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Synthesis and mesogenic properties of three- and four-ring compounds with a fluoroisothiocyanatobiphenyl moiety

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The syntheses and mesomorphic properties of 4-alkylcyclohexyl- and 4-alkylcyclohexylethyl and 4-alkylbicyclohexyl-3-fluoro- and 3,5-difluorobiphenyl-4-isothiocyanates are described. The compounds are low melting, very broad range nematic liquid crystals and are very useful for the formulation of nematic mixtures of low viscosity and with a moderately high birefringence (0.3–0.35). The refractive indices, bulk viscosity and dielectric anisotropy extrapolated from Demus' ester mixture for the prepared compounds are presented.

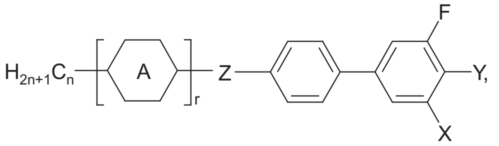
Keywords: nematic isothiocyanates; syntheses; phase transitions; bulk viscosity; refractive indices; dielectric anisotropy; nematic mixtures

1. Introduction

Fluorosubstituted biphenyl, terphenyl, tolane and phenyl tolane isothiocyanates are very useful liquid crystalline compounds because of their high birefringence [1–6]. In the case of fluorosubstituted isothiocyanates, placing fluorine atoms, especially in the vicinity of terminal isothiocyanato (NCS) group is an excellent way to cancel or diminish the strong smectic tendency observed for isothiocyanates with an unsubstituted aromatic rigid core [7]. Due to their high polarity and low viscosity, isothiocyanates can be very useful components of liquid crystalline mixtures for various applications. However, a wider variety of nematic isothiocyanates is needed to adjust and modify the properties of the high birefringence liquid crystalline mixture in the broader range of different parameters such as viscosity, refractive indices, elastic constants and dielectric constants.

Among known isothiocyanates, alkylbicyclohexylbenzene isothiocyanates exhibit a very broad range nematic phase [8, 9]. Their birefringence is too low to obtain a high enough value of the Figure of Merit, $\frac{\Delta n^2 \cdot k_{ii}}{\gamma_1}$ – critical for thin and fast operating displays and other electro-optical devices [5]. Alkylcyclohexylbiphenyl isothiocyanates seem more preferable in this respect due to their higher birefringence. The unsubstituted compounds of this series, which have been prepared in the past with exception of compounds with a Z = CH_2CH_2 bridge, have a high melting point and melting enthalpy. Moreover, the presence of a broad temperature range of smectic phases [10] in their mesomorphism excludes these components in practice from a mixture formulation standpoint.

Presented in this article are studies of the influence of structural transformations of compounds of general formula:



(I)

where Y = NCS, A = cyclohexane or benzene ring, Z = single bond or CH_2CH_2 bridge, r = 1 or 2, X = H or F, n = 2–5 (compounds I.1) on their mesogenic properties. These compounds are compared with benzene analogues (A = benzene) or with analogues where Y = H (compound I.2), Y = F (compound I.3) and Y = CN (compound I.4). The properties of three- and four-ring compounds of the general structure I.3 with X = F have been already documented [11].

The aim of this work was to:

- enhance understanding of the correlations between molecular units comprising the liquid crystalline molecules with NCS terminal group necessary for them to show strong nematic character;
- select low melting and high clearing components suitable for the formulation of mixtures with a low viscosity and high birefringence.

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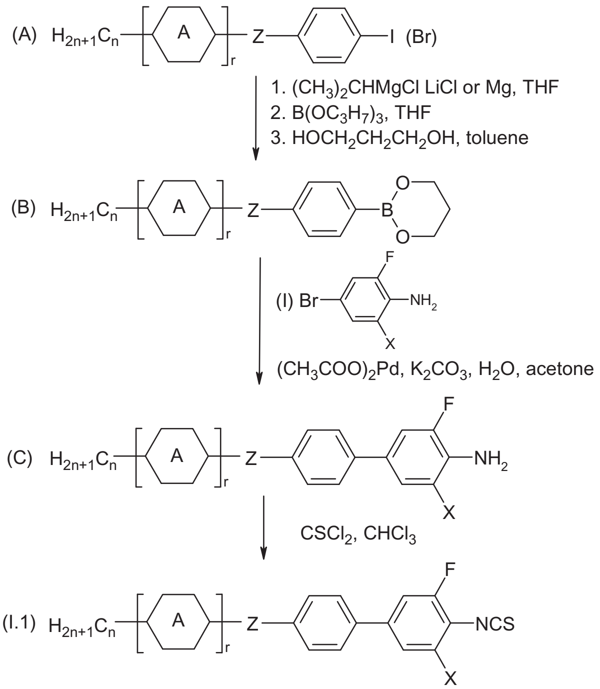
2. Syntheses

