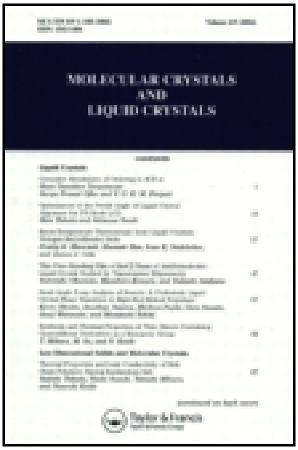


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

(Iso)Thiocyanato Substitution in Calamitic Liquid Crystals

Vladimir F. Petrov [a] [b] & Yo Shimizu [a]

[a] Department of Organic Materials, Osaka National Research Institute, 1-8-31 Midorigaoka, Ikeda, Osaka, 563-8577, Japan

[b] LC Works, 6/68 Brinsley Road, Camberwell, VIC. 3124, Australia

Version of record first published: 24 Sep 2006

To cite this article: Vladimir F. Petrov & Yo Shimizu (2001): (Iso)Thiocyanato Substitution in Calamitic Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 363:1, 107-121

To link to this article: http://dx.doi.org/10.1080/10587250108025262

Mol. Cryst. Liq. Cryst., Vol. 363, pp. 107-121
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group.
Printed in the USA

(Iso)Thiocyanato Substitution in Calamitic Liquid Crystals

VLADIMIR F. PETROV* and YO SHIMIZU

Department of Organic Materials, Osaka National Research Institute,
1–8–31 Midorigaoka, Ikeda, Osaka 563–8577, Japan

(Received November 8, 2000)

The effect of the terminal substitution of calamitic liquid crystals by the (iso)thiocyanato groups on the appearance of the mesophases and their physico-chemical properties is discussed and compared with that of other well-known groups.

Keywords: (iso)thiocyanato groups; physico-chemical properties; liquid crystals

1. INTRODUCTION

The strong polar liquid crystals, such as the cyano derivatives, are still the most important components for the liquid crystal materials for nematic display applications.(1–4) In continuation of our study of the structure-property relationships in the strong polar liquid crystals {see, for example our previous publications which discuss the effects of the terminal CN and NO_2 substitutions(5–11)}, we present here our results on the study of the effect of the terminal substitution of calamitic liquid crystals by the NCS and SCN groups on the appearance of the mesophases and their physico-chemical properties. The results of this study will be compared with those of the corresponding liquid crystals having other polar terminal groups.

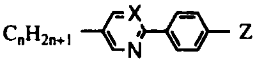
---

* Author for correspondence. Present address: LC Works, 6/68 Brinsley Road, Camberwell, VIC. 3124, Australia.

2. MESOMORPHIC PROPERTIES

The phase transition temperatures of some (iso)thiocyano substituted liquid crystals and the corresponding reference compounds are summarized in tables I–V, where Cr, SmA, SmB, N and I are the crystalline, smectic A, smectic B, nematic and isotropic phase, respectively.

TABLE I Physico-chemical properties of liquid crystals:



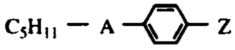
No.	*n*	x	*Z*	*Phase transitions, °C*	*L, Å*	d_2^a, Å	d_l^a, Å	*Reference*
1–1	3	H	NCS	Cr 64 SmA 99 I				(5, 12)
1–2	4	H	NCS	Cr 37.6 SmA 100 I				(5)
1–3	5	H	NCS	Cr 34 SmA 98.5 I	19.7		19.9	(5, 12, 13)
1–4	6	H	NCS	Cr 27 SmA 99 I				(5)
1–5	7	H	NCS	Cr 26.1 SmA 99.2 I				(5, 12)
1–6	3	H	CN	Cr 43.4 N 43.8 I				(6)
1–7	4	H	CN	Cr 32.3 N (26.5) I				(6)
1–8	5	H	CN	Cr 33.6 N 43.5 I	18.5	22.7	15.4	(6, 7)
1–9	6	H	CN	Cr 29 N 32.5 I				(6)
1–10	7	H	CN	Cr 30.9 N 47 I				(6)
1–11	5	H	OCF_3	Cr 18.6 SmB 38.5 SmA 52.4I	19.5		18.7	(12, 13)
1–12	5	H	OCF_2H	Cr 26 Sm 43.6 I				(12)
1–13	5	N	NCS	Cr 46 SmA 85.5 I				(14)
1–14	5	N	CN	Cr 70.8 N (51.9) I				(15)
1–15	5	N	OCF_3	Cr 32 SmA 45.2 I				(12)
1–16	5	N	OCF_2H	Cr 20.1 Sm 24 I				(12)

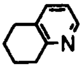
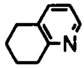
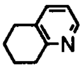
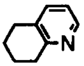
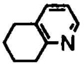
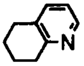
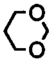
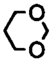
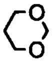
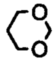
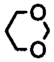
a. $T_{meas} = T_{N\text{-}I}$ or $T_{SmA\text{-}I} - 10$ °C

It is evident from tables I, II and the references$^{(3, 4, 24)}$ that the isothiocyanato substituted aromatic and hetero-aromatic liquid crystals exhibit mainly smectic phases, with a higher thermostability than that of the corresponding strong polar (CN) and moderate polar (OCF_3, OCF_2H, SCF_2H, F) derivatives (compounds **1–1** and **1–6**; **1–2** and **1–7**; **1–3** and **1–8**; **1–4** and **1–9**; **1–5** and **1–10**; **1–13** and **1–14** – **1–16**; **2–1** and **2–2** - **2–6**; **2–7** and **2–8** – **2–11**, **2–12** and **2–13**). From table I, it follows that the terminal NCS substitution of pyridin-2,5-diyl derivatives changes the efficiency of alkyl groups (compounds **1–1** – **1–5** and **1–6** – **1–10**):

