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Liquid Crystals

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New liquid-crystalline isothiocyanates with high clearing points, low viscosities and strong nematic character

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Bi-, tri- and tetra-ring liquid-crystalline compounds with an isothiocyanate group in the terminal position of the molecule and with an ethylene group in the central position have been synthesized. Phenyl, cyclohexyl, bicyclo[2,2,2]octyl, 1,3-dioxane and pyrimidinyl were used as the ring systems. Their transition temperatures and melting enthalpies have been determined. The relationship between the order of the rings in the molecule and the clearing points and melting points of the compounds is discussed. It is shown that these compounds are valuable components of liquid crystal mixtures, since they effectively raise their clearing points yet only have a small effect on the viscosity.

1. Introduction

Liquid crystal bi-ring compounds with the isothiocyanato (NCS) terminal group, especially the derivatives of cyclohexylbenzene and pyrimidine, are potentially an important family of compounds for use in displays. They have low melting points and low viscosities, and always reveal a lower value of the elastic constant ratio k_{33}/k_{11} than the analogous cyano derivatives [1, 2]. Our interest in isothiocyanates is now continued with the aim of finding such multi-ring compounds that would possess high clearing points, low viscosities and excellent solubility in mixtures composed of bi-ring compounds; especially those made of 4-(*trans*-4-alkylcyclohexyl)isothiocyanatobenzenes [1]. We have found that such properties are possessed by some compounds of the general formula



Their mesomorphic properties, synthesis and use as components of liquid crystal mixtures are considered here.

2. Results and discussion

2.1. Mesomorphic properties of the isothiocyanates

In table 1 the transition temperatures are compared for compounds of general formula **1** with different kinds of rings *A*, *B*, *C* and various values of *k*, *l*, *m*. The melting temperatures and enthalpies, as well as the clearing points of the compounds **1** depend not only on the kind and number of rings *A*, *B*, *C* in the molecule, but also decisively on their arrangement with respect to the central ethylene group. In bi-ring compounds ($k = 1$, $l = 0$ and $m = 0$)

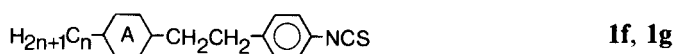
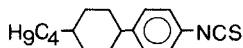


Table 1. Transition temperatures and melting enthalpy of compounds

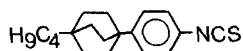
No.	<i>n</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>k</i>	<i>l</i>	<i>m</i>	Transition temperature/°C	$\Delta H_m/\text{kJ mol}^{-1}$
1a	5		X		1	0	1	C95.5N190I	
1b	5			X	1	1	0	C65N126I	33.9
	4			X				C ₁ 49C ₂ 61N113.5I	8.1, 15.8
1c	5			X	1	2	0	C123S _A 161.5N280I	19.5
1d	4				1	1	1	C86.5N260I	18.8
1e	5		X		1	0	1	C70S _A 120N183I	
1f	5		X	X	1	0	0	C38.5N47I	
	4		X	X				C23N33.5I†	
1g	4		X	X	1	0	0	C64N105.5I	10.4
1h	4		X		1	0	1	C138N256I	23.0
1i	4			X	1	1	0	C133N153I	
1j	4				1	1	1	C153N269I	29.0
1k	4		X		1	0	1	C58N110I	
	5		X					C69N119I	16.2
1l	4		X		1	0	1	C94N113I	35.5
1m	4			X	1	1	0	C ₁ 82C ₂ 87(S _B 83)N131I	3.3, 24.3
1n	4			X	1	1	0	C137S _A 142I	

† From [3].

only those compounds in which ring *A* is *trans*-substituted cyclohexyl (**1f**) or bicyclo[2,2,2]octyl (**1g**) are mesogenic. Compounds **1f** have clearing temperatures comparable with, and compounds **1g** even higher than, the compounds in which the cyclohexyl or bicyclo[2,2,2]octyl ring is directly attached to a phenyl ring (see compounds **2** and **3**)



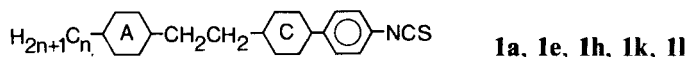
C 34.5°C (N32°C) I ([1])



C 93°C (N82°C) I

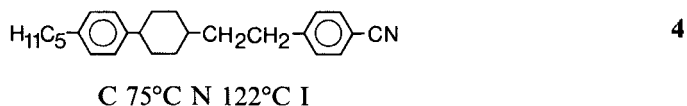
In analogous compounds with the cyano terminal group Gray and his colleagues observed identical correlations [4].