The developed method of the synthesis of alkylcyclohexylbiphenyl isothiocyanates is shown in Scheme 1. Iododerivatives A were prepared from either amines [12] being also intermediates for alkylcyclohexylbenzene isothiocyanates and alkylcyclohexylethylbenzene isothiocyanates [8, 13], or by direct iodination of hydrocarbons [14]. They were subsequently transformed to halogenomagnesium derivatives via Krasovskiy's transmetalation method [15]. Given the relatively easy preparation by acylation with bromophenylacetic acid chloride followed by hydrogenation in the case of compounds where A is a benzene ring and Z = CH_2CH_2, a substituted bromobenzene was starting intermediate A. The Grignard's reagent being intermediate for B was prepared directly by treating a bromoderivative with magnesium foil scraps.

The magnesium intermediate obtained in the first step was treated with tri-isopropyl borate giving, after acidification, a derivative of boronic acid. The boronic acid was rather difficult to separate and purify. We found that transforming it to the cyclic ester of boronic acid (compound B) by treating it with 1,3-propanediol was a more efficient route. Such esters easily crystallise from a non-polar solvent like hexane. Compound B was coupled with a bromo- or iodofluoroaniline. Although commercially available, these amines are relatively expensive and so we proposed a simple way to prepare them. 2,6-Difluoroaniline treated with bromine results in pure 4-bromo-2,6-difluoroanile in excellent yield. In the case of bromination of 2-fluoroaniline, a mixture of isomers arises and thus iodination is a better method here because only 4-iodo-2-fluoroaniline is formed.



Scheme 1. Synthesis route of the fluorosubstituted isothiocyanatobiphenyls.

The presence of palladium acetate or chloride as catalyst in the alkaline acetone–water medium improved the coupling of compound B to C. We found that it was not, as is often suggested, necessary to use the triphenylphosphine palladium catalyst $(Ph_3P)_4Pd$. The amine C was not separated but it was treated directly with thiophosgene. This reaction proceeds extremely well in acidic medium and so it is not necessary to add calcium carbonate to bond hydrochloride.

Compounds I.2, I.3 and I.4 were prepared in the way shown in Scheme 2. In this case, 1,2,3-dioxaborolane B was coupled using 1-bromo-3,5-difluorobenzene or 1-bromo-3,4,5-trifluorobenzene to compounds I.2 or I.3 under the same conditions as for amine C shown in Scheme 1. Furthermore, compound I.2 was an intermediate material for the preparation of compound I.4. A common carbonisation procedure involving treatment of the lithium derivative with carbon dioxide was used for this purpose (see Scheme 2).

