and enantiotropic for the butyl homologue. Compound **I.7c** has the lowest melting point in the **I.7** series. The

Table 1. Phase transition temperatures (onset temperature, upper line) (°C) and associated enthalpy changes (kcal mol^{-1}) (lower line) for two-ring ($r = 0$) isothiocyanatotolanes, **I** ($X_1 = X_2 = $ H), **II** ($X_1 = $ F, $X_2 = $ H) and **III** ($X_1 = $ H, $X_2 = $ F), obtained from DSC measurements. () = monotropic transition.
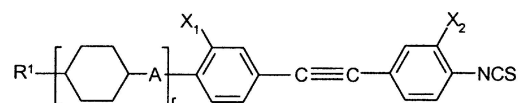
| Compound	R^1	X_1	X_2	Cr		CrK		CrE		N		I
I.7a	C_2H_5	H	H	•	88.1^a; 94.4	(•	85.8)	(•	90.5)	—		•
					2.95; 4.85		0.42		4.12			
III.7a	C_2H_5	H	F	•	71.3	—		—		—		•
					6.3							
I.7b	C_3H_7	H	H	•	96.6	(•	78.2)	(•	90.6)	—		•
					4.70		0.58		4.3			
I.7c	C_4H_9	H	H	•	44.0	•	70.5	•	86.9	—		•
					3.8		0.2		3.20			
III.7c	C_4H_9	H	F	•	38.4; 40.5	—		—		—		•
					2.91; 2.88							
I.7d	C_5H_{11}	H	H	•	90.5	—		(•	84.0)	—		•
					6.49				3.36			
II.7e	CH_3O	F	H	•	155.5	—		—		—		•
					8.82							
I.7f	C_2H_5O	H	H	•	90.0; 127.3	—		—		—		•
					3.10; 5.71							
II.7f	C_2H_5O	F	H	•	65.4; 96.1	—		—		(•	71.1)	•
					0.64; 6.78						0.14	
III.7f	C_2H_5O	H	F	•	103.2	—		—		(•	93.6)	•
					7.39						0.13	
I.7g	C_3H_7O	H	H	•	125.3	—		—		—		•
					5.67							
II.7g	C_3H_7O	F	H	•	73.5	—		—		(•	56.0)	•
					6.30						0.075	
I.7h	C_4H_9O	H	H	•	112.7	—		(•	112.0)	•	116.0	•
					5.36				3.16		0.19	
II.7h	C_4H_9O	F	H	•	64.2	—		—		•	71.6	•
					5.72						0.13	
III.7h	C_4H_9O	H	F	•	96.7	—		—		(•	89.9)	•
					8.53						0.15	
I.7i	$C_5H_{11}O$	H	H	•	69.6	—		•	112.8	—		•
					5.83				3.30			
II.7i	$C_5H_{11}O$	F	H	•	61.1	—		—		•	65.4	•
					7.25						0.83	
I.7j	$C_6H_{13}O$	H	H	•	58.4	—		•	112.7	•	113.6	•
					6.28				3.10		0.28	
II.7j	$C_6H_{13}O$	F	H	•	49.7	—		—		•	71.7	•
					7.05						0.115	
I.7k	$C_7H_{15}O$	H	H	•	60.3	—		•	111.6	—	112.9^b	•
					7.06				0.37		2.87	

^{a} Transition in solid state. ^{b} SmB.

of characteristic microscopic patterns. The phase transition from the crystal E phase to the lower temperature phase is very difficult to observe using POM. Only a small change in the colour of the texture was observed, but the transition was clearly seen in the DSC trace. The phase transition is first order in nature with an enthalpy change of 0.2 kcal mol^{-1}. X-ray investigations of the temperature dependence of the layer spacing,

figure 1(*b*), show that it does not change with temperature in the orthogonal CrE phase ($d = 21.53$ Å, $d/l = 0.87$). For the lower temperature phase, d decreases slowly with temperature. This suggests that the phase may be a tilted crystal K phase, with the cell parameters $a = 5.26$ Å, $b = 8.04$ Å, and $c = 23.8$ Å. More detailed studies are in progress to exclude, or otherwise, the possibility that the phase is in fact the crystal H phase.

