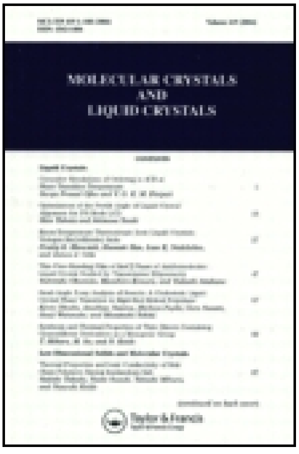

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Isothiocyanates and their Mixtures with A Broad Range of Nematic Phase

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ISOTHIOCYANATES AND THEIR MIXTURES WITH A BROAD RANGE OF NEMATIC PHASE*

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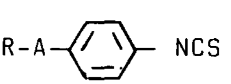
Abstract Results referring to liquid crystalline isothiocyanates especially as components of liquid crystal mixture were summarized. The outstanding feature of liquid crystalline isothiocyanates is the possibility to make mixtures with a wide range of nematic phase low viscosity and weak temperature dependence of viscosity. The compounds exhibit good chemical stability; they are especially resistant to humidity and UV radiation. Their thermal stability is not extremely high but this disadvantage is overcome by a suitable selection of the mixture components.

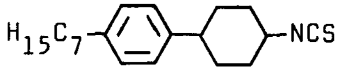
Investigations conducted in my laboratory, as well as those conducted in other laboratories shown that liquid crystalline isothiocyanates are a family of liquid crystal compounds atractive from the applicational point of view. Several invention in this field have been filled in the Patent Offices, by us[1] as well as by manufacturers of liquid crystals: Hoffmann La Roche[2], Merck[3], and Chisso[4] and others[5,6].

Almost all the liquid crystal isothiocyanates so far prepared and tested are derivatives of phenylisothiocyanates,



(1)

wherein the moiety A is a combination of different kinds of rings and bridging groups usually used for bulding liquid crystalline molecules. From among other isothiocyanates so far only single examples of cyclohexylisothiocyanates are known:



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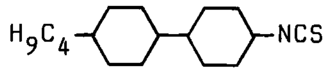
T_m=43°C, $T_c \sim$(-20°C) , ref.(7)



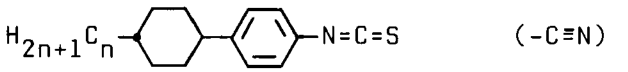
(3)

T_m=23°C, T_c=72.9°C , ref.(3c)

The attractiveness of isothiocyanates as materials for displays will become more obvious if we compare their physicochemical properties with those of analogous cyano compounds, Table 1. The derivatives of cyclohexylbenzene are the most suitable for this purpose in view of their importance and strongly exhibited nematic character.

The bulk viscosity of 4-(isothiocyanatophenyl)-1-(trans-4-alkyl)cyclohexane (n-CHBT) is almost half that of 4-(cyanophenyl)-1-(trans-4-alkyl)cyclohexane (n-PCH) and its bend elastic constant (k_{33}) is also by almost twice smaller, and hence the ratio of the bend to splay elastic constants (k_{33}/k_{11}) is also small. The -NCS compound has a somewhat smaller dipole moment as compared with the -CN group.[9] Therefore the isothiocyanates exhibit a lower dielectric anisotropy than the cyano compounds, but their birefringence Δn are higher.[10] Similar relations are observed between the physicochemical properties when nematic pairs of compounds of other homologous series are compared.[8] This is due to the different association ability of compounds with the terminal groups -NCS and -CN. Isothiocyanates do not form dimers in mesogenic state or if so, the concentration of the latter is small. In distinction to isothiocyanato cyano compounds form in the isotropic, nematic and smectic phases dimers with antiparallel orientation of the cyano group dipoles. The degree of dimerization depends on the molecular structure of the mesogene and the solvent. The differences in the near ordering of the nematic phases of isothiocyanato and cyano compounds are the reason why the properties of their mixtures do not show additivity.