3. Experimental

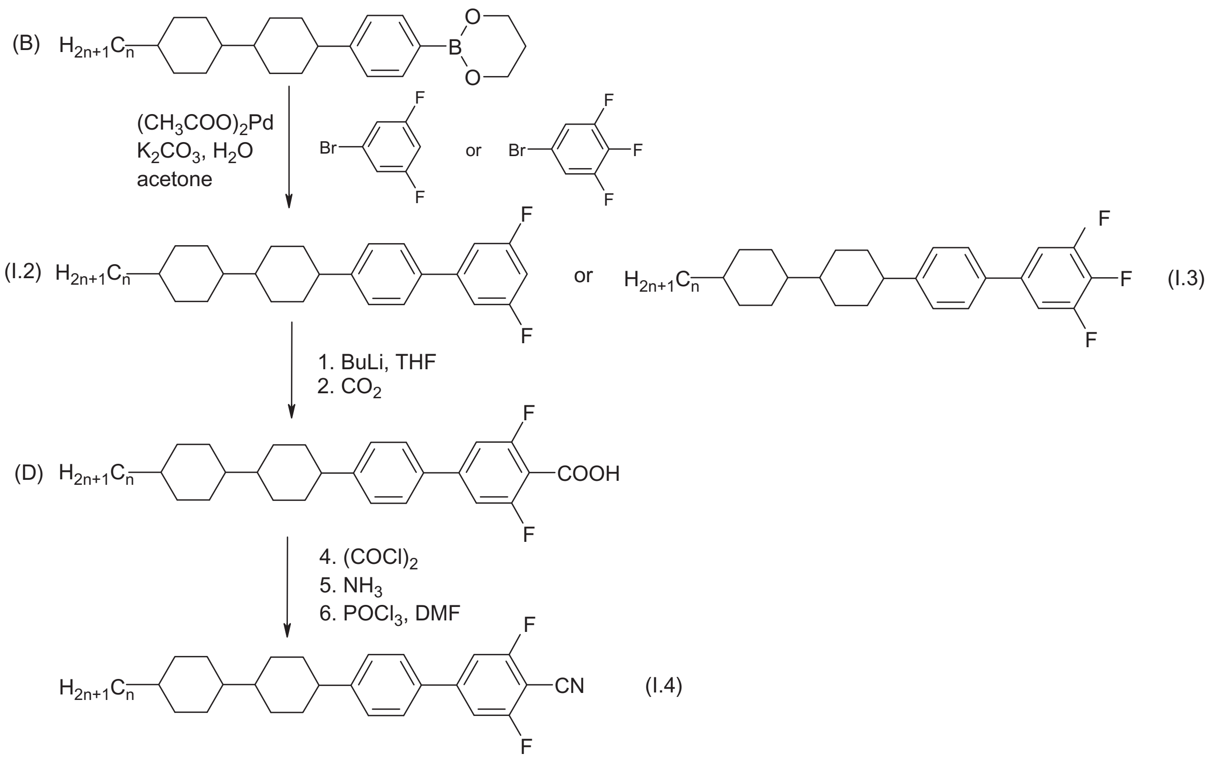
3.1 General method of preparation of compounds I.1

The example of compound **I.1.3d** (4′-(4″,4″-*trans*,*trans*-pentylbicyclohexyl)-4-isothiocyanatobiphenyl) is used.

3.1.1 Compound (B) 4-(4′,4′-trans,trans-pentylbicylohexyl)phenyl[1,2,3]dioxaborolane

To a mixture consisting of 4-(4′,4′-*trans*,*trans*-pentylbicyclohexyl)iodobenzene (43.8 g, 0.1 mol) and 500 cm^3 THF under inert atmosphere (N_2), a solution of the isopropyl magnesium chloride/lithium chloride complex (0.11 mol) in 130 cm^3 THF was dropped in at temperature 0°C and then stirred for 2 h. The mixture was then cooled to –65°C and tri-isopropylborate (24.8 g, 0.132 mol) was dropped in and stirred at this temperature for 0.5 h. Then it was left to reach room temperature. Then 10 wt.% solution of H_2SO_4 (0.15 mol) was dropped in and the solvent was evaporated. Water (300 cm^3) and hexane (200 cm^3) were added to the solid residue and stirred for 2 h. Separated boronic acid was filtered off. The yield was 28 g (85.6%).

The boronic acid, toluene (100 ml) and 1,3-propanediol (7.6 g, 0.1 mol) were refluxed until water stopped separating out. The resulting toluene solution was washed with water, dried over $MgSO_4$ and the



Scheme 2. Synthesis route of the fluoro- and cyano-terminated bicyclohexylbiphenyls.

solvent was evaporated. The solid residue was crystallised from hexane. The yield of 4-(4′,4′-*trans*,*trans*-pentylbicylohexyl)phenyl[1,2,3]dioxaborolane (B) was 27.0 g (68.2%) and the phase transition sequence was Cr 145 S 176°C Iso.

^{1}H NMR (CDCl$_3$) δ: 0.88 (3H, t, CH$_3$), 0.96–1.3 (16H, m), 1.44 (2H, m), 1.75–1.9 (9H, m), 2.02 (2H, m, **CH$_2$**CH$_2$O), 2.47 (1H, m, **CH**-Ph), 4.13 (4H, t, O-CH$_2$), 7.18, 7.68 (4H, 2d, Ph).

IR (diamond prism), strongest bonds [cm^{-1}]: 2911 and 2844 (CH$_2$, v), 1424 and 1341 (CH$_2$, d), 1266 cm^{-1} (v, B-O-C), 1154 (v, C-O), 826 (d, CH, in *p*-substituted benzene) MS m/Z: 396, 395 (M$^+$), 187, 188 (M-C$_{15}$H$_{28}$), 174, 175 (M-C$_{16}$H$_{29}$).