Table 2. Phase transition temperatures (onset temperature, upper line) (°C) and associated enthalpy changes (kcal mol^{-1}) (lower line) of three-ring ($r = 1$) isothiocyanatotolanes **I** ($X_2 = $ H) and **III** ($X_2 = $ F) obtained from DSC measurements.

$$R^1 \text{---} \left[\bigcirc \text{---} A \right]_r \text{---} \bigcirc \text{---} C{\equiv}C \text{---} \bigcirc^{X_2} \text{---} NCS$$
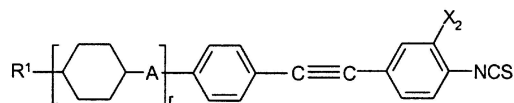
Compound	R^1	X_1	X_2	A	Cr			SmA		N		I
I.7l	C_2H_5	H	H	single bond	•	140.2 *6.14*		—		•	243.0 *0.20*	•
I.7m	C_3H_7	H	H	single bond	•	137.2 *6.34*		—		•	265.4 *0.36*	•
I.7n	C_4H_9	H	H	single bond	•	76.2; 106.9 *1.12; 5.03*		•	139.9 *0.14*	•	257.4 *0.26*	•
III.7n	C_4H_9	H	F	single bond	•	77.1 *4.96*		—		•	238.9 *0.29*	•
I.7o	C_5H_{11}	H	H	single bond	•	119.5 *6.42*		•	147.6 *0.15*	•	254.9 *0.25*	•
III.7o	C_5H_{11}	H	F	single bond	•	63.0; 85.2 *0.91; 4.52*		•	112.6 *0.00*	•	243.2 *0.29*	•
III.7oB[b]	C_5H_{11}	H	F	single bond	•	151 *5.78*		•		•	284.8 *0.28*	•
I.7p	C_3H_7	H	H	$-CH_2CH_2-$	•	130.0 *6.22*		—		•	211.4 *0.64*	•
I.7r	C_4H_9	H	H	$-CH_2CH_2-$	•	70.4; 102.3 *4.16; 5.49*		(•	99.3) *0.025*	•	207.0 *0.52*	•
I.7s	C_5H_{11}	H	H	$-CH_2CH_2-$	•	114.1 *6.58*		(•	100.5) *0.000*	•	207.0 *0.70*	•

[b] Bicyclo[2,2,2]octane ring instead of cyclohexane ring.

Exchanging the alkyl chain for an alkoxy one increases the melting points for members with short alkoxy chains (ethoxy and propoxy, compounds **I.7f** and **I.7g**). Here the smectic-like phases are not observed.

The crystal E phase was found for the butoxy to heptoxy homologues (compounds **I.7h**–**k**). The thermal stability of the CrE phase is up to 111.6°C. The nematic phase was also observed over very short temperature ranges for the butoxy and hexyloxy members (total number of atoms is odd). The heptoxy derivative (**I.7k**) has also a crystal B phase seen over a short temperature range.

The introduction of a fluorine atom in the *ortho*-position (3′) to the alkoxy group or to the isothiocyanato group (3) extinguishes the smectic-like behaviour and only a nematic phase with a moderately high clearing point is observed. The nematic phase is monotropic for the short chain homologues (ethoxy, propoxy) and enantiotropic for the higher members. Compounds of series **II** have lower melting points, smaller melting enthalpies and lower clearing points than members of series **III**, cf. **II.7f** and **III.7.f**, or **I.7h** and **III.7h** in table 1.

The introduction of a fluorine atom in the neighbourhood of the terminal NCS group in the case of three-ring tolanes decreases the stability of all the phases, but of the smectic A phase a little more effectively than of

the nematic phase. The smectic A phase appears in the higher members (from pentyl, **III.7o**, instead of butyl, **I.7n**). The enthalpy of the smectic–nematic transition is also smaller, see table 2.

The compounds containing the $-CH_2CH_2-$ link between the cyclohexane ring and the tolane unit show lower thermal stabilities for the smectic A and nematic phases in comparison with those of the compounds containing the cyclohexane ring linked directly; compare **I.7m, n, o** with **I.7p, r, s**. This is typical behaviour and is observed also for structures with other terminal groups.

The intermediate nitroketones of series **I.2** and **II.2** are not liquid crystalline in the case of two-ring and three-ring compounds, see table 3. Also, the two ring nitrotolanes, series **I.5**, are not mesomorphic except for the heptyloxy derivative (**I.5k**), see table 4. All the three-ring nitrotolanes, compounds **I.5l, m, n, o, p, r** show nematic phases over a broad temperature range. Their melting points are higher than those of the analogous isothiocyanates except for the compounds with $-CH_2CH_2-$ link (**I.5p, r**).