Z = NCS $T_{cl} \rightarrow C_nH_{2n+1}$: $C_5H_{11} < C_3H_7 \approx C_6H_{13} < C_7H_{15} < C_4H_9$

Z = CN $T_{cl} \rightarrow C_nH_{2n+1}$: $C_4H_9 < C_6H_{13} < C_5H_{11} < C_3H_7 < C_7H_{15}$,

TABLE II Physico-chemical properties of liquid crystals: 

No.	*A*	*Z*	*Phase transitions, °C*	*L, Å*	d_2^a, *Å*	d_l^a *Å*	*Reference*
2–1		NCS	Cr 92 Sm 104 N 115.1 I				(12)
2–2		CN	Cr 96.2 N 98 I				(12)
2–3		OCF_3	Cr 57.5 N 63.2 I				(12)
2–4		OCF_2H	Cr 61.8 N (59.1) I				(12)
2–5		SCF_2H	Cr 40.9 I				(12)
2–6		F	Cr 65 N (55.1) I				(12)
2–7		NCS	Cr 60 SmA 79 I	21.3		19.6	(16)
2–8		CN	Cr 56 N (49) I	18.0	22.0		(17, 18)
2–9		OCF_3	Cr 23.6 SmB 34.9 I				(12)
2–10		OCF_2H	Cr 23 Sm (4) N (8) I				(12)
2–11		SCF_2H	Cr 42.5 I				(12)
2–12		NCS	Cr 53 SmE 74.5 I	20.3		20.0	(19, 20)
2–13		CN	Cr 22.5 N 35 I	18.0	24.8	14.3	(7, 21)
2–14		NCS	Cr 68 N (51.8) I	21.4	22.5^b		(22)
2–15		CN	Cr 30 N 55 I	20.0	25.9		(7, 23)

a. $T_{meas} = T_{N\text{-}I}$ or $T_{SmE\text{-}I} - 10$ °C.
b. $T_{meas} = T_{N\text{-}I} - 1.8$ °C.

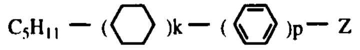
where T_{cl} is the nematic-isotropic or smectic-isotropic phase transition temperature. Interestingly, the butyl group is most and less effective for the NCS and CN derivatives, respectively. Similar results have been found for other homologous series of the NCS derivatives.(16, 24, 25)

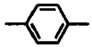
The terminal isothiocyanato substitution of two-ring trans-1,4-disubstituted cyclohexylene derivatives creates only nematic phase {compounds **2–14, 5–1, 5–3**, tables II, V and the references(14, 24, 26)}, while three ring trans-1,4-disubstituted cyclohexylene derivatives exhibit the nematic and smectic phases (compounds **3–1, 3–7, 3–12**, table III). It is important to note that the efficiency of the terminal NCS group depends on the molecular core structure. So far for two-ring trans-1,4-disubstituted cyclohexylene derivatives the NCS group is less efficient than the CN group (compounds **2–14** and **2–15, 5–1** and **5–2, 5–3** and **5–4**), while for three-ring derivatives the opposite situation has been found (compounds **3–1** and **3–2, 3–7** and **3–8, 3–12** and **3–14**). Interestingly, increasing the quantity of the cyclohexane rings in the molecular core of liquid crystals reduces the difference in the clearing points (nematic-isotropic phase transition temperatures) between the NCS and CN derivatives (compounds **3–1** and **3–2, 3–7** and **3–8**). The isothiocyanato group is also more efficient than other terminal polar groups (OCF_3, OCF_2H, F) attached to the core of three-ring trans-1,4-cyclohexylene derivatives (compounds **3–1** and **3–3** – **3–6**; **3–7** and **3–9** – **3–11**, table III). As can be seen from table V, the fifth member of two-ring 1,4-bicyclo[2.2.2]octylene derivatives exhibits only nematic phase, with slightly decreased thermostability in comparison with that of the corresponding cyano derivative (compounds **5–5** and **5–6**). However, changing the alkyl group length may lead to the opposite situation.(25,29) Similar results have been found for other isothiocyanates.(42–44)

Considering the effect of the terminal substitution of calamitic liquid crystals by the thiocyanato group, we would like to point out that no mesomorphic two-ring SCN derivatives have been reported yet.(45)

It is evident from tables III, IV and the references(45, 46) that the thiocyanato group promotes the formation of mostly smectic mesophases in the aromatic systems, and it is less effective than the corresponding terminal isothiocyanato and cyano groups attached to the core of three-ring derivatives (compounds **3–13** and **3–12, 3–14; 4–1** and **4–2; 4–6** and **4–7; 4–11** and **4–12**). It is also less effective than the corresponding NO_2, OCF_3 and F groups {compounds **4–1** and **4–3** – **4–5; 4–6** and **4–8** – **4–10**, and the references(45, 46)}. The decreased thermostability of the thiocyanato group has been explaineed in terms of increased bent angle (~ 80 °) of the cyano moiety in this group.(45,46) Similar results have been found for other SCN derivatives.(51)

TABLE III Physico-chemical properties of liquid crystals:



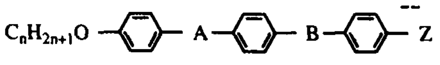
No.	*k*	*p*	*Z*	*Phase transitions, °C*	$\varepsilon_\perp^a$	$\Delta\varepsilon^a$	*Ref.*
3–1	1	2	NCS	Cr 123 Sm 133 N 233.5 I			(35)
3–2	1	2	CN	Cr 96 N 222 I			(36)
3–3	1	2	OCF_3	Cr 43 SmB 128 N 147.4 I			(37)
3–4	1	2	OCF_2H	Cr 69.5 Sm 119.6 N 167.5 I			(12)
3–5	1	2	SCF_2H	Cr 56.2 Sm 94.7 N 114 I			(12)
3–6	1	2	F	Cr 100 N 153 I			(36)
3–7	2	1	NCS	Cr_1 38.4 Cr 55.5 N 237 I			(38)
3–8	2	1	CN	Cr 53.8 Sm 60.3 N 234.4 I			(39)
3–9	2	1	OCF_3	Cr 52 SmB 73 N 156.1 I			(37)
3–10	2	1	OCF_2H	Cr 37 SmB 102 N 170 I			(37)
3–11	2	1	F	Cr 69.4 Sm 75.5 N 157.5 I			(40)
3–12	1	1	COO  NCS	Cr 118.5 SmA 129 N 235 I	3.3	3.4	(41)
3–13	1	1	COO  SCN	Cr 104 N 124.5 I	5.2^b	4.5^b	(41)
3–14	1	1	COO  CN	Cr_1 82 Cr 111 N 225.5 I	5.8	7.9	(41)

a. $T_{meas} = T_{N\text{-}I} - 30$ °C.
b. $T_{meas} = T_{N\text{-}I} - 10$ °C.

According to the theory of Maier and Saupe the nematic-isotropic phase transition temperature is proportional to the anisotropy of polarizability of the molecules forming the nematic phase.(52) In such case, isothiocyanato substituted derivatives, having increased values of the anisotropy of polarizability compared to those of corresponding cyano derivatives,(27) consequently should exhibit the increased values of the nematic-isotropic phase transition temperatures in comparison with those of the cyano substituted liquid crystals. However, some of the presented results and the results reported in the references(53, 54) are found to be difficult to follow the Maier and Saupe theory.

It has been proposed that the packing of the molecules predominantly influences the nematic thermostability.(55, 56) The anisotropic dispersion interactions and consequently the anisotropy of polarizability, which depend on the electronic structure of the NCS and SCN groups,(57–60) also influence the packing and hence the stability of the mesophases but play a secondary role compared to the steric factors.(56) Other molecular aspects such as the association(61) or dipole-dipole attraction in polar liquid crystalline derivatives which can influence the packing of the molecules also affect the stability of the mesophases.(56)

TABLE IV Physico-chemical properties of liquid crystals:



No.	*n*	*A*	*B*	*Z*	*Phase transitions, °C*	*d^a, Å*	*d^a/L*	*Ref.*
4–1	8	COO	COO	SCN	Cr 110 SmA 179 N 179 I	32.1	1.063	(45, 47)
4–2	8	COO	COO	CN	Cr 116 N 229 I			(48)
4–3	8	COO	COO	NO_2	Cr 114 SmA 210 N 224 I	36.2	1.237	(8, 47)
4–4	8	COO	COO	OCF_3	Cr 122 SmA 216 I	32.1	1.039	(47)
4–5	8	COO	COO	F	Cr 120 SmA 176 N 185 I	28.6	0.993	(8, 47)
4–6	8	OOC	COO	SCN	Cr 138 SmB 165 SmA 173 N 178 I	32.5	1.069	(46, 47)
4–7	8	OOC	COO	CN	Cr 148 SmA 158 N 233 I			(49)
4–8	8	OOC	COO	NO_2	Cr 153 SmA 190 N 220 I	38.8	1.320	(8, 47)
4–9	8	OOC	COO	OCF_3	Cr 193 SmA 225 I	31.5	1.026	(47)
4–10	8	OOC	COO	F	Cr 173 SmA 196 I	30.0	1.053	(8, 47)
4–11	7	–	COO	SCN	Cr 102 SmA 176 I			(46)
4–12	7	–	COO	CN	Cr 114.5 N 228 I			(50)

a. $T_{meas} = T_{SmA\text{-}N}$ or $T_{SmA\text{-}I} - 10$ °C.

It has been shown that X-ray diffraction of liquid crystals is one of the useful methods to study the effects of the association of liquid crystalline molecules on the structure of their mesophases and consequently on the properties of liquid crystals formed by these molecules.(7, 18, 62–64)

The investigation of polar liquid crystals by X-ray diffraction has revealed not only existence of a layer structure in the smectic phase of these compounds but also periodic density fluctuations in the nematic phase having a period d. They involve swarms containing tens to hundreds of molecules and are characterized by a correlation length ξ defined directly from the width of the diffraction peak. For the nematic phase of some two-ring cyano derivatives it has been shown that the ratio d / L, where L is a molecular length, is about 1.2–1.5.(7, 18, 63, 64) Hence the period of the fluctuating layer structure significantly exceeds a single molecular length, and should be related to the size of the molecular dimer. Such a dimer is formed by two polar molecules being mutually antiparallel. Experimental values of the layer structure period d, for some other cyano derivatives belonging to the different chemical classes showed that d depends on the molecular structure of the polar liquid crystals and characterizes in particular the degree of overlap of the molecular cores on dimer formation. Further X-ray diffraction investigations of the nematic phase of polar liquid crystals revealed in some cases the simultaneous existence of two fluctuation layer structures with incommensurate periods d_l and d_2, where $d_l < L$ and $L < d_2 < 2L$.(7, 62–64)

It has been found two incommensurate density waves: monomeric with period d_l (period d_l is related to the fluctuation layer structure formed by separate molecules) and dimeric with the period d_2 for two-ring 2,5-disubstituted pyridine derivatives having cyano terminal group (compound **1–8**, table I).(7,63,65) The replacement of the cyano group by the NCS and OCF_3 groups in this compound to obtain compounds **1–3** and **1–11**, respectively results in the creation of only smectic phases which exhibit only monomeric density waves in X-ray diffraction experiments. Similar results have been found for 4,4′-n-pentyl substituted biphenyls (compounds **2–12** and **2–13**, table II).