3.1.2 *Compound C and final compound **I.1.3d***

The mixture consisting of 4-(4′,4″-*trans*,*trans*-pentylbicyclohexyl)phenyl-[1,3,2]-dioxaborolane (9.9 g, 0.025 mol), 4-bromo-2,6-difluoroaniline (5.2 g, 0.025 mol), anhydrous K$_2$CO$_3$ (13.8 g, 0.10 mol), 100 cm^3 acetone and 100 cm^3 H$_2$O was refluxed under inert atmosphere (N$_2$) for 0.5 h. Then 0.1 g (CH$_3$COO)$_2$Pd was added and stirred at boiling temperature for 1 h. The acetone was distilled off. After the residue had cooled to room temperature, chloroform (50 cm^3) and hydrochloric acid were added to obtain a pH < 7. CSCl$_2$ (3.45 g) was then dropped in with stirring for 12 h until the amine was totally converted. The mixture was filtered and chloroform phase was separated. It was further dried over MgSO$_4$ and filtrated again. CHCl$_3$ was evaporated and the residue was crystallised from acetone. The yield was 5.3 g.

The product was then dissolved in the hexane at 60°C and eluted on a silica gel chromatographic column at 60°C. The colourless solid obtained was recrystallised from acetone (250 cm^3). The yield was 4.8 g (42%) and the phase transition was Cr 60.3 N > 350°C Iso.

^{1}H NMR (CDCl$_3$) δ: 0.86 (3H, t CH$_3$), 0.95–1.32 (16H, m), 1.44 (2H, m, CH), 1.73–1.94 (9H, m), 2.49 (1H, m, **CH**-Ph), 7.17 (2H, d, **H**-Ph-F), 7.28 and 7.4 (4H, 2d, **H**-Ph)

IR (diamond prism), strongest bonds [cm^{-1}]: 2924, 2848 (v, CH$_2$), 2027 (v, NCS), 1442 (d, CH$_2$), 1035 (v, (-C-N), 819 (d, **CH** in *p*-substituted benzene) MS m/Z: 481 (M$^+$), 273 (M-C$_{15}$H$_{28}$)$^+$, 260 (M-C$_{16}$H$_{29}$)$^+$, 228 (M-C$_{16}$H$_{29}$S)

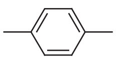
4. Results

4.1 Mesomorphic properties

Phase transition temperatures and enthalpies were measured using a SETARAM 141 differential scanning calorimetry (DSC) instrument. The liquid crystalline phases and phase transition temperatures were confirmed by texture identification under a OLYMPUS polarising microscope (POM) equipped with a LINKAM hot stage.

The prepared new isothiocyanato series I.1.1–I.1.7 showed only nematic phase (Table 1). Mono- and difluorosubstituted three-ring compounds I.1.1 and I.1.2, with the cyclohexane biphenyl rings bonded directly (Z-single bond), have a clearing point

Table 1. Phase transition temperatures and enthalpies (kJ/mol) of compounds measured by DSC method (onset point) in a heating cycle at 2°/min.

Compound I (Y = NCS)						Phase transition temperature (°C)									
No	A	n	r	Z	X	Cr$_1$		Cr		SmA		N		Iso	Crystallisation (°C)
I.1.1a		3	1	–	H	–		*	108.3	–		*	222.6	*	88
									23.5				*0.96*		
I.1.1b		5	1	–	H	*	57.8	*	86.5	–		*	220.7	*	56
							2.7		*4.5*				*0.17*		
I.1.2a		3	1	–	F			*	53.4			*	199.2	*	
									24.9				*0.76*		
I.1.2b		4	1	–	F	–		*	48.9	–		*	135.2	*	
									21.4				*0.12*		
I.1.2c		5	1	–	F	–		*	50.5	–		*	196.3	*	
									23.9				*0.78*		
I.1.3a		2	2	–	F	–		*	85.3	–			>350	*	58
									19.3				decomp.		
I.1.3b		3	2	–	F	*	63.3	*	80.2	–		*	>350	*	71
							13.1		*15.3*				decomp.		
I.1.3c		4	2	–	F	–		*	57.9	–			>350	*	
									34.1				decomp.		
I.1.3d		5	2	–	F	–		*	60,3	–			>350	*	
									30.1				decomp.		
I.1.4a		3	1	CH_2CH_2	H	–		*	68.6	–		*	179.8	*	56
									33.2				*2.13*		
I.1.4b		5	1	CH_2CH_2	H	–		*	72.0	–		*	162.2	*	
									24				*1.92*		
I.1.5a		3	1	CH_2CH_2	F	–		*	66.3	–		*	162.0	*	35
									20.2				*2.07*		
I.1.5b		5	1	CH_2CH_2	F	–		*	72.0	–		*	162.1	*	
									24.0				*1.92*		
I.1.6a		3	1	CH_2CH_2	H	–		*	75.5	–		*	123.3	*	
									28.4				*1.62*		
I.1.6b		4	1	CH_2CH_2	H	–		*	57.7	–		*	111.8	*	48
									1.12				*24.4*		
I.1.7a		3	1	CH_2CH_2	F	–		*	66.7	–		*	95.9	*	47
									23.9				*1.04*		
I.1.8a		3	1	–	F			*	106.4	–		*	204.8[16]	*	
I.1.8b		4	1	–	F			*	95.4	*	144.4	*	187.3[16]	*	
I.1.8c		5	1	–	F			*	95.3	*	107.5	*	187.1[16]	*	
									10.3						
Compound I (Y = H)															
I.2a		3	2	–	F			*	107	*	119.2	*	239	*	90.5
									16.5		*3.09*		*0.94*		
Compound I (Y = F)															
I.3a		3	2		F	*	35.5	*	103.1	–		–	260	*	81
							5.8		*11.8*						
													>250[11]		
									105.8						
Compound I (Y = CN)															
I.4a		3	2		F			*	159.6	–		–	>350	*	152
									27.3				decomp.		