4. Electronic absorption spectra

The UV absorption spectra of compounds **I.7h, II.7h** and **III.7h** are compared in figure 2. The compounds

Table 3. Melting points (onset temperatures, upper line) (°C) and enthalpy changes (kcal mol^{-1}) (lower line) of the nitroketones **I** (X_1 = H) and **II**; (X_1 = F).

$$R^1 -\!\!\left[\text{cyclohexyl}-A\right]_r\!\!-\overset{X_1}{\text{benzene}}-COCH_2-\text{benzene}-NO_2$$
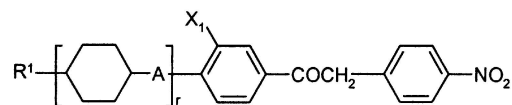
Compound	R^1	r	X_1	A	Cr		I
I.2a	C_2H_5	0	H	—	•	112.2	•
						6.1	
I.2d	C_5H_{11}	0	H	—	•	90.0	•
						7.04	
II.2e	CH_3O	0	F	—	•	139.7	•
						8.42	
I.2f	C_2H_5O	0	H	—	•	117.1	•
						6.74	
II.2f	C_2H_5O	0	F	—	•	117.9	•
						6.80	
I.2g	C_3H_7O	0	H	—	•	99.2	•
						7.65	
II.2g	C_3H_7O	0	F	—	•	95.7	•
						7.80	
I.2h	C_4H_9O	0	H	—	•	62.9	•
						5.96	
II.2h	C_4H_9O	0	F	—	•	78.1; 87.5	•
						4.28; 5.0	
I.2i	$C_5H_{11}O$	0	H	—	•	80.2	•
						6.47	
II.2i	$C_5H_{11}O$	0	F	—	•	71.5	•
						8.2	
I.2j	$C_6H_{13}O$	0	H	—	•	77.6	•
						7.0	
II.2j	$C_6H_{13}O$	0	F	—	•	76.8	•
						7.26	
I.2k	$C_7H_{15}O$	0	H	—	•	71.7; 74.4	•
						3.0; 6.55	
I.2l	C_2H_5	1	H	single bond	•	171.9	•
						8.92	
I.2m	C_3H_7	1	H	single bond	•	163.3	•
						9.29	
I.2n	C_4H_9	1	H	single bond	•	153.7	•
						8.70	
I.2o	C_5H_{11}	1	H	single bond	•	142.7	•
						8.24	
I.2p	C_3H_7	1	H	$-CH_2CH_2-$	•	146.9	•
						8.50	
I.2r	C_4H_9	1	H	$-CH_2CH_2-$	•	135.4	•
						8.58	
I.2s	C_5H_{11}	1	H	$-CH_2CH_2-$	•	135.9	•
						9.07	

absorb in the range 270–340 nm and two distinct maxima are seen. Such spectra are characteristic of compounds containing a triple bond, for which a vibrating structure in the spectrum is seen. For the unsubstituted tolane, **I.7h**, the absorption maxima are observed at 317 and 338 nm. The substitution of the benzene ring by a fluorine atom in the 3 position (in the neighbourhood of the NCS group) causes a slight red shift to 320 and 340 nm, while in the 3′ position (near to the alkoxy group) involves a blue shift to 315 and 335 nm, respectively. A steric interaction involving the fluorine atom with the non-bonding electron pair of oxygen in the alkoxy group probably disturbs its conjugation with the π-electrons of the tolane unit, while such an interaction did not occur with the NCS group, because the fluorine atom and the isothiocyanato group have the same electron-withdrawing character. Similar differences are seen for infrared bands (COC bond).

Table 4. Phase transition temperatures (onset temperatures, upper line) (°C) and enthalpy changes (kcal mol^{-1}) (lower line) of the nitrotolanes **I** ($X_1 =$ H) and **II**; ($X_1 =$ F). () = monotropic transition.