It has been reported that for two-ring trans-1,4-disubstituted cyclohexylene and trans-1,3-dioxan-2,5-diyl derivatives having cyano terminal groups, only one density wave with a characteristic period d_2 has been observed(7, 18, 63, 65) (compounds **2–8, 2–15** table II), while the replacement of the cyano group by the NCS group in these compounds to obtain compounds **2–7, 2–14**, respectively results in an appearance of only monomeric density wave with $d_l < L$ for the trans-1,3-dioxan-2,5-diyl isothiocyanato derivative **2–7**, and the dimeric density wave for the trans-1,4-disubstituted cyclohexylene derivative **2–14**. The d_2 values of compounds **2–14** and **2–15** differ significantly, indicating different degrees of molecular core overlap in the dimer formation.(61, 66) The different d_2 values probably result from significantly different electron density distributions in the molecular structure {for the pyridine derivatives this is shown in the reference(67)} and steric factors which are responsible for the type of dimerization. Similar results have been demonstrated for other liquid crystalline isothiocyanates.(16, 19, 22, 43)

X-ray diffraction study of some three-ring thiocyanato substituted ester derivatives has shown only one density wave with the period d which is slightly larger than the molecular length. According to this data and the classification of the smectic A phases,(13) the smectic A phases, which are observed in compounds **4–1** and **4–6**, have been classified as the partially bilayer smectic Ad phases with an antiparallel arrangement of the molecules in their dimers.(47) These compounds exhibit the ratios d / L which are larger and lower than that of the corresponding trifluoromethoxy, fluoro (compounds **4–1** and **4–4, 4–5; 4–6** and **4–9, 4–10**, table IV) and nitro (compounds **4–1** and **4–3; 4–6** and **4–8**) derivatives, respectively. The difference in the d / L values for compounds **4–1** and **4–6** shows the influence of the orientation of ester groups on the structure of the smectic A phases, with a higher level of molecular overlapping in the formation of the dimers of the former compound. Similar conclusions can be derived for the corresponding nitro (compounds **4–3** and **4–8**, table IV) and fluoro (compounds **4–5** and **4–9**) derivatives, while for the trifluoromethoxy derivatives (compounds **4–4** and **4–9**) the opposite situation has been found.

3. STATIC DIELECTRIC PROPERTIES

The relationship between the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are, respectively, dielectric constants, that are parallel and perpendicular to the nematic director **n**; and molecular structure of liquid crystals is described by the theory of Maier and Meier:(68)

$$\Delta\varepsilon = \mathrm{NhF}/\varepsilon_{\mathrm{O}}[\Delta\alpha - \mathrm{F}\mu^2/\mathrm{kT}(1 - 3\cos^2\beta)]\mathrm{S}, \qquad (1)$$

where $h = 3\varepsilon^*/(2\varepsilon^* + 1)$, $\varepsilon^* = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$; $\Delta\alpha = (\alpha_{\parallel} - \alpha_{\perp})$ is the polarizability anisotropy; F is the cavity reaction field; μ is the dipole moment; β is the angle between the molecular long axis and the dipole moment and N is the number of molecules per unit volume; S is the order parameter.

It has been shown that meaningful comparisons of the dielectric (as well as optical and elastic) properties of liquid crystals with different nematic-isotropic phase transition temperatures $T_{N\text{-}I}$ can only be made at constant reduced temperature $\tau = T_{meas} / T_{N\text{-}I}$.(1) Tables III, V present some data on the dielectric properties of liquid crystalline compounds measured at a constant reduced temperature and extrapolated from the liquid crystalline mixtures at 20 °C. According to,(1) the extrapolations are not meaningful, however these estimations are only one way to obtain a rough definition of the dielectric (as well as optical and elastic) properties of non-mesomorphic compounds, smectic liquid crystals, and liquid crystals with narrow nematic range.

It is evident from tables III, V and the references(12, 26, 69) that the replacement of the cyano group by the thiocyanato and isothiocyanato groups lowers the dielectric anisotropy of liquid crystals due to the dipole moments being decreased (compounds **3–12** – **3–14**; **1–3** and **1–8**; **5–1** and **5–2**; **5–3** and **5–4**; **5–5** and **5–6**; **2–12** and **2–13** - dipole moments). For the definite molecular core of liquid crystals, their dielectric anisotropy decreases in the same sequence as values of dipole moments for the terminal groups CN, SCN and NCS diminish: 3.93 D, 3.62 D, 2.85 D.(70) These results are found to be in an agreement with the equation (1). Similar results have been reported for other liquid crystalline isothiacyanates.(27, 29, 38, 43, 71)

TABLE V Physico-chemical properties of liquid crystals: **R — A** —— **Z, R = C_nH_{2n+1}**

No.	*n*	*A*	*Z*	*Phase transitions, °C*	k_p *40 °C*	μ, *D 25 °C*	$\varepsilon_\perp$	$\Delta\varepsilon$	g^a	Δn	K_{11}^b	$\frac{K_{33}}{K_{11}}$	ν mm^2s^{-1}	*Reference*
1–3	5		NCS	Cr 34 SmA 98.5 I	0.6645	4.46		15.5^c	0.533	0.220^c			18^c	(12, 32)
1–8	5		CN	Cr 33.6 N 43.5 I	0.6538	6.00	10.9^e	17.8^e	0.518	0.214^c			50^c	(2, 5, 12)
2–12	5		NCS	Cr 53 SmE 74.5 I		3.23			0.577	0.330^d				(2, 20, 33)
2–13	5		CN	Cr 22 5 N 35 I		4.80			0.530	0.178^f				(2, 21, 34)
5–1	7		NCS	Cr 38.1 N 52.1 I	0.6430		4.6^f	5.1^f		0.140^f				(22, 27)
5–2	7		CN	Cr 30 N 59 I	0.6306		4.9^f	7.3^f		0.083^f				(23, 28)
5–3^u			NCS	Cr 2 N 19.8 I			5.1^f	5.6^f		0.130^f	4.65^f	1.07^f		(26)
5–4^u			CN	Cr 19 N 32.2 I			5.9^f	8.4^f		0.086^f	4.79^f	1.14^f		(26)
5–5	5		NCS	Cr 74 N 99.5 I				6.4^e		0.186^e				(29)
5–6	5		CN	Cr 62 N 100 I				10.0^t		0.140^t				(30, 31)

