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R. Dabrowski^a, J. Dziaduszek^a & T.

Szczuciński^a

^a Military Technical Academy, 00-908 Warsaw, Poland

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Mesomorphic Characteristics of Some New Homologous Series with the Isothiocyanato Terminal Group†

R. DABROWSKI, J. DZIADUSZEK and T. SZCZUCIŃSKI

Military Technical Academy, 00-908 Warsaw, Poland

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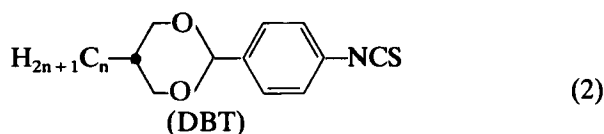
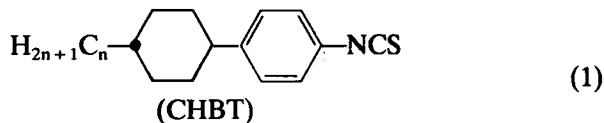
The synthesis is described and the mesomorphic properties have been tested for two homologous series of compounds with the isothiocyanato ($-\text{NCS}$) terminal group: 4-(*trans*-4'-*n*-alkylcyclohexyl)isothiocyanatobenzenes (CHBT— formula 1) and 5-*trans*-*n*-alkyl-2-(4'-isothiocyanatophenyl)-1,3-dioxans (DBT— formula 2). CHBT are nematics, and reveal low viscosity and low melting points, DBT are A_1 smectics. In this work, binary phase diagrams are presented for mixtures of CHBT or DBT with compounds with the $-\text{CN}$ terminal group. CHBT and DBT yield with the latter simple eutectics. Moreover, DBT when mixed with A_d smectics at an appropriate smectic layer spacing ratio, yield nematic mixtures. The suitability of CHBT as components of display mixtures is postulated.

INTRODUCTION

Various liquid crystal compounds including a 1,4-disubstituted cyclohexane ring or a 2,5-disubstituted 1,3-dioxan ring have been synthesized and tested in recent years.¹⁻⁶ Among these compounds, derivatives having the cyano group in the terminal position have gained particular interest as the principal components of many liquid crystal commercial mixtures for displays. These derivatives reveal low viscosity or low threshold voltage. When testing esters obtained from 4-(*trans*-4'-*n*-pentylcyclohexyl) benzoic acid and *para*-substituted phenols we found that the isothiocyanatophenyl ester has a wide range nematic phase,⁷ its clearing point being even higher than those of

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analogous esters with cyano or nitro groups. This encouraged us to synthesize and test the mesogenic properties of two homologous series of binuclear compounds with the isothiocyanato group instead of the cyano group in the terminal position: 4-(*trans*-4'-*n*-alkylcyclohexyl)-1-isothiocyanatobenzenes (CHBT— formula 1) and 5-*trans*-*n*-alkyl-2-(4'-isothiocyanatophenyl)-1,3-dioxans (DBT— formula 2)