R^1—[cyclohexyl—A]$_r$—(benzene with X$_1$)—C≡C—(benzene)—NO$_2$
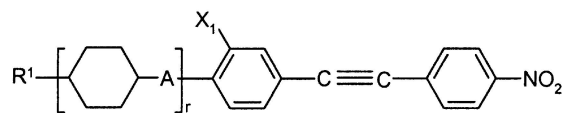
Compound	R^1	r	X_1	A	Cr		N		I
I.5a	C_2H_5	0	H	—	•	116.3	—		•
						6.16			
I.5b	C_3H_7	0	H	—	•	78.1	—		•
						5.57			
I.5c	C_4H_9	0	H	—	•	68.9	—		•
						4.4			
I.5d	C_5H_{11}	0	H	—	•	69.5	—		•
						5.1			
II.5e	CH_3O	0	F	—	•	127.4	—		•
						7.49			
I.5f	C_2H_5O	0	H	—	•	113.5	—		•
						6.10			
I.5g	C_3H_7O	0	H	—	•	103.9	—		•
						7.51			
II.5g	C_3H_7O	0	F	—	•	99.2	—		•
						7.04			
I.5h	C_4H_9O	0	H	—	•	101.5	—		•
						5.22			
II.5h	C_4H_9O	0	F	—	•	82.6	—		•
						6.78			
I.5i	$C_5H_{11}O$	0	H	—	•	86.7	—		•
						8.02			
II.5i	$C_5H_{11}O$	0	F	—	•	60.6	—		•
						6.35			
I.5j	$C_6H_{13}O$	0	H	—	•	89.1	—		•
						7.82			
II.5j	$C_6H_{13}O$	0	F	—	•	58.3	—		•
						6.62			
I.5k	$C_7H_{15}O$	0	H	—	•	73.6	(•	69.6)	•
						8.78		0.08	
I.5l	C_2H_5	1	H	single bond	•	163.9	•	210.0	•
						6.13		0.14	
I.5m	C_3H_7	1	H	single bond	•	164.2	•	231.8	•
						6.71		0.22	
I.5n	C_4H_9	1	H	single bond	•	136.2	•	224.7	•
						5.66		0.21	
I.5o	C_5H_{11}	1	H	single bond	•	135.1	•	224.3	•
						6.51		0.21	
I.5p	C_4H_9	1	H	$-CH_2CH_2-$	•	102.9	•	182.7	•
						5.25		0.52	
I.5r	C_5H_{11}	1	H	$-CH_2CH_2-$	•	119.3	•	183.1	•
						6.05		0.50	

5. Physical properties of multicomponent mixtures

Two eutectic mixtures, A and B, were calculated and prepared from the compounds listed in tables 1 and 2 and **5CHBT**, 4-(*trans*-4-pentylcyclohexyl)isothiocyanatobenzene. These are nematic over a broad temperature range. Their physical properties and compositions are given in table 5.

6. Experimental

The structures of the intermediates and final products were confirmed by mass spectrometry (Hewlett Packard MSD HP5972), infrared spectrometry (FTIR Biorad FTS-175C) and UV-Vis spectrometry (Carry 3E UV-Vis spectrophotometer). Transition temperatures were measured using DSC (Setaram141) and a polarizing
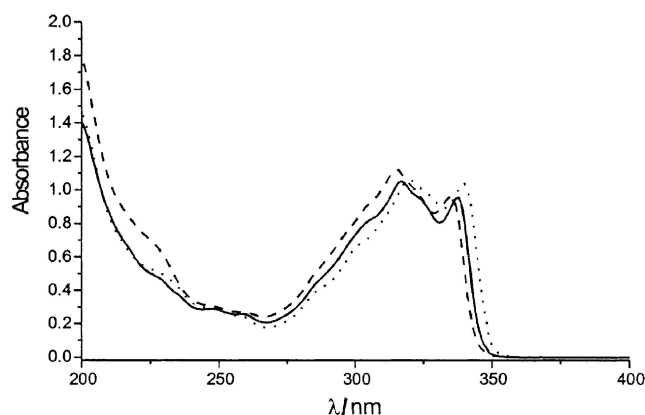
Figure 2. Absorption spectra of compounds **I.7h** -, **II.7h** --, **III.7** …. Each compound was dissolved in hexane to give a solution of concentration 2×10^{-4} M; $T \sim 22°C$ and quartz cell length ~ 1 cm.

Table 5. Physical properties of multicomponent mixtures.

Mixture components, wt %	A	B
II.7f	5.57	4.95
II.7h	22.98	20.53
II.7i	17.64	15.76
III.7f	4.30	3.84
III.7h	3.56	3.18
III.7n	24.43	21.86
III.7o	21.52	19.23
5CHBT	—	10.64
Parameter		
Nematic range/°C	0–152	(−5)–141
Viscosity at 20°C, v/mm^2 s^{-1}		48.5
at 0°C, v/mm^2 s^{-1}		235.5
Birefringence*, Δn	0.4492	0.3988
Threshold voltage, V_{10}/V	2.16	2.09
k_{33}/k_{11}[a]	1.64	1.61
$\varepsilon_\perp$[a]	15.4	15.1
$\varepsilon_\parallel$[a]	4.8	4.6

[a] All measured at 23.3°C.

optical microscope (Biolar-PZO) linked to a Linkam THMS-600 heating stage. The dielectric and elastic constants and threshold voltages were measured using a computer controlled APT III instrument (Displaytech).