TABLE I Comparison of the physical properties of 4-(isothiocyanatophenyl)-1-(trans-4-hexyl)cyclohexane (6CHBT) and 4-(cyanophenyl)-1-(trans-4-pentyl)cyclohexane (5PCH) at 22°C

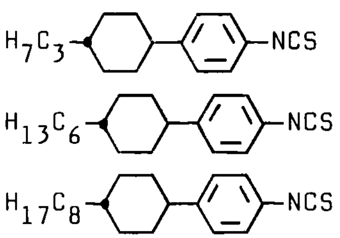


n-CHBT (n-PCH)

Properties, 22°C	6CHBT	(5PCH)
1. Dipole moment, $\mu(10^{-30}$C m)	11.2	15.6
2. Dielectric constant: $\varepsilon_{\parallel}$	12.0	17.0
$\varepsilon_{\perp}$	4.0	4.8
$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$	8.0	12.2
3. Refractive indeces: n_o	1.52	1.49
n_e	1.67	1.61
$\Delta n = n_e - n_o$	0.15	0.12
4. Bulk viscosity, η (mPa·s)	13.3	21.5
5. Rotational viscosity γ (mPa·s)	83	123
6. Elastic constant: $k_{11}(10^{-12}$N)	8.57	8.98
k_{22}	3.70	4.73
k_{33}	9.51	18.3
k_{33}/k_{11}	1.11	2.03
$k = k_{11} + (k_{33} - 2k_{22})/4$	9.1	11.2
7. Visco-elastic ratio, γ/k (10^{10} sm^{-2})	0.91	1.14
8. Decay time, t_{off}(ms)	41	43
9. Treshold, V_{10}(volt)	1.63	1.55

Raszewski found for instance, that the parallel component of the effective dipole moment ($\mu_{\parallel}$) of the mixture of 6CHBT and 5CB shows a positive deviation[11] what results from the decomposition of the antiparallel 5CB molecule dimers. The lowering of the dimer concentration results in in the lowering of viscosity, threshold voltage, the k_{33}/k_{11} ratio, etc. of the mixtures. These effects are accompanied by a negative effect, i.e. increased mobility of current carriers. The mixtures composed of isothiocyanato and cyano compounds exhibit a higher electric conductivity than the individual components.

The compounds of the n-CHBT homologous series[1a,12] are those of the so far known isothiocyanates which are the most suitable for obtaining base mixtures with low melting point. The compound with the propyl substituent deserves particular attention since it reveals a very low melting enthalpy and the compound with the hexyl substituent as the latter has very low melting point.
For obtaining the base mixture we usually use propyl, hexyl and octyl derivatives. The ternary eutectic mixture obtained from the above three mentioned compounds

I


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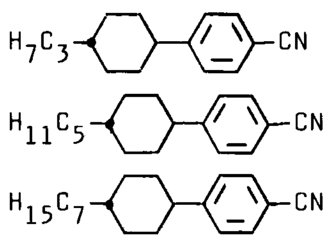
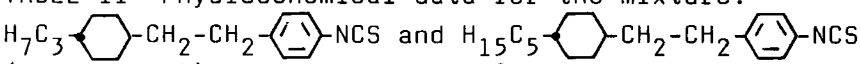


has the following properties:	I	II
Melting point (°C)	-8	-5
Clearing point (°C)	41.5	52
$\eta_{20°}$ (mPa·s)	11	21
E_a of η (eV)	0.28	0.31
Δn	0.17	0.14
$\Delta\varepsilon$	7.9	10,6
V_{10} (volt)	1.6	1.75

The theoretic melting point of mixture I is -8°C but it becomes easily supercooled to -25°C and even lower. Besidies the temperature dependence of viscosity is lower as compared with the analogous mixture II composed of PCH compounds.

Low-melting eutectic mixtures can also be obtained from compounds belonging to the 1-(4-trans-alkylcyclohexyl)-2-(4-isothiocyanatophenyl)ethane homologous series. As it was shown by Dr Schadt et al.[8], these compounds have a higher value elastic constant ratio k_{33}/k_{11} but their visco-elastic ratio is smaller and hence the time of switching of the liquid crystal cell is shorter, see properties of the bicomponent mixture, Table II.