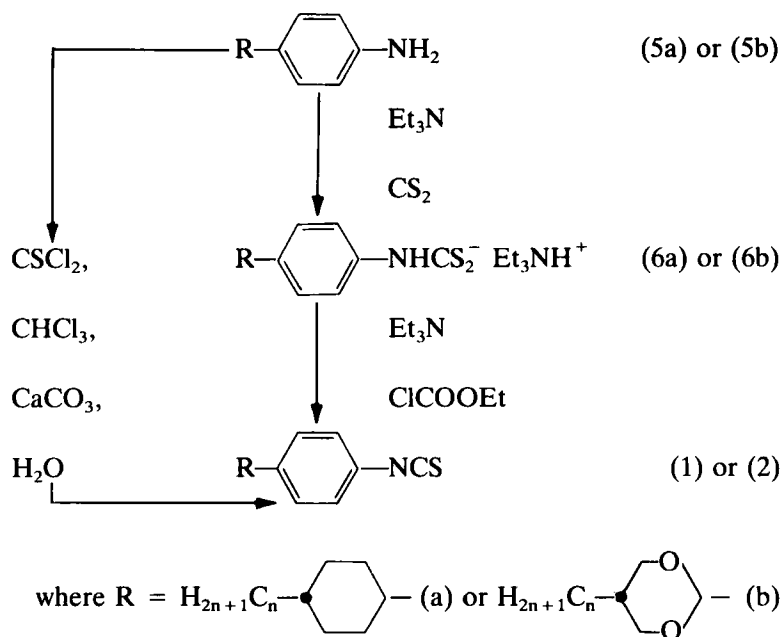
The mesogenic properties of both series of compounds proved very interesting. CHBT are low melting nematics, and DBT have an A_1 smectic phase of high thermal stability. These properties are quite unexpected if we compare them with those found for two other series of compounds with the isothiocyanato group: 4-*n*-alkyl-4'-isothiocyanatobiphenyls^{8,9} (formula 3) and 4'-isothiocyanatophenyl 4-*n*-alkylbenzoates⁸ (formula 4). The above mentioned biphenyl derivatives (3) only reveal a highly ordered smectic E phase, while the esters (4) are mainly monotropic A_1 smectics with fairly high melting points.¹⁰ In a short report¹⁰ we have discussed some properties of the compounds (1). In the present paper we discuss the properties of the compounds (1) in greater detail and describe for the first time the properties of the compounds (2).

EXPERIMENTAL

Preparation of materials

Compounds (1) and (2) have been obtained from the corresponding 4-(*trans*-4'-*n*-alkylcyclohexyl)anilines (5a) or 5-*trans*-*n*-alkyl-2-(4'-aminophenyl)-1,3-dioxans (5b) by treating these compounds with dicyclohexylcarbodiimide, thiophosgene or carbon disulfide in the presence of a tertiary amine followed by treatment with ethyl or methyl

chloroformate according to generally known methods.¹¹ The method involving carbon disulfide (scheme 1), in which a crystalline triethylammonium dithiocarbamate salt (6a) or (6b) is obtained as an intermediate product, allows one to obtain particularly pure compounds (1) and (2).



Scheme 1—conversion of amines into isothiocyanates

Amine (5a) was prepared by alkaline hydrolysis of acetanilides obtained from 4-(*trans*-4'-alkylcyclohexyl)acetophenones through reaction with sodium azide.¹²

Amine (5b) was obtained by reduction of *trans*-5-*n*-alkyl-2-(4'-nitrophenyl)-1,3-dioxans obtained using hydrazine in the presence of Raney nickel.

The preparative procedure will be illustrated by the following representative examples:

4-(*trans*-4'-*n*-hexylcyclohexyl)isothiocyanatobenzene (6CHBT). A portion of 25.8 g (0.1 mole) of 4-(*trans*-4'-*n*-hexylcyclohexyl)aniline was dissolved in a mixture of 80 ml benzene and 20 ml hexane, then 7.5 ml (0.1 mole) of carbon disulfide and 15 ml of triethylamine were added and the mixture was left to stand for 45 h at 0°C. The yellow

triethylammonium dithiocarbamate precipitate was filtered off, washed with hexane and dried. The crystalline product was dissolved in 100 ml of chloroform and 15.5 ml of triethylamine added. The solution was cooled to 0°C and at this temperature 15.5 ml of ethyl chloroformate were added with stirring. Then the mixture was allowed to warm up to room temperature, when stirring was continued for 1 hour; it was then poured into 500 ml of a 3M hydrochloric acid. The organic layer was separated from the aqueous one, washed with water, dried down and the residue crystallized from ethanol. The yield was 15 g of 6CHBT having the following phase transition points: Cr 12.5°C N 43.0°C I.