[a] $T_{meas} = T_{N\text{-}I}$ or $T_{Sm\text{-}I}$; [b] K_{11} in [x 10^{-12} N]; [c,d] Extrapolated from 10 wt % and 5–25 mol. % solutions in ZLI-1132 and liquid crystal mixture, at 20 and 25 °C, respectively. [e] $\tau = T_{meas}/T_{N\text{-}I} = 0.95$, T_{meas}, $T_{N\text{-}I}$ in [K]; [f] $T_{meas} = T_{N\text{-}I} - 10$ °C; [t] $\tau = 0.96$; [u] R is equal to $CH_2{=}CH\text{-}C_5H_{10}$

It has been shown that mesogenic molecules possessing strongly polar terminal groups form associated pairs. Both head-to-head and head-to-tail pairing occurs(66, 72–74) but antiparralel association predominates and reduces the effective dipole moment(61):

$$\mu_{\text{eff}}{}^2 = g\mu^2 \tag{2}$$

$$\mu_{\text{eff}}{}^2 = \frac{9kT(\varepsilon_i - \varepsilon_i{}^{\infty})(2\varepsilon_i + \varepsilon_i{}^{\infty})}{4\pi N\varepsilon_i(\varepsilon_i{}^{\infty} + 2)^2}, \tag{3}$$

where $\varepsilon_i{}^{\infty} = 1.05n_i{}^2$; g – is the correlation factor characterizing the association tendency. For non-associating systems g is equal to 1. The data collated in table V reveal that compounds **1–3** and **1–8, 2–12** and **2–13** exhibit the values of g which are smaller than 1, indicating an antiparallel association. The replacement of the cyano group by the isothiocyanato group in 2,5-disubstituted pyridine derivatives and 4,4′-disbstituted biphenyls increases the factor g, i.e. lowers the association tendency. Similar results have been reported for other liquid crystalline isothiocyanates.(75)

4. OPTICAL PROPERTIES

The phenomenological relation between the refractive index and the electric polarization is defined as(76,77):

$$(n^{*2} - 1)/(n^{*2} + 2) = N\alpha^{*}/3\varepsilon_O, \tag{4}$$

where the mean polarizability $\alpha^{*} = (\alpha_{\parallel} + 2\alpha_{\perp})\ /\ 3$; the mean refractive index $n^{*2} = (n_e{}^2 + 2n_o{}^2)\ /\ 3$; n_o is the ordinary and n_e is the extraordinary refractive indices. From equation (4) and previous paragraph, it follows that the NCS substituted compounds which have a larger induced polarizability of their highly conjugated π-electron system exhibit the optical anisotropy $\Delta n = n_e - n_o$ which is much larger than that of the corresponding cyano derivatives {compounds **1–3** and **1–8, 2–12** and **2–13, 5–1** and **5–2**, **5–3** and **5–4**, table V and the references(26, 27, 29, 44, 69)}.

Similar results have been found for other liquid crystalline isothiocyanates:

Compound **2–1**	$\Delta n = 0.254^{*}$, reference(12)
Compound **2–2**	$\Delta n = 0.214^{*}$, reference(12)

*Extrapolated from 10 wt % solution in ZLI-1132 at 20 °C

Compound **2–14**	$\Delta n = 0.163$, $T_{\text{meas}} = T_{\text{N-I}} - 10$ °C, reference(27)
Compound **2–15**	$\Delta n = 0.092$, $T_{\text{meas}} = T_{\text{N-I}} - 10$ °C, reference(28)

These can be explained in terms of a reduction the effective conjugation length of π-electron system resulting in shorter resonance wavelength of UV absorption spectrum for the liquid crystals having terminal CN group than for the corresponding NCS derivatives.(69)

5. VISCO-ELASTIC PROPERTIES

It has been shown that the nematic liquid crystalline materials for display applications should have a low viscosity for giving the acceptable response times to Liquid Crystal Displays.(1, 78) According to the results on the kinematic viscosity ν presented in table V (compounds **1–3** and **1–8**) and the reference,(71) the isothiocyanato derivatives show lower values of the viscosity in comparison with those of the corresponding cyano derivatives:

4-(trans-4′-propylcyclohexyl)isothiocyanatobenzene

$\nu = 8\ \mathrm{mm^2 s^{-1}}$, extrapolated from 10 wt % solution in ZLI-1132 at 20 °C, reference(69)

4-(trans-4′-propylcyclohexyl)cyanobenzene

$\nu = 20\ \mathrm{mm^2 s^{-1}}$, extrapolated from 10 wt % solution in ZLI-1132 at 20 °C, reference.(79)

The viscous behavior of cyano derivatives can be explained in terms of changed association tendency(80) expressed by the the correlation coefficient g (see paragraph 3). It has been shown that for the fifth and greater homologues of two-ring cyano derivatives the balance in the monomer-dimer system 2M ↔ D is biased towards dimers which define the liquid crystal properties.(7, 54, 81)