Notes: Cr$_1$: transition in solid phase, Cr: crystal mesophase transition (melting point), SmA: smectic A phase, N: nematic phase, Iso: isotropic phase.

temperature of about 200°C or higher. Their clearing points are similar to terphenyl derivatives I.1.8, but the much lower melting point temperature and stronger nematic character differentiate them clearly from I.1.8.

The only exception is butyl derivative I.1.2b, which has a clearing point temperature ~60°C lower than other members of the series. This low clearing point is accompanied by a very small clearing enthalpy of only 0.12 kJ/mol. Such a small enthalpy Iso-N transition shows that the increase in molecular ordering in the nematic phase in comparison to the isotropic phase is low. Usually it is observed that homologues with a butyl chain have lower clearing points than adjacent ones, but never so large an observed decrease as in this case (owing to the well-known even–odd effect of the alkyl chain). We tested the purity of this compound and no trace of the *cis*-isomer was found. That the observed decrease is an intrinsic feature of compound I.12b is confirmed by much higher viscosity (38 mPa·(s) than observed for other members (see Table 2). Further experiments are necessary to explain this phenomenon.

Cyclohexylethyl derivatives ($Z = CH_2CH_2$), compounds I.1.4 and I.1.5, show a clearing point temperature 30°C lower than the corresponding compounds of I.1.1 and I.1.2 with a direct bond between the cyclohexane ring and biphenyl core. Phenylethyl derivatives, compounds I.1.6 and I.1.7, show a low clearing point and slightly higher melting point temperature compared to cyclohexyl analogues.

The clearing enthalpies of cyclohexyl derivatives I.1.1 and I.1.2 are small or moderate, but they are very high for phenylethyl derivatives I.1.6 and I.1.7, and especially for cyclohexylethyl compounds I.1.4 and I.1.5. We understand that these compounds with an ethane bridge have a strongly broken conformation in the isotropic phase. During the transition to the nematic phase, this conformation changes to a linear form and thus there is a significant increase in molecular order and intermolecular interaction.

Four-ring bicyclohexylbiphenylisothiocyanates, compounds I.1.3a–d, have an extremely high clearing point temperature of greater than 350°C. Moreover, these compounds show only a slightly higher melting point than the three-ring analogue I.1.2a–c. Therefore, the range of the nematic phase is larger than 250°C for these compounds. The four-ring fluoro analogue I.1.3a and especially the cyano compound I.1.4a are high melting point temperature compounds.

4.2 *Physical properties*

The values of the optical indices n_o, n_e, birefringence Δn, dielectric anisotropy $\Delta\varepsilon$ and combined parameter $M = \eta/\Delta n^2 \cdot T_{N\text{-}I}$ (where η bulk viscosity, $T_{N\text{-}I}$ is the nematic–isotropic transition temperature) for characteristic representative of compound I are listed in Table 2.

Values were extracted from a guest–host system as follows. A three-component host mixture of

Table 2. Value of optic indices n_o, n_e and optical birefringence Δn ($\lambda = 589$ nm), dielectric anisotropy $\Delta\varepsilon$ at 20°C, extrapolated from the host Demus' esters mixture and bulk viscosity extrapolated from 6CHBT, $M = \eta/\Delta n^2 \cdot T_{N\text{-}I}$ (mPa·s/°C).