Anal. calcd for $C_{19}H_{27}NS$:

C = 75.68%, H = 9.02%, N = 4.64%

Found:

C = 75.66%, H = 9.09%, N = 4.51%

IR spectrum (film):

very strong band at 2100 cm^{-1} (—NCS group)

5-trans-n-hexyl-2-(4'-aminophenyl)-1,3-dioxan. A mixture of 29.3 g (0.1 mole) of *5-trans-n-hexyl-2-(4'-nitrophenyl)-1,3-dioxan*, 250 ml of methanol and 15.5 g (0.25 mole) of 80% hydrazine hydrate were heated to 40°C with stirring. At this temperature, the first portion of a Raney nickel suspension in methanol was added when the temperature of the mixture increased spontaneously and evolution of nitrogen started. When the temperature ceased to rise, a further portion of Raney nickel was added. This procedure was repeated until the addition of more Raney nickel did not produce any increase in temperature. Next, the mixture was heated for 1 hour under reflux. The hot solution was filtered, and the filtrate left to crystallize. After cooling to 0°C, the solid was separated and recrystallized from methanol. We obtained 16 g (yield 60%) of the *5-trans-n-hexyl-2-(4'-aminophenyl)-1,3-dioxan* with m.p. 85–87°C.

Anal. calcd for $C_{16}H_{25}NO_2$:

C = 72.96%, H = 9.57%, N = 5.32%

Found:

C = 72.92%, H = 9.56%, N = 5.27%

IR spectrum (KBr):

3360 cm^{-1} (—NH₂ group)

5-*trans-n*-hexyl-2-(4'-isothiocyanatophenyl)-1,3-dioxan (6DBT). A mixture of 40 ml of water, 6 g (0.06 mole) of calcium carbonate, 20 ml of chloroform and 5.2 g (0.046 mole) of thiophosgene was cooled to 0–5°C when a solution prepared from 10.5 g (0.04 mole) of 5-*trans-n*-hexyl-2-(4'-aminophenyl)-1,3-dioxan and 40 ml of chloroform was added with vigorous mixing. Next the mixture was heated at 35°C for 1 hour and poured into water (50 ml). The layers were separated, and the chloroform layer was washed with 1% hydrochloric acid, water and dried over anhydrous magnesium sulfate. The solution was filtered through a layer of silica gel, and the chloroform was distilled off; the precipitate was recrystallized from methanol, and then hexane. A white crystalline product (6. g, 50%) was obtained with the phase transition temperatures: Cr 35°C S_A 79°C I.

Anal. calcd for C₁₇H₂₃NO₂S:

C = 66.85%, H = 7.59%, N = 4.59%, S = 10.48%

Found:

C = 66.62%, H = 7.69%, N = 4.60%, S = 10.66%

Measurement of the phase transition temperatures and enthalpies

The phase transition temperatures were determined using a PHMK Analytik (Dresden) polarizing microscope with a heated stage. The phase transition enthalpies were measured by means of a Du Pont 910 calorimeter. The binary mixture diagrams were plotted from the phase transition points for samples prepared by weighing out the pure compounds in adequate proportions.

RESULTS

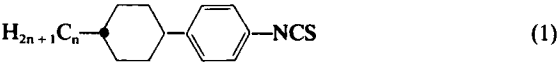
Mesomorphic properties

The phase transition temperatures and enthalpies are summarized in Table I for compounds (1) and in Table II for compounds (2). The compounds of series (1) and (2) reveal totally different liquid crystal properties. In compounds (1), we observe solely the nematic phase, even if the alkyl chain is very long. Even in 10CHBT we did not detect the presence of a smectic phase when its nematic phase was supercooled to 0°C.