The regularity observed in bi-ring compounds is also characteristic of tri-ring systems **1**. Among the compounds with the subformula



only those in which the external ring *A* is a cyclohexyl or bicyclo[2,2,2]octyl ring have high clearing temperatures, irrespective of the character of the ring *C*. If the order is changed, and ring *A* becomes a phenyl ring, then irrespective of the character of ring *C*, whether it is aromatic or saturated (cyclohexyl, dioxane; **1,3**), the compounds possess low clearing temperatures.

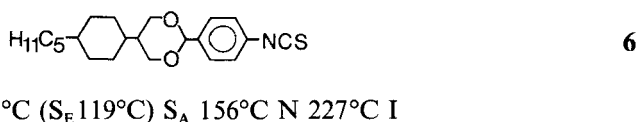
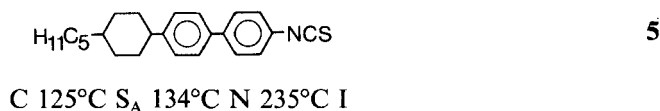
Clearing temperatures as low as those for the isothiocyanato compound **1k** have been observed by us for the cyano compound



Considering the results of Gray and co-workers [4, 5] and those of Takatsu *et al.* [6] for other liquid crystal derivatives of ethane with the CN or a halo terminal group we can conclude that for polar compounds (*Y* = NCS, CN, Cl, Br, etc.) only the arrangement of the rings



gives mesogens (for $m = 0$ and $m = 1$) with transition temperatures comparable with those of compounds without the ethylene-bridging group. In addition, when *Y* = NCS this bridging group reveals another advantageous effect in that the nematic properties of the compounds are better developed. This can be seen if we compare, for instance, the mesogenic properties of compounds **1a** and **1e** with those of the compounds



In compounds **5** and **6** we also observe a smectic A phase which is absent in **1a** or has a lower stability in **1e**. In cyano compounds with the central ethylene group the smectic phases are created more easily and they are observed already in compounds with shorter alkyl chains [4].

In tetra-ring compounds **1c**, **1d** and **1j** we do not observe significant differences in the clearing temperatures, but large differences occur in their melting points and the capacity of creating smectic phases. The lowest melting points, lowest melting enthalpy and the widest range of the nematic phase occur for compounds with the subformula

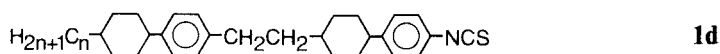


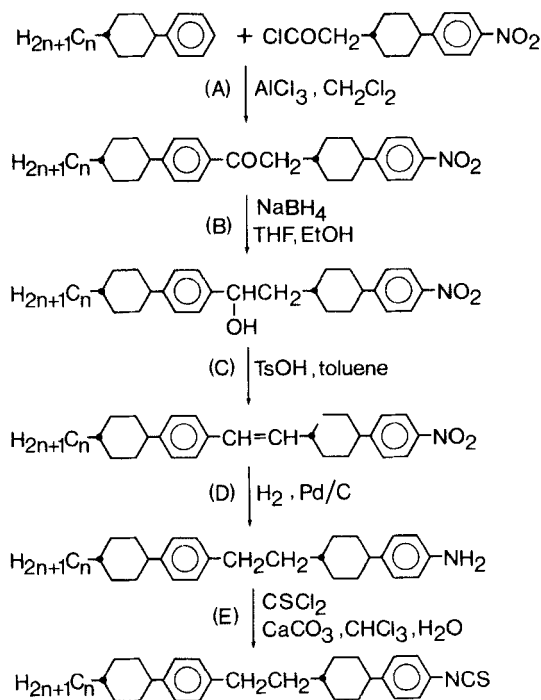
Table 2. Transition temperatures and melting enthalpy of compounds