In combination with the better development of the monomeric density wave as compared to the dimeric one {for most NCS derivatives and two-ring OCF_3 derivatives which also have a lower viscosity than the corresponding CN derivatives(13,37,82)}, it can be proposed that for the isothiocyanato derivatives the balance in the monomer-dimer system 2M ↔ D (considering the data on the correlation factor g in table V) is biased towards monomers which define the liquid crystal properties. The similar effects on their viscous properties of introducing the NCS group in the terminal position of the molecular cores of other liquid crystalline derivatives have been found in the reference.(71)

The elastic constant ratio K_{33} / K_{11} of liquid crystalline materials is very important parameter for Super Twisted Nematic-Liquid Crystal Displays (STN-LCDs), defining their electro-optical performance.(83)

It is evident from table V and the reference(26) *that the replacement of terminal* NCS group by the CN group increases the ratio K_{33} / K_{11}. It corresponds to an increase in the period of dimeric density wave d_2 (obtained from X-ray diffraction experiment) for two-ring trans-1,4-disubstituted cyclohexylene cyano derivatives in comparison with that of the corresponding isothiocyanato derivatives(7,22) and can be explained in terms of a linear proportionality between the ratio K_{33} / K_{11} and the squared dimeric density wave period d_2^2.(7,81)

The similar effects on their elastic properties of introducing the NCS group in the terminal position of the molecular cores of other liquid crystalline derivatives have been reported in the references.(14, 26)

6. MOLECULAR PACKING

It has been shown that liquid crystal molecular packing plays a very important role in creation of their mesophases(55) and defines their optical properties.(76) Molecular packing coefficient is expressed in(84) as:

$$k_p = N_A V_\rho / M, \qquad (5)$$

where N_A is Avogadro number, ρ is the density, M is the molecular weight, V is intrinsic (van der Waals) volume of the molecule, calculated from the van der Waals volume increments of the individual atoms or by using the average atomic radii and chemical bond lengths.(85)

As can be seen from table V, the NCS derivatives exhibit a higher molecular packing than the corresponding CN derivatives (compounds **1–3** and **1–8, 5–1** and **5–2**). Similar results have been found for other NCS derivatives (table II):

Compound **2–14** $k_p = 0.6472$, $T_{meas} = 40$ °C, references(27, 85)

Compound **2–15** $k_p = 0.6333$, $T_{meas} = 40$ °C, reference(84)

These results can be associated with the difference in the energy of intermolecular interactions {and therefore with the difference in the activation energy of the rotational viscosity of these compounds(84)}

CONCLUSION

Systematic studies on the effect of terminal substitution of calamitic liquid crystals by the NCS and SCN groups on the creation of the mesophases and their physico-chemical properties have been performed, with attempts to correlate the molecular level parameters with the observed properties. The information here presented may lead to a better understanding of the nature of liquid crystals.

Acknowledgements

V. F. Petrov would thank Osaka National Research Institute and STA for providing an opportunity to work with Osaka National Research Institute under the STA Fellowship Program.

References

(1) M. Schadt, Displays, **13**, 11 (1992).
(2) V. F. Petrov, *Proc. SPIE*, **2408**, 84 (1995).
(3) A. I. Pavluchenko, G. V. Purvanyatskas, N. I. Smirnova, M. F. Grebyonkin, V. F. Petrov, M. I. Barnik, V. V. Titov, A. V. Ivaschenko, N. I. Korotkova, E. I. Kovshev, A. Z. Rabinovich, N. A. Bumagin, N. P. Andrjukhova, I. P. Beletskaya, S. D. Maltsev, and V. V. Titov, PCT WO 88/7992, 1988.
(4) A. I. Pavluchenko, V. F. Petrov, M. F. Grebyonkin, A. V. Ivaschenko, N. I. Korotkova, N. I. Smirnova, L. V. Kruchkova, L. A. Karamysheva, I. F. Agafonova, P. P. Dakhnov, R. Kh. Geyvandov, E. P. Pozhidaev, and B. M. Bolotin, Eur. Pat. Appl., EP 374 849, 1989.
(5) A. I. Pavluchenko, N. I. Smirnova, V. F. Petrov, M. F. Grebenkin, and V. V. Titov, *Mol. Cryst. Liq. Cryst.*, **209**, 155 (1991).
(6) M. F. Grebenkin, V. F. Petrov, V. V. Belyaev, A. I. Pavluchenko, N. I. Smirnova, E. I. Kovshev, V. V. Titov, and A. V. Ivashchenko, *Mol. Cryst. Liq. Cryst.*, **129**, 245 (1985).
(7) M. F. Grebenkin, V. F. Petrov, and B. I. Ostrovskii, *Liq. Crystals*, **7**, 367 (1990).
(8) S. Takenaka, Y. Sakurai, H. Takeda, T. Ikemoto, H. Miyake, S. Kusabayashi, and T. Takagi, *Mol. Cryst. Liq. Cryst.*, **178**, 103 (1990).
(9) H. Takeda, Y. Sakurai, S. Takenaka, H. Miyake, T. Doi, S. Kusabayashi, and T. Takagi, *J. Chem. Soc. Faraday Trans.*, **86**, 3429 (1990).
(10) Y. Sakurai, S. Takenaka, H. Sugiura, S. Kusabayashi, Y. Nishihata, H. Terauchi and T. Takagi, *Mol. Cryst. Liq. Cryst.*, **201**, 95 (1991).
(11) H. Sugiura, Y. Sakurai, Y. Masuda, H. Takeda, S. Kusabayashi, and S. Takenaka, *Liq. Crystals*, **9**, 441 (1991).
(12) A. I. Pavluchenko, N. I. Smirnova, V. F. Petrov, Yu. A. Fialkov, S. V. Shelyazhenko, and L. M. Yagupolskii, *Mol. Cryst. Liq. Cryst.*, **209**, 225 (1991).
(13) T. A. Lobko and B. I. Ostrovskii, *Mol. Mats.*, **1**, 99 (1992).
(14) M. Schadt, R. Buchecker, A. Villiger, F. Leenhouts, and J. Fromm, *IEEE Trans. Electron De.*, **ED-33**, 1187 (1986).
(15) A. Boller, M. Cereghetti, M. Schadt, and H. Scherrer, *Mol. Cryst. Liq. Cryst.*, **42**, 215 (1977).
(16) K. Czuprynski, R. Dabrowski, J. Baran, A. Zywocinski, and J. Przedmojski, *J. Physique*, **47**, 1577 (1986).
(17) H. M. Vorbrodt, S. Deresch, H. Kresse, A. Wiegeleben, D. Demus, and H. Zaschke, *J. Prakt. Chem.*, **323**, 902 (1981).
(18) M. J. Bradshaw, E. P. Raynes, I. Fedak, and A. J. Leadbetter, *J. Physique*, **45**, 157 (1984).
(19) J. van der Veen, *J. Physique Colloque*, **37**, C3–13 (1976).
(20) R. Dabrowski, J. Dziaduszek, and T. Szczucinski, *Mol. Cryst. Liq. Cryst.*, **102**, 155 (1984).
(21) G. W. Gray, *J. Physique Colloque*, **36**, C1–337 (1975).