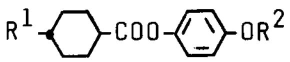
TABLE II Physicochemical data for the mixture:



(40:60 mole%) at temperature 22°C

η	γ	k	γ/k	V_{10}	t_{off}	T_c
(mPa·s)	(mPa·s)	(10^{-12}N)	($\cdot 10^{10}$s m^{-2})	(volt)	(ms)	(°C)
11.5	105	15.2	0.69	2.18	21	43.4

The workers of the Hoffmann La Roche laboratory have shown, besides that the phase transition points, viscosities and elastic constants of the above discused isothiocyanates (and also of other compounds) may be varied in a wide range by introducing a double bond into the alkyl side chain[13]. It makes possible to obtain from cyclohexylphenyl and cyclohexylethylphenylisothiocyanates base mixtures with very differentiated visco-elastic properties and clearing points in the range of 40-50°C and melting points down to -40°C. Compounds of the mentioned n-CHBT series can be obtained in a state of high purity. The most difficult to purify member of this series, 6CHBT, when is purified by a standart procedure consisting of distillation and crystallization shows a specific resistivity exceeding 10^{11}ohm cm. The conductivity may be effectively lowered and the temperature stability increased by passing the liquid crystal through a layer of alumina, silicagel and active carbon[14]. Besides, the conductivity may be effectively lowered by dilution with compounds of low polarity. Very suitable for this purpose are esters of alkylcyclohexanecarboxylic acids and hydrocarbons, for example the compounds: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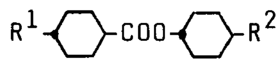
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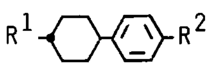
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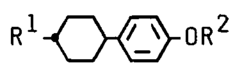
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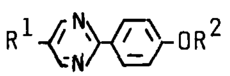
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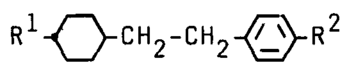
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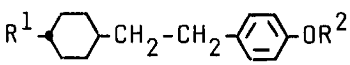
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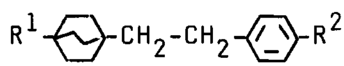
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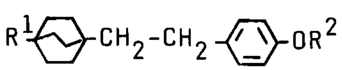
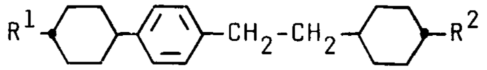

(12)

The low viscosity of isothiocyanato compounds also allows to use for this purpose compounds of higher viscosity, as for instance, bicyclo(2,2,2)octane or pyrimidine derivatives.

Cyano compounds are less advantageous as components of isothiocyanato mixtures, especially in cases when these mixtures are to operate at higher temperatures or when the cyano compounds are mixed with unsufficiently purified isothiocyanates[14].

In order to obtain mixtures with clearing points above 50°C one should add to mentioned two ring isothiocyanato base mixtures additional components exhibiting high clearring points. Most suitable for this purpose are high clearing isothiocyanates, fluoro compounds, ethers, esters and hydrocarbons. These groups of compounds make it possible to obtain mixtures of highest stability and lowest conductivity. By using solely isothiocyanates mixtures are obtained of lowest viscosities but of high optical anisotropy 0.16.

Mixtures of moderate anisotropy, 0.1 - 0.16 are obtained by adding in adequate properties such compounds as, for example: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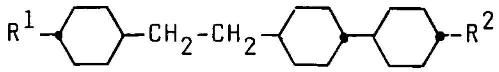
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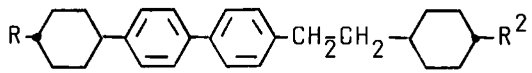
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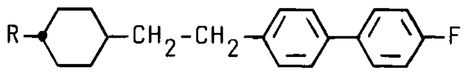
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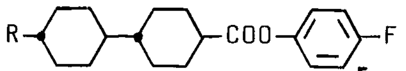
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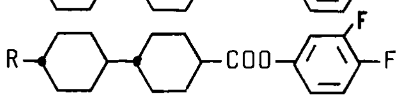
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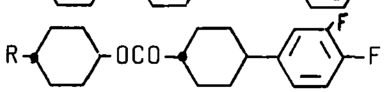
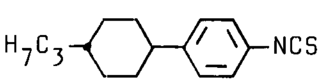
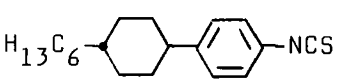
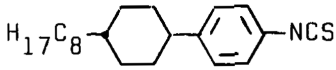
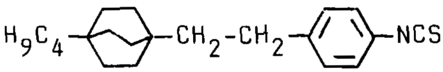

(19)

The increase of the amount of non-polar compounds in the mixture contributes to the lowering of Δn and the raising of the threshold voltage proportionally to their concentration in the mixture.
High clearing isothiocyanates are two ring bicyclooctane derivatives or multiring compounds of other classes.