The compounds of series (2) are all A₁ smectics from $n = 2$ to $n = 10$. The smectic phase reveals a fairly high thermal stability,

TABLE I

Phase transition temperature (in the upper line, °C) and molar enthalpies (in the lower line, kJmole⁻¹) for the compounds:



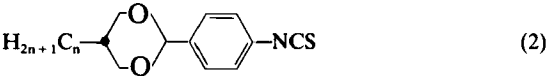
Acronym	n	Cr	N		I
2CHBT	2	•	23.0 12.0	• (-4.0) ^a	•
3CHBT	3	•	38.5 13.1	• 41.5 0.9	•
4CHBT	4	•	34.5 25.2	• 32.0 0.45	•
5CHBT	5	•	67.5 30.7 36.0 ^b	• 49.5 1.1	•
6CHBT	6	•	13.6 12.5 26.8	• 43.0 1.6	•
7CHBT	7	•	37.0 32.1	• 52.0 1.1	•
8CHBT	8	•	28.0 35.3	• 48.0 1.1	•
9CHBT	9	•	38.5	54.0	•
10CHBT	10	•	42.0 37.8	• 50.0 0.8	•

^a This temperature was an estimate from the clearing points of 2CHBT–3CHBT mixtures.

^b The metastable crystalline form which grows upon cooling the nematic phase.

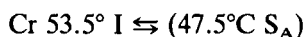
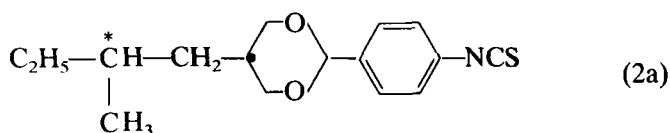
TABLE II

Phase transition temperatures (°C) for the compounds:



Acronym	n	Cr	S _{A1}		I
2DBT	2	•	74	• (54)	•
3DBT	3	•	79	• (65)	•
4DBT	4	•	60	• 75	•
5DBT	5	•	60	• 79	•
6DBT	6	•	35	• 79	•
7DBT	7	•	51.5	• 81.5	•
8DBT	8	•	47.5	• 80	•
9DBT	9	•	57.0	• 81	•
10DBT	10	•	61	• 79.5	•

even for the compound with $n = 2$. Its clearing temperature (monotropic) is high and amounts to 54°C . In series (1) the clearing temperature for the compound with $n = 2$ is only -4°C , what is drastically lower as compared with the successive members of this series. The fairly strong stabilization of the A_1 smectic phase by the structure of compound (2) is confirmed by (i) the high value of enthalpy of the $S \rightarrow I$ phase transition on average about 4 kJmole^{-1} , and (ii) the high clearing temperature of the optically active compound (2a)



The branching of the alkyl chain lowers the clearing temperature of compounds (2a) by only 30°C as compared with the series (2) compound with the alkyl chain of the same length ($n = 4$). In nematic series of compounds, e.g., biphenyl derivatives, the observed differences in the clearing temperatures of compounds with normal and branched alkyl chains are much greater.¹³

In the nematic series (1), the alteration of the melting points with change of n is very strong, whereas the melting enthalpy increases more systematically. Much higher melting points are observed for compounds with an odd number of carbon atoms in the alkyl chain. 5CHBT, melting only at 67.5°C and revealing also a high melting enthalpy of 30.7 kJmole^{-1} , deserves particular attention in this respect. This compound has also an unstable form with a lower melting point (36°C) and a lower melting enthalpy (13.6 kJmole^{-1}). The metastable form of 5CHBT is formed above 30°C when the nematic phase is cooled slowly. At lower temperatures, however, this form is unstable and converts spontaneously into the form with the higher melting point. The series (1) compounds with even numbers of carbon atoms in the alkyl chain reveal lower melting points as compared with those observed for an analogous series of compounds with the $-\text{CN}$ group in the terminal position. 6CHBT melting at 12.5°C deserves particular attention in this respect, since it is one of the lowest low-melting polar nematics known so far. Also in series (2), 6DBT relates to the compounds with the lowest melting points.

Physical properties

Values for viscosity coefficients, electric permittivity and refractive indices are summarized in Table III for 6CHBT.