The preparative procedures are given for compounds **II.7h** and **III.7h** as representative examples; all other compounds were similarly obtained.

6.1. *4-Nitrobenzyl 4-butoxy-3-fluorophenyl ketone **II.2h***

To a mixture of AlCl$_3$ (42 g, 0.31 mol) and CH$_2$Cl$_2$ (700 ml) a solution of 4-nitrophenylacetic acid chloride (49.9 g, 0.25 mol) was added dropwise and then 4-butyloxy-3-fluorobenzene (42 g, 0.25 mol) was added similarly at 0–5°C. The mixture was stirred at this temperature for 4 h and poured into ice-water. The organic layer

was separated, washed three times with water and dried over anhydrous magnesium sulphate. The solution was filtered and the solvent evaporated. The residual solid was crystallized from methanol (300 ml) and acetone (100 ml) mixture; yield 76 g (91%), yellow crystals, purity 99.4% (GCh), m.p. 87.5°C. MS m/z 331 (very weak M$^+$), 195, 139 (strongest), 111, 83, 57, 41, 29. IR v_{max} (CCl$_4$)/cm^{-1}: 1282 (COC), 1683 and 1691 (CO).

6.2. *4′-Butoxy-3′-fluoro-4-nitrotolane **II.5h***

A mixture of compound **II.2h** (74 g, 0.22 mol), PCl$_5$ (59 g, 0.28 mol) and benzene (600 ml) was heated at reflux for 8 h. It was then poured onto ice-water and the organic layer was separated, washed three times with water and dried over anhydrous MgSO$_4$. The solution was filtered and the solvent evaporated. The yellow solid residue was dissolved in diglyme (250 cm^3) and KOH solution was added (74 g, 1.32 mol, dissolved in 150 ml of water). The mixture was heated at reflux (105°C) for 8 h and then diluted with water (1000 ml). The precipitated solid was filtered off and washed with water; yield 48 g (70%), purity 99.2% (GCh), m.p. 82.6°C. MS m/z 331 (M$^+$) 257, 227, 181, 163, 87, 57, 29. IR v_{max} (CCl$_4$)/cm^{-1}: 1271 (COC), 1344 and 1523 (NO$_2$ sym and asym), 2214 (triple bond).

6.3. *4′-Butoxy-3′-fluoro-4-isothiocyanatotolane **II.7h***

A mixture of compound **II.5h** (48 g, 0.15 mol), iron dust (42 g, 0.75 mol), ethanol (220 ml), H$_2$O (90 ml), THF (550 ml) and concentrated hydrochloride acid (4 ml, 0.11 mol) was heated at reflux for 6 h. The mixture was then cooled and filtered, and the solvents were evaporated. Next 200 ml of 1,2-dichloroethane was added to the solid residue and was then distilled off to remove completely traces of ethanol that would affect the next reaction. The crude amine **II.6h** was dissolved in chloroform (200 ml) and the solution was added slowly to a mixture of chloroform (100 ml), water (100 ml), CaCO$_3$ (30 g, 0.3 mol) and thiophosgene (13 ml, 0.16 mol), while cooling to 0–3°C. The mixture was then stirred for 8 h at room temperature and the organic layer separated. The solvent was evaporated and the solid residue crystallized from acetone. A yellow product was obtained; yield 35 g (71%). To remove the colour the product was dissolved in hexane (700 ml) and the solution eluted through a column filled with silica gel. The colourless hexane solution was evaporated and the solid residue crystallized from acetone (500 ml), three times. White crystals were obtained; yield 25 g (51%), purity 99.7% (GCh), phase transitions: Cr 64.2 N 71.6 I (°C). MS m/z 325 (M$^+$ strong), 269 (strongest), 237, 181, 157, 137, 57, 41, 29. IR v_{max} (CCl$_4$)/cm^{-1}: 1269 (COC), 2044 (NCS, very strong), 2190 (triple bond).