We synthetized several homologous series of compounds containing the bicyclooctane ring and met compounds of fairly low melting and often very low melting enthalpies[15]. Low melting enthalpies of bicyclooctane derivatives ensure them very good solubility in mixtures and allow to obtain eutectic mixtures with low melting points. For instance, the quaternary mixture has a following properties.

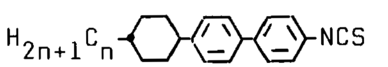
Composition	wt%	Properties, 20°C	
	29.16	T_m	-18
	27.70	$T_{N\rightarrow I}$	61

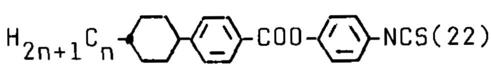
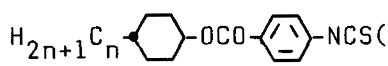
 9.34

 33.80

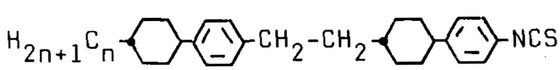
η (mPa·s)	12.9
E_a (eV)	0.31
$\Delta\varepsilon$	7.3
Δn	0.20
V_{10}(volt)	1.8
V_{90}(volt)	2.7
T_{off}(ms)	40
T_{on}(ms)	60

Mixtures with low viscosity including mentioned two ring isothiocyanato bicyclooctane derivatives have not high clearing points. To obtain mixtures of a broader nematic range and low viscosity at low temperatures other compounds should be considered as components raising the claearing point. In our laboratory, in that to Hoffmann La Roche and that of Chisso triring and tetraring compounds with and without bridging groups have been synthetized. The more interesting compounds are given below:

 (20)  (21)

 (22)  (23)

and especially compounds

 (24)

The compounds (24) exhibit the widest range of the nematic phase and lowest melting points and enthalpies. The strongly nematic character of this structure is also shown by that the smectic phase is observed for the members of the homologous series only with 8 or more carbon atoms in the alkyl tail[16], Table III, whereas in analogous cyano compounds it is observed already for compounds with a shorter alkyl chain[17].

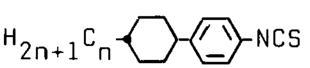
The compounds of this series have excellent solubilities in mixtures, the butyl and heptyl derivatives are outstanding in this respect.

TABLE III Phase transition temperatures (°C) and melting enthalpy ($kJmol^{-1}$) of compounds (24)

Transition temperature						ΔH_m
n	C_1	C_2	S_B	N	I	
2	* 83	* 105	-	* 249	*	9.9; 16.7
3		* 123	-	* 266	*	18.6
4		* 86.5	-	* 260	*	18.9
5		* 105	*	* 257	*	22.1
6	* 57	* 76	-	* 248	*	13.1; 14.6
7	* 52.5	* 78.5	-	* 244	*	2.1; 17.0
8		* 59	* 75	* 235	*	28.4
10		* 76.5	* 94	* 225	*	21.4

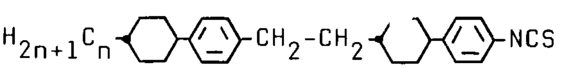
The former dissolves at room temperature and -10°C in amounts of 30 wt% and 15 wt%, respectively. These compounds raise effectively the clearing point of the base mixtures increasing only slightly the viscosity, the temperature dependence of viscosity is small. These compounds when used as components of mixtures yield mixtures with a nematic phase range of -40°C to 100°C and more and low temperature dependence of the threshold voltage. To illustrate this we can present as example the properties of the mixture:

1. Composition wt%



68

(n=3, 4, 6, 8)



32

(n=2, 4, 6)

2. Clearing point (°C) 111
3. Melting point (°C) -30
4. Viscosity, $\eta_{20°}$ (mPa·s) 15.4
5. Energy activation of η, Ea (eV) 0.31

6.	Threshold voltage V_{10} (volt)	2.0
7.	Saturation voltage V (volt)	2.9
8.	Temp.dependence of V_{10}(-20-60°C)(%/grad)	-0.26
9.	Optical anisotropy Δn	0.26
10.	Dielectric anisotropy $\Delta\varepsilon$	8.7
11.	Response time, t_{off}(ms)	60
12.	Decay time , t_{on} (ms)	40

CONCLUSION

Liquid crystal isothiocyanates make possible to obtain a wide assortment of liquid crystalline mixtures with high or moderate optical anisotropies and revealing good chemical stability and high displaying dynamics in a wide temperature range.

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