Members of the CHBT series are distinguished for their low viscosity. The viscosity of 6CHBT as measured by a capillary viscometer is 21 mPa·s at 20°C. This value is close to the viscosity found for the PCH series.¹⁴ Probably, however, the CHBT compounds reveal, as distinguished from the PCH compounds, a strong variation of viscosity with length of the alkyl chain; the CHBT compounds with odd *n* have a lower viscosity than those with even *n* values. This observation is supported by the values of viscosity measured for mixtures. For instance, the mixture of composition:

3CHBT	42.9% wt.
6CHBT	57.1% wt.

has at 20°C $\eta = 13.5$ mPa·s, whereas the mixture consisting of

2CHBT	44.9% wt.
6CHBT	55.1% wt.

has at the same temperature $\eta = 21$ mPa·s

TABLE III

Physical parameters of 6CHBT determined at 20°C.

Parameter	Notation	Value at 20°C
1. Viscosity*	η	21 mPa·s
2. Viscosity coefficients: ¹⁵		
$\theta = 90^\circ, \phi = 90^\circ$	η_a	28 mPa·s
$\theta = 0^\circ, \phi = 0^\circ$	η_b	12 mPa·s
$\theta = 90^\circ, \phi = 0^\circ$	η_c^{**}	93 mPa·s
$\theta = 45^\circ, \phi = 0^\circ$	η_{45°	48 mPa·s
3. Refractive indices:		
ordinary ray	n_o	1.52
extraordinary ray	n_e	1.68
4. Electric permittivity: ²¹		
parallel component	$\epsilon_{ }$	12.0
perpendicular component	ϵ_{\perp}	4.5
5. Density		$1.01 \cdot 10^3$ kg/m ³

* by capillary viscometer,

** at temperature 23°C.

6CHBT being a nematic in the range from 12.5°C to 43.0°C, it is particularly suitable for testing the variation of viscosity coefficients with temperature. The values of the anisotropic viscosity coefficients at 20°C are summarized in Table III; the viscosity coefficient η_b , corresponding to the orientation of the long axes of the molecules in the direction of flow, is very low and amounts to hardly 12 mPa·s. The value of the viscosity determined by the capillary method is only twice as large as the value η_b ; this points to a considerable orientation of the long axes of the molecules in the direction of flow in the capillary. The detailed results of studies of the viscosity of the compounds (1) will be presented in a separate paper.¹⁵

The refractive indices of CHBT are higher than those of an analogous series of compounds with the —CN terminal group, while their anisotropy of the electric permittivity is smaller; this is related to the lower value of the dipole moment of the —NCS group as compared with the —CN group. The CHBT compounds show a high resistance to U.V. light; irradiation with a U.V. lamp or heating at 120°C for many hours does not affect the color or conductivity of the compound. They are also resistant to hydrolysis and are not hygroscopic; there is therefore no great problem in obtaining samples of conductivity of $10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$. The DBT compounds are much less stable to elevated temperatures and undergo visible destruction at 120°C.

Diagrams of binary mixtures

CHBT and DBT compounds yield in most cases simple eutectics both when they are mixed with each other (Figures 1a and 1b) and with other compounds, especially cyanoderivatives (Figures 1c and 2a, 2b, 2c, 2d). In the latter case, eutectic mixtures are obtained even in the case of mixtures composed of compounds with alkyl tails of the same length; for instance 3CB—3CHBT (Figure 2a) or 4'-cyanophenyl 4-*trans*-n-propylcyclohexanoate—3CHBT. The 3CHBT—3PCH system is an exception, since in the solid phase it reveals unlimited mutual solubility of the components with a minimum on the solidus (Figure 2c). The two components are, however, very similar: they have the same type of rigid core in the molecule, the same alkyl group, and differ only as regards one terminal polar group.