(22) P. Sarkar, P. Mandal, S. Paul, P. Paul, R. Dabrowski, and K. Czuprynski, *Mol. Cryst. Liq. Cryst.*, **330**, 159 (1999).

(23) L. Pohl, R. Eidenschink, G. Krause, and D. Erdmann, *Phys. Lett.*, **A60**, 421 (1977).

(24) R. Dabrowski, J. Dziaduszek, and T. Szczucinski, *Mol. Cryst. Liq. Cryst. Lett.*, **102**, 155 (1984).

(25) R. Dabrowski, J. Dziaduszek, W. Drzewinski, K. Czuprinski, and Z. Stolarz, *Mol. Cryst. Liq. Cryst.*, **191**, 171 (1990).

(26) R. Buchecker and M. Schadt, *Mol. Cryst. Liq. Cryst.*, **149**, 359 (1987).

(27) J. W. Baran, Z. Raszewski, R. Dabrowski, J. Kedzierski, and J. Rutkowska, *Mol. Cryst. Liq. Cryst.*, **123**, 237 (1985).

(28) S. Sen, K. Kali, S. K. Roy, and S. B. Roy, *Mol. Cryst. Liq. Cryst.*, **126**, 269 (1985).

(29) H. Herba, B. Zywicki, G. Czechowski, D. Bauman, A. Wasik, and J. Jadzyn, *Acta Phys. Pol. A*, **87**, 985 (1995).

(30) G. W. Gray and S. M. Kelly, *J. Chem. Soc. Perkin Trans.* II, 26 (1981).

(31) D. A. Dunmur and A. E. Tomes, *Mol. Cryst. Liq. Cryst.*, **97**, 241 (1983).

(32) V.F. Petrov, Ph. D. Thesis, Organic Intermediates and Dyes Institute, Moscow, 1990.

(33) G. J. Cross, A. J. Seed, K. J. Toyne, J. W. Goodby, M. Hird, and M. C. Artal, *J. Mater. Chem.*, **10**, 1555 (2000).

(34) M. Schadt, M. Petrzilka, P. R. Gerber, and A. Villiger, *Mol. Cryst. Liq. Cryst.*, **122**, 241 (1985).

(35) M. Petrzilka, M. Schadt, and A. Villiger, US Patent 4 980 486, 1990.

(36) R. Eidenschink, *Mol. Cryst. Liq. Cryst.*, **94**, 119 (1983).

(37) E. Bartmann, D. Dorsch, U. Finkenzeller, H. A. Kurmeier, and E. Poetsch, 19 Freiburger Arbeitstagung Flussigkristalle, P. 8, 1990.

(38) S. Urban, R. Dabrowski, J. Dziaduszek, J. Janik, and J. K. Moscicki, *Liq. Crystals*, **26**, 1817 (1999).

(39) T. Kojima, M. Tsuji, and S. Sugimori, German Pat. Appl., DE 3 223 637, 1982.

(40) S. Sugimori, T. Kojima, and M. Tsuji, German Pat. Appl., DE 3 139 130, 1982.

(41) R. Dabrowski, J. Dziaduszek, T. Szczucinski, and Z. Raszewski, *Mol. Cryst. Liq. Cryst.*, **107**, 411 (1984).

(42) T. Sawada, H. Satonaka, and I. Arai, Proceedings of the 11th Japanese Liquid Crystal Conference, p. 190, 1985; R. Dabrowski, J. Dziaduszek, T. Szczucinski, Z. Stolarzowa, and K. Czuprynski, *Liq. Crystals*, **5**, 209 (1989); R. Dabrowski, *Mol. Cryst. Liq. Cryst.*, **191**, 17 (1990); V. S. Bezborodov, V. F. Petrov, and V.I. Lapanik, *Liq. Crystals*, **20**, 785 (1996).

(43) R. Dabrowski, K. Czuprynski, J. Przedmojski, J. Baran, J, Jadzyn, and G. Czechowski, *Mol. Cryst. Liq. Cryst.*, **249**, 51 (1994).

(44) A. J. Seed, K. J. Toyne, J. W. Goodby, and D. G. Mcdonnell, *J. Mater. Chem.*, **5**, 1 (1995).

(45) H. Okamoto, M. Hayashi, and S. Takenaka, *Liq. Crystals*, **20**, 647 (1996).