6.4. 4′-Butoxy-3-fluoro-4-aminotolane III.6h

To a mixture of 2-fluoro-4-iodoaniline (29 g, 0.1 mol), triethylamine (21.2 g, 0.21 mol), THF (500 ml), $(Ph_3P)_2PdCl_2$ (0.2 g, 0.0003 mol), $(Ph)_3P$ (0.2 g, 0.0008 mol) and CuI (0.1 g, 0.0003 mol) a solution of 4-butoxyphenyl-acetylene (25 g, 0.14 mol in 100 ml THF) was slowly added over 6 h at room temperature under argon. The mixture was stirred for 5 days and poured into water (1000 ml). The product was extracted with ethyl acetate, the extract washed with water, dried over $MgSO_4$ and the solvent evaporated. The yields of the crude amine III.6h was 39 g; after crystallization from hexane (300 ml) the yield was 29 g (70%), purity 94% (GCh). MS m/z 283 (strong M^+), 227 (strongest), 170, 151, 125, 105, 86, 57, 41, 29.

6.5. 4′-Butoxy-3-fluoro-4-isothiocyanatotolane III.7h

A solution of the prepared amine III.6h (28 g, 0.1 mol in 150 ml $CHCl_3$), was added dropwise to a stirred mixture of $CHCl_3$ (100 ml), water (100 ml), $CaCO_3$ (20 g, 0.2 mol) and thiophosgene (9 ml, 0.11 mol) at 0–3°C. The mixture was stirred for 8 h at room temperature; it was then filtered and the organic layer separated and dried over $MgSO_4$. The solvent was evaporated and solid residue crystallized from acetone (200 ml); yield 25 g (77%), yellow crystals. This product was dissolved in hexane at 60°C and eluted at 60°C on a chromatographic column filled with silica gel. The colourless hexane eluent was concentrated to dryness and the solid crystallized from acetone (200 ml); final yield 18.8 g (58%), purity 99.9% (GCh). Phase transition: Cr 96.7 (N 89.9) I (°C). MS m/z 325 (strong M^+), 269 (strongest), 237, 181, 155, 126, 57, 41, 29. IR v_{max} $(CCl_4)/cm^{-1}$: 1249 (COC), 2024 (NCS, very strong), 2209 (triple bond).

7. Conclusion

Two-ring 4′-alkoxy-4-isothiocyanatotolanes laterally substituted by a single fluorine atom in either the 3 or 3′ position exhibit only a nematic phase with clearing temperature between 60 and 90°C, while the unsubstituted corresponding compounds show smectic-like crystal phases. The placement of the fluorine atom in the neighbourhood of the alkoxy group gives compounds with lower melting enthalpies than the compounds with the fluorine atom located in the neighbourhood of the NCS group. Therefore these are better components to use in multicomponent eutectic mixtures although they have lower clearing points. Three-ring 4′-alkylcyclohexyl-4-isothiocyanatotolanes, laterally substituted as well as unsubstituted, exhibit nematic behaviour over a broad temperature range (clearing points up to 260°C). There are members in this family with low melting points and small heats of fusion. They mixed well with the two-ring tolanes resulting in eutectic mixtures with clearing points as high as 150°C, optical anisotropies approaching 0.5 and modest viscosities at room temperature.

References

[1] Wu, S. T., and Yang, D. K., 2001, *Reflective Liquid Crystal Displays* (Wiley-SID).
[2] McManamon, P. F., *et al.,* 1996, *Proc. IEEE*, **84,** 268.
[3] Wu, S. T., 1986, *Phys. Rev. A*, **33,** 1270.
[4] Khoo, I. C., and Wu, S. T., 1993, *Optics and Nonlinear Optics of Liquid Crystals* (Singapore: World Scientific), Chap. 1.
[5] Dąbrowski, R., 1990, *Mol. Cryst. liq. Cryst.*, **191,** 17.
[6] Cross, G. J., Seed, A. J., Toyne, K. J., Goodby, J. W., Hird, M., and Artal, M. C., 2000, *J. mater. Chem.*, **10,** 1555.
[7] Seed, A. J., Toyne, K. J., Goodby, J. W., and McDonnell, D. G., 1995, *J. mater. Chem.*, **5,** 1.
[8] Seed, A. J., Toyne, K. J., Goodby, J. W., and Hird, M., 2000, *J. mater. Chem.*, **10,** 2069.
[9] Spadło, A., Dziaduszek, J., Dąbrowski, R., Czupryński, K., and Wu, S. T., 2002, *SPIE*, **4759** (in press).
[10] Urban, S., Czupryński, K., Dąbrowski, R., Gestblom, B., Janik, J., Kresse, H., and Schmalfuss, H., 2001, *Liq. Cryst.*, **28,** 691.