Compound	n_o**	n_e**	Δn**	Viscosity η	M	$\Delta\varepsilon$***
I.1.1a	1.5078	1.8774	0.3696	16.0	0.52	11.6 7.1*
I.1.2a	1.5208	1.8551	0.3343	16.7	0.74	13.9 16.5*
I.1.2b				38,0		
I.1.3a	1.4933	1.8767	0.3834	28.5	0.55	19.8
I.1.3b	1.5119	1.9099	0.3980	26.0	0.46	21.6
I.1.3c	1.5299	1.9055	0.3756	26.7	0.54	20.2
I.1.3d	1.5239	1.9086	0.3847	27.0	0.52	21.3
I.1.4a				11.7		11.0*
I.1.5a	1.5416	1.9092	0.3681	23.3	1.06	16.5 13.5*
I.1.7a	1.5267	1.8484	0.3217	41.2	3.22	12.8 13.9*
I.1.8a	1.5585	2.0442	0.4857	35.6	0.83	17.9 17.5*
I.2a	1.4617	1.6572	0.1955	22.1	6.25	8.2
I.3a	1.4593	1.6603	0.2010	17.2	1.50	14.3 12.6[11]
I.4a	1.4668	1.7289	0.2621	–		–

Notes: *Near melting point in pure compound [17]. **Extrapolated from Demus' mixture. ***Extrapolated from 6CHBT.

Demus' ester or 6CHBT [4-(isothiocyanotophenyl)-1-(trans-4-hexyl)cyclohexane] was doped with 10% wt. of a single compound being investigated and its refractive indices, permittivity constants and bulk viscosity were measured with temperature using an Abbe refractometer or an impedance analyser HP 4191 at a frequency of 1 kHz as described in Czub *et al.* [17] or using Ostwald's capillary viscometer. The Demus' ester mixture and pure 6CHBT were measured under the same conditions.

The properties of the investigated compounds were calculated for the chosen temperature from the relationship:

$$AB = X.B + (1 - X).A,$$

where AB is the measured property of the mixture, B is the unknown property of an investigated compound, A is the measured property of the host, and X is the mole ratio of the guest.

It is likely that the elongated molecular rigid core and resulting very high clearing point temperature of compounds I influence the order parameter of the host nematic material. Therefore the calculated ordinary index n_e and Δn may be higher than estimated ones with a high clearing host mixture and their real values. However, it seems that the optical and dielectric properties of dopants in the moderately high clearing nematic medium are well approximated. For example, the birefringence $\Delta n = 0.201$ and $\Delta\varepsilon = 14.3$ of compound I.3a was estimated by us at 20°C and the corresponding values given by Demus *et al.* [11] are 0.154 and 12.6, respectively.

The investigated polar compounds have a relatively low viscosity except for I.4a. The bulk viscosity of the members with the same propyl chain increases as follows:

$$\begin{gathered}\text{I.1.4a} < \text{I.1.1a} < \text{I.1.2a} < \text{I.3a} < \text{I.2a} < \text{I.1.5a} \\ < \text{I.1.3b} < \text{I.1.8a} < \text{I.1.7a} < \text{I.4a}.\end{gathered}$$

The monofluorosubstituted compounds I.1.4a, I.1.1a (and also the difluorosubstituted one I.1.2a) have the lowest viscosity, while the difluorosubstituted terphenyl analogue I.1.8a and especially I.1.7a have a much higher bulk viscosity. The combined parameter of compound I.1.1a is low ($M = 0.52$), while $M = 0.74$ for I.1.2a and $M = 0.83$ for the terphenyl derivative.

The four-ring compound I.1.3a has the lowest value ($M = 0.46$), although its viscosity is nearly two times higher than that of I.1.1a. As well as their combined properties expressed by the M index, the individual properties of compounds with an ethane bridge are in most cases worse in comparison with those compounds with a direct bond between the cyclohexane or benzene ring and the biphenyl core. Several compounds of I listed in Table 1 appear to be excellent components with which to formulate mixtures with moderately high birefringence values (in the range 0.2 to 0.35).

Table 3. Properties of mixture A composed of alkylfluoroisothiocyanatotolanes and alkylfluoroisothiocyanatobiphenyls, and three- and four-ring isothiocyanates presented in Table 1.