<i>n</i>	Transition temperature/°C					Enthalpy/ kJ mol ⁻¹	
	C ₁	C ₂	S _B	N	I		
2	83	105		249		9.9	16.7
3		123		266			18.6
4		87.5		260			18.9
6	57	78		248		13.1	14.6
7	52.5	78.5		244		2.1	17.0
8		60	75	235			28.4
10		94	96	225			

for which the relevant data are summarized in table 2. The strong nematic character of compounds **1d** is demonstrated in that the smectic B phase is only observed for molecules with $n > 8$, whereas for similar cyano compounds it is observed for molecules with shorter alkyl chains ($n = 5$) [7]. We should also note the very low melting enthalpy of molecules of that size, especially with $n = 3, 4$ and 7 . This gives compounds **1d** excellent solubility in liquid crystal mixtures. For instance, compound **1d** ($n = 4$) dissolves in a mixture composed of compound **2** up to 30 wt % and 15 wt % at 20 and -10°C , respectively.

2.2. Synthesis

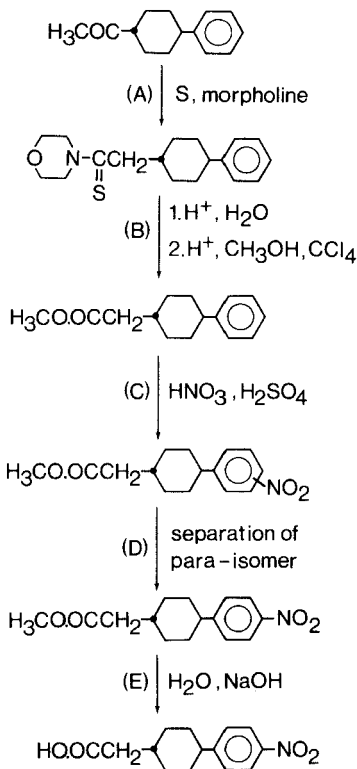
Scheme 1 shows the procedure developed by us to obtain compounds **1d** of high purity.



Scheme 1.

The yield of the final product depends largely on the purity of the substrates: *trans*-4-alkylcyclohexylbenzene and *trans*-4-(4-nitrophenyl)cyclohexylacetic acid. The procedure shown in scheme 1 is a multistep one, but it is not recommended to shorten it by reducing the ketone obtained in step A under the conditions of the Wolff-Kishner reaction, since it is difficult to isolate the amine obtained in a pure form. The procedure used also leads to many intermediate compounds which have liquid-crystalline properties and may, therefore, also be used for the synthesis of many attractive liquid crystal compounds, among them ones with long lateral substituents of the type described recently by Weissflog *et al.* [8]. The *trans*-4-alkylcyclohexylbenzene was obtained from *trans*-4-alkanoylcyclohexylbenzene which was isolated in a pure form from the mixture of *cis*- and *trans*-isomeres formed in the condensation reaction of alkanoyl chloride, benzene and cyclohexane [9].

The *trans*-4-(4-nitrophenyl)cyclohexylacetic acid was obtained according to scheme 2.



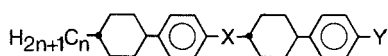
Scheme 2.

In this procedure the greatest difficulties were encountered in the separation of the mixture of *ortho*- and *para*-isomers formed in the process of nitrating *trans*-4-phenylcyclohexylacetic acid. Nitration of the methyl ester of this acid and not the free acid is recommended, because the separation of the *para*- from the *ortho*-isomer by crystallization presents no problems for the ester.

2.3. Mesomorphic properties of the intermediate compounds

Table 3 summarizes the transition temperatures of the compounds shown in scheme 1. The intermediate compounds with the terminal group $Y = \text{NO}_2$ and the