(46) H. Okamoto, M. Hayashi, and S. Takenaka, *Bull. Chem. Soc. Jpn.*, **69**, 1437 (1996).

(47) M. Duan, T. Tasaka, H. Okamoto, V. F. Petrov, and S. Takenaka, *Liq. Crystals*, **27**, 1195 (2000).

(48) G. Sigaud, H. T. Nguyen, F. Hardouin, and H. Gasparoux, *Mol. Cryst. Liq. Cryst.*, **69**, 81 (1981).

(49) H. T. Nguyen, *Mol. Cryst. Liq. Cryst.*, **127**, 143 (1985).

(50) D. Coates and G. W. Gray, *Mol. Cryst. Liq. Cryst.*, **31**, 275 (1975).

(51) H. Okamoto, V.F. Petrov, and S. Takenaka, *Liq. Crystals*, **26**, 691 (1999).

(52) W. Maier and A. Saupe, *Z. Naturforsch.*, **14a**, 882 (1959).

(53) D. A. Dunmur and A. E. Tomes, *Mol. Cryst. Liq. Cryst.*, **97**, 241 (1983).

(54) V. F. Petrov, S. I. Torgova, L. A. Karamysheva, and S. Takenaka, *Liq. Crystals*, **26**, 1141 (1999).

(55) M. A. Osman, *Z. Naturforsch.*, **38A**, 693 (1983).

(56) M.A. Osman and L. Revesz, *Mol. Cryst. Liq. Cryst., Lett.*, **82**, 41 (1982).

(57) C. I. Beard and B. P. Dailey, *J. Am. Chem. Soc.*, **71**, 929 (1949).

(58) M. D. Danford and R. L. Livingston, *J. Am. Chem. Soc.*, **77**, 2944 (1955).

(59) L. Pauling, *The Nature of The Chemical Bond* (Cornell University Press, New York, 1960), p. 269f.

(60) J. W. Rabalais, J. M. McDonald, V. Scherr, and S. P. Glynn, *Chem. Rev.*, **71**, 73 (1971).

(61) Hp. Schad and M.A. Osman, *J. Chem. Phys.*, **75**, 880 (1981).

(62) G. J. Brownsey and A.J. Leadbetter, *Phys. Rev. Lett.*, **44**, 1608 (1980).

(63) V. F. Petrov, S. A. Ivanov, M. F. Grebenkin, and A. I. Pavluchenko, *Rus. J. Phys. Chem.*, **64**, 421 (1990).

(64) B. I. Ostrovskii, A. I. Pavluchenko, V. F. Petrov, and M. A. Saidachmetov, *Liq. Crystals*, **5**, 513 (1989).

(65) V. F. Petrov, M. F. Grebenkin, A. I. Pavluchenko. and N. I. Smirnova, *Rus. J. Phys. Chem.*, **65**, 447 (1991).

(66) W. H. de Jeu, *Phil. Trans. R. Soc. A*, **309**, 217 (1983).

(67) V. T. Grachev, B. E. Zaitsev, E. M. Itskovich, A. I. Pavluchenko, N. I. Smirnova, V. V. Titov, and K. M. Djumaev, *Mol. Cryst. Liq. Cryst.*, **65**, 133 (1981).

(68) W. Maier and G. Meier, Z. *Naturforsch.* A, **16**, 262.

(69) S. T. Wu, E. Ramos, and U. Finkenzeller, *J. Appl. Phys.*, **68**, 78 (1990).

(70) A. L. McClellan, *Tables of Experimental Dipole Moments* (W. H. Freeman and Company, San Francisco and London, 1963).

(71) R. Dabrowski, J. Dziaduszek, and T. Szczucinski, *Mol. Cryst. Liq. Cryst.*, **124**, 241 (1985).

(72) I. T. Shabatina, T. V. Khasanova, E. V. Vovk, and G. V. Sergeev, *Thin Solid Films*, **284–285**, 573 (1996).

(73) K. Toriyama and D. A. Dunmur, *Mol. Phys.*, **56**, 479 (1985).

(74) D. A. Dunmur and P. Palffy-Mohoray, *Mol. Phys.*, **76**, 1015 (1992).

(75) P. Kedziora and J. Jadzyn, *Mol. Cryst. Liq. Cryst.*, **192**, 31 (1990).

(76) W.H. de Jeu, *Physical Properties of Liquid Crystalline Materials* (Gordon & Breach, New York, 1980).

(77) W. H. de Jeu, C. J, Gerristma, P. van Zanten, and W. A, Goosens, *Phys. Lett.*, **39A**, 355 (1972).

(78) E. Jakeman and E. P. Raynes, *Phys. Lett.*, **39A**, 69 (1972).

(79) V. F. Petrov, M. F. Grebenkin, L. A. Karamysheva, and R. Kh. Geivandov, *Rus. J. Phys. Chem.*, **65**, 716 (1991).

(80) A. Raviol, W. Stille, and G. Strobl, *J. Chem. Phys.*, **103**, 3788 (1995).

(81) A. I. Pavluchenko, V. F. Petrov, and N. I. Smirnova, *Liq. Crystals*, **19**, 811 (1995).

(82) T. A. Lobko. B. I. Ostrovskii, A. I. Pavluchenko, and S. N. Sulianov, *Liq. Crystals*, **15**, 361 (1993).

(83) S. C. Guy, Displays, 32, 1993.

(84) V. V. Belyaev, M. F. Grebyonkin, and V. F. Petrov, *Rus. J. Phys. Chem.*, **64**, 509 (1990).

(85) A. Bondi, *Physical Properties of Molecular Crystals, Liquids, and Glasses* (John Wiley & Sons, New York, 1968).