Property		Value
Cr-N		<−20°C
N-Iso		128°C
η	at (−10)°C	203 mPa·s
	at 20°C	25 mPa·s
	at 50°C	8 mPa·s
n_o at 633	at 25°C	1.5320
	at 35°C	1.5320
n_e	at 35°C	1.8582
Δn	at 35°C	0.3273
$\varepsilon_\perp$	at 25°C	4.46
$\varepsilon_\parallel$	at 25°C	21.76
$\Delta\varepsilon$	at 25°C	17.30

4.3 *Mixture formulation*

An example multicomponent mixture marked as A and consisting of two-ring alkylfluoroisothiocyanatotolanes and alkylfluoroisothiocyanatobiphenyls and a few compounds listed in Table 1 was formulated. Its properties are given in Table 3.

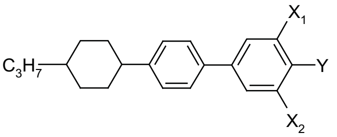
The nematic phase of mixture A has a broad temperature range, its viscosity is low both at and below room temperature, and its dielectric and optical anisotropy are both high.

5. Discussion

An isothiocyanato group (NCS) placed on the terminal position of a molecule with a cyclohexylbiphenyl or cyclohexylethylbiphenyl core provides strong mesogenic stability. Such compounds show a very high clearing point temperature, which decreases as the result of fluorosubstitution but much less than is observed for analogous cyano- or fluoro- terminated compounds as seen from the comparison given below for compounds I.A and I.B, respectively, in Tables 4 and 5.

A three-ring laterally unsubstituted 4-(4-propylcyclohexyl)biphenyl-4-isothiocyanate has a higher clearing point than CN or F terminated analogues, about 10 and 70°C, respectively, as shown in

Table 4. Comparison of phase transition temperatures (°C) of compounds I.A upon the change of terminal substituent Y and lateral substituent X.

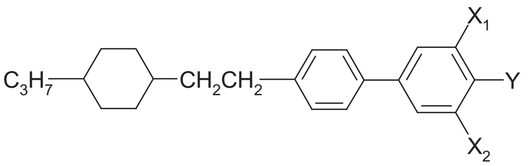


I.A

Y	X_1	X_2	Cr		N		Iso	$T_{NCS}-T_Y$*
F [18]	H	H	*	99	*	160	*	79.9
CN [19]	H	H	*	133	*	230	*	9.9
NCS	H	H	*	147.5	*	239.9	*	0
F [20]	H	F	*	69.7	*	98.6	*	124
CN [21]	H	F	*	104	*	183	*	39.6
NCS	H	F	*	108.3	*	222.6	*	0
F [11]	F	F	*	40.7	(*	33.2)	*	166
NCS	F	F	*	53.4	*	199.2	*	0

Note: *Difference in clearing point.

Table 5. Comparison of phase transition temperatures (°C) for compounds I.B upon the change of terminal substituent Y and lateral substituent X.



I.B

Y	X_1	X_2	Cr		N		Iso	$T_{NCS}-T_Y$*
F [22]	H	H	*	76	*	125	*	67.5
NCS	H	H	*	113.4	*	192.6	*	0
F	H	F	*	69.7	*	98.6	*	81.2
CN [23]	H	F	*	76.4	*	153	*	26.8
NCS	H	F	*	68.6	*	179.8	*	0
F [11]	F	F	*	48.0	*	51.8	*	111.2
NCS	F	F	*	66.3	*	162	*	0

Note: *Difference in clearing point.

the last column of Table 4. The difference increases for monofluorosubstituted compounds ($X_1 = H$, $X_2 = F$) to about 40 and 125°C for respective homologues. A difluorosubstituted compound with Y = F has a clearing point at about 160°C lower than is observed for one with Y = NCS. A similar relationship is seen with propylcyclohexylethylbiphenyl derivatives (compounds I.B) (Table 5). Difluorosubstituted three-ring isothiocyanates I.B have a clearing point temperature near 200°C while that for fluoro-terminated analogues is only 30–50°C. The same tendency in relation to clearing point temperature is observed for the four-ring compounds investigated in this work; see the comparison in Table 6 for compounds I.1.3b, I.2a, I.3a and I.4a with the same propyl terminal chains. The length of molecules *l* in the most extended structure was calculated by HyperChem 7.5 molecular modelling software. The shape and length of the isothiocyanato group was taken from recent X-ray studies [24, 25] because the HyperChem's calculation approximates NCS group as tilted to the benzene axis when it is nearly linear.