The clearing temperatures of mixtures composed solely of CHBT compounds or solely of DBT compounds, when the differences in the lengths of the alkyl chains in their molecules are moderate, vary according to the CSL equation, and lie in the vicinity of the straight

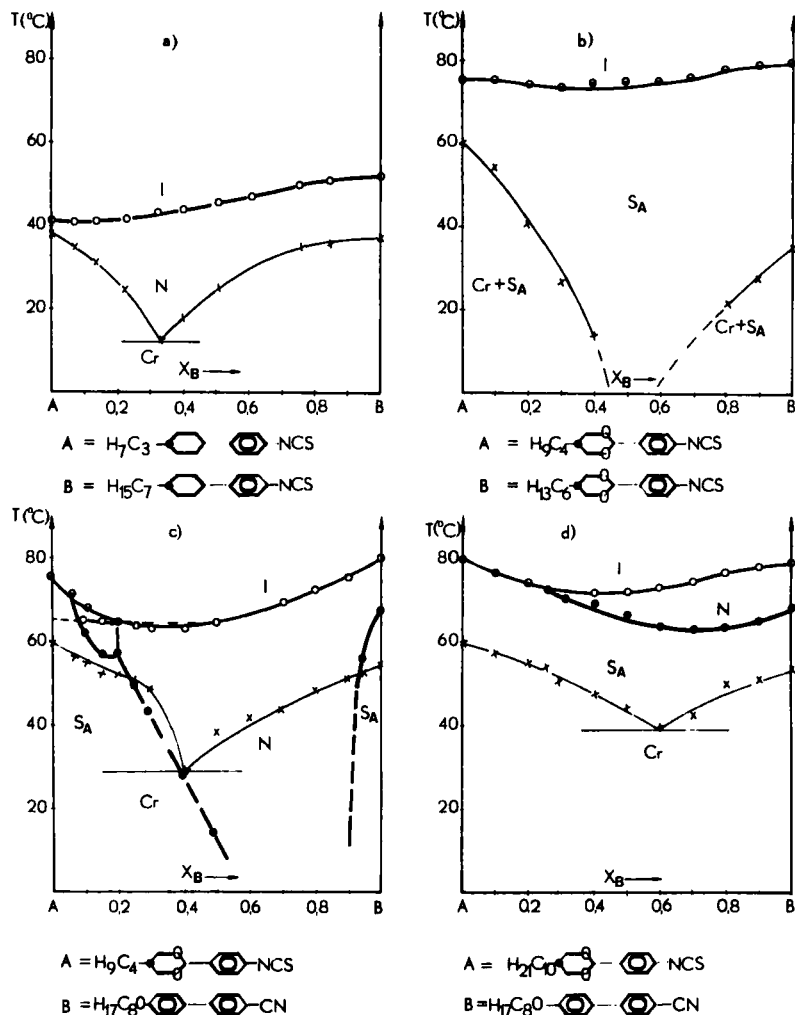


FIGURE 1 Phase diagrams of binary systems composed of: *a*—4-(*trans*-4'-*n*-alkyl-cyclohexyl)isothiocyanatobenzenes, *b*—*trans*-5-*n*-alkyl-2-(4'-isothiocyanatophenyl)-1,3-dioxans, *c* and *d*—*trans*-5-*n*-alkyl-2-(4'-isothiocyanatophenyl)-1,3-dioxans and 4-oc-tyloxy-4'-cyanobiphenyl.

line connecting the clearing points of the pure components (Figures 1a and 1b). The clearing temperatures of all mixtures composed of compounds (1) or (2) and cyano-compounds always reveal smaller or larger negative deviations (Figures 2a, 2b, 2c and 2d). Negative deviations are observed even for molecules of the same length, and these deviations increase with growing difference in the alkyl chain