Table 3. Transition temperatures of compounds



No.	<i>n</i>	<i>X</i>	<i>Y</i>	Transition temperatures/°C
1	2	COCH ₂	NO ₂	C183N198I
2	3	COCH ₂	NO ₂	C175N217I
3	4	COCH ₂	NO ₂	C160N214I
4	6	COCH ₂	NO ₂	C152N219I
5	7	COCH ₂	NO ₂	C136N196I
6	8	COCH ₂	NO ₂	C130N201I
7	10	COCH ₂	NO ₂	C132N192I
8	2	CHOHCH ₂	NO ₂	C128N195I
9	3	CHOHCH ₂	NO ₂	C123N213I
10	4	CHOHCH ₂	NO ₂	C117N215-5I
11	6	CHOHCH ₂	NO ₂	C107N192I
12	8	CHOHCH ₂	NO ₂	C94N195-5I
13	10	CHOHCH ₂	NO ₂	C91S160N189I
14	2	CH=CH	NO ₂	C178N > 310decomp.
15	3	CH=CH	NO ₂	C183N > 310decomp.
16	4	CH=CH	NO ₂	C172N > 310decomp.
17	6	CH=CH	NO ₂	C143N > 310decomp.
18	7	CH=CH	NO ₂	C140N > 310decomp.
19	8	CH=CH	NO ₂	C139N > 310decomp.
20	10	CH=CH	NO ₂	C134N > 310decomp.
21	2	CH ₂ CH ₂	NH ₂	C180N209I
22	4	CH ₂ CH ₂	NH ₂	C176N222I
23	6	CH ₂ CH ₂	NH ₂	C169N214I
24	8	CH ₂ CH ₂	NH ₂	C170N202I
25	10	CH ₂ CH ₂	NH ₂	C164N192I

bridging group $X = -\text{CO}-\text{CH}_2-\text{CHOH}-\text{CH}_2-$, or $-\text{CH}=\text{CH}-$ produced in steps A, B and C are nematic for those members of the homologous series with $n = 2$ to $n = 10$ with the exception of the compound with $Y = -\text{CHOH}-\text{CH}_2-$ and $n = 10$ which also has a smectic phase. The amino derivative obtained in step D ($Y = -\text{NH}_2$, $X = -\text{CH}_2-\text{CH}_2-$) is also a nematic, which is rarely encountered. The presence of a nematic phase for compounds having a hydroxy group in the lateral position or an amine group in the terminal position allows us to suppose that the structure of the molecule does not favour the formation of intermolecular hydrogen bonds. Neither are smectic phases observed when two strongly smectogenic groups, $-\text{NO}_2$ and $-\text{CO}-$, are present simultaneously, this also suggests that the intermolecular attractive forces are weak.

2.4. Compounds 1 as components of liquid-crystalline mixtures

In table 4 the viscosity, measured at 20°C, of the base mixture A composed of three *trans*-4-(4-alkylcyclohexyl)-isothiocyanatobenzenes (CHBT) is compared with that of mixtures obtained by adding to mixture A compounds 1. All compounds 1 raise the clearing temperature of the base mixture significantly, and yet its viscosity is only slightly increased. Compound 1a affects the viscosity of the base mixture least, but its solubility is fairly low. Its 10 per cent solution is already supersaturated and so on

Table 4. The influence of 10 per cent of compounds **1** on the viscosity and the clearing temperature of the basic mixture A (comprising three 4-*trans*-(4-alkylcyclohexyl)isothiocyanatobenzenes in weight ratio C₃H₇:C₆H₁₃:C₈H₁₇ = 40:42:18)

	Compound in A	η (mPa s at 20°C)	$T_{Ni}/^{\circ}\text{C}$
	Mixture A	10.8	41.5
1a		10.8	50.0
1b		12.7	48.5
1d		12.1	61.0
1d		12.2	56.0
1g		11.5	47.5
1h		12.5	66.0
1m		11.6	50.0

Table 5. Viscosity (mPa s) and its temperature dependence.

Mixture	Nematic range	Temperature/ $^{\circ}\text{C}$						
		-10	0	10	20	30	40	50
A	-8† to 41.5	43.1	14.1	15.2	10.8	8.2	7.2	—
I	-30 to 111	89.9	34.6	25.7	15.4	10.3	7.5	5.8
II	-40 to 96	73.3	32.7	24.0	15.1	10.4	7.8	6.2

† Supercooled (-30°C).

longer storage crystals of compound **1a** precipitate. Compounds **1d** are the most soluble in the base mixture and so we consider them as the most suitable for making up mixtures with a wide nematic range (-40 to 100°C or above) and low viscosity. The viscosities of two examples of such mixtures are compared at various temperatures in table 5. Mixture I consists only of compounds CHBT and compounds **1d**, mixture II contains in addition compounds **1d** and tri-ring compounds **1b** and **1m**. The presence of the latter effects advantageously the properties of the mixture, lowering the dependence of viscosity on temperature. Compounds **1** are very favourable components of mixtures, since they allow us to obtain mixtures with a small dependence of the threshold voltage on temperature (0.2 – 0.3 per cent per $^{\circ}\text{C}$), which results from the low dependence of their viscosity on temperature.

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