The difference in clearing point temperature between fluorosubstituted compound I.3a and cyano

Table 6. Comparison of clearing point temperature for compounds I.1.3b, I.4a, I.3a and I.2a with the same propyl terminal chains.

Y	$T_{N\text{-}I}$ (°C)	Length of molecule (l) (nm)
NCS	~350	2.46
$\text{-C}\equiv\text{N}$	~350	2.31
-F	260	2.19
-H	239	2.16

or isothiocyanato compounds (I.4a and I.1.3b) is smaller than in case of three-ring compounds, but still relatively large of about 100°C.

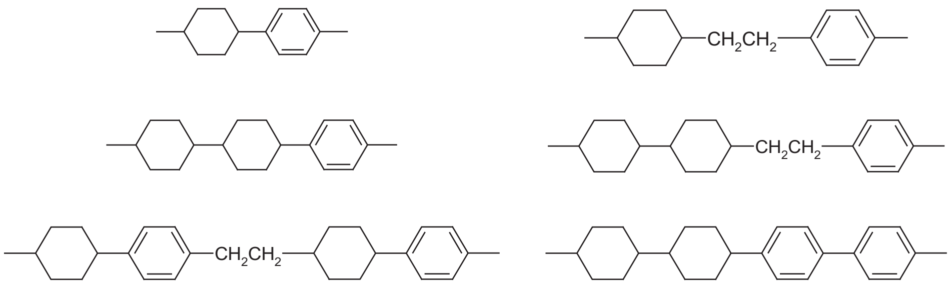
The increase in the length of molecule I.2a in comparison with I.3a is only ~1% and involves an increase in $T_{\text{N-I}}$ of 21°C, while the increase in length of molecule I.3a and I.1.3b compared with to I.2a is 5 and 11%, respectively. It seems likely that the difference in the length of the molecules is not the only cause for such extensive change to the mesomorphic properties of the compounds. In the case of cyano compounds, a strong side-by-side charge–transfer interaction leads to partial dimerisation and effectively elongates the molecular aggregates to 1.4 l [8, 26–28]. In isothiocyanates, dimerisation is very limited but X-ray studies show that apparent length is slightly larger than l even in two-ring compounds [28]. In four-ring molecules it may be more pronounced. Dipole–dipole interaction may be also responsible for longer aggregates than l for compounds with F, CN and NCS substituents.

In the case of isothiocyanates I.1, fluorosubstitution reduces their melting points strongly, so not only three-ring compounds have low melting points but also four-ring compounds have acceptable melting points for use as mixture components, as seen from a comparison of compounds I.1.2a–c with I.1.3a–d.

Four-ring isothiocyanates I.1.3a–d are strongly mesogenic compounds. The temperature range of the nematic phase is extremely broad for these compounds and, for compound I.1.3b, it is about 300°C. It is the individual compound probably with the broadest nematic phase. For this reason it may be interesting to study the order parameter at a large distance from the clearing point.

The isothiocyanato terminal group not only promotes smectogenicity in some structures (biphenyl or terphenyl core), but also results in strong nematogens if the molecular core contains cyclohexane and benzene rings in an appropriate ratio.

Combining the results of this work with early recognised structures [9, 29, 30], the following molecular cores which are terminally substituted by an alkyl group and the isothiocyanato group promote the presence of nematic phase with low viscosity:



A ratio of cyclohexane to benzene ring of 1:1 or higher leads to a shape of the rigid core in which intermolecular interactions are rather weak and the translation of molecules is less hindered than in the case when an aromatic ratio rings prevails.

In parallel work [31], it was found that the four-ring compound series I.1.3 shows a strong dependence of the parallel electric permittivity constant on frequency, which makes them especially interesting for the formulation of low viscosity dual frequency (DF) addressed mixtures. Examples of such DF mixtures with low crossover and frequency, with low conductivity suitable for active matrix addressing, is given in our patent application [31].

6. Conclusions

4′-Alkylcyclohexyl- and 4′-alkylcyclohexylethyl-3-fluoro(or 3,5-difluro)-4-isothiocyanatobiphenyls, and 4′-alkylbicyclohexyl-3,5-difluoro-4-isothiocyanatobiphenyls are strongly nematic liquid crystals with a high or very high clearing point and relatively low melting point temperature. The melting enthalpies of these compounds are relatively low. Moreover, the viscosity of these compounds in the relation to their high dielectric anisotropy is low. These are excellent components for formulation of nematic mixtures with a moderately high birefringence (*Δn*~0.35) with a broad range.

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