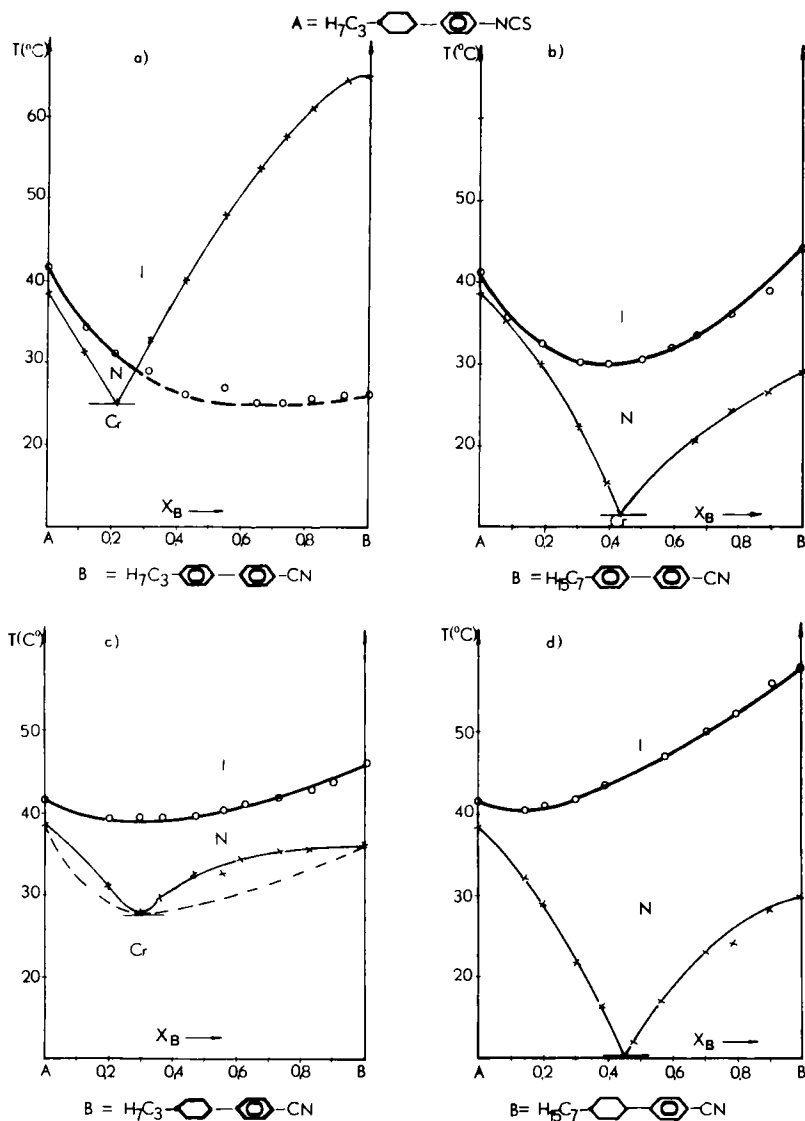


FIGURE 2 Phase diagrams of binary system composed of 4-(*trans*-4'-*n*-propylcyclohexyl)isothiocyanatobenzene and 4-*n*-alkyl-4'-cyanobiphenyls—*a* and *b* or 4-(*trans*-4'-alkylcyclohexyl)cyanobenzenes—*c* and *d*.

lengths in the pair of molecules forming the mixture or with growing difference of shape of the rigid cores of the molecules. A particularly deep minimum is observed on the $N \rightarrow I$ curve for mixtures including cyanobiphenyls (Figure 2b).

The clearing temperatures of mixtures composed of CHBT compounds and compounds without strongly polar groups in the terminal position, e.g., molecules of esters or azoxy compounds with alkyl or alkoxy groups, reveal, in the concentration range close to equimolar, a positive deviation from additivity (Figures 3a and 3b). At the same time, we observe in this concentration range induction of the smectic phase from the components of the nematic phase. In this respect, the compounds with the $-\text{NCS}$ terminal behave analogously to those with the $-\text{CN}$ terminal.^{16,17} Mixtures of concentrations at which the smectic phase is induced supercool very easily, and this state is fairly stable for quite a long time; difficulties are therefore, encountered in determining the melting temperature of such a mixture. Phase diagrams of DBT compounds which are A_1 smectics in mixtures with other A smectics and especially with A_d smectics deserve special attention. The character of the phase diagram depends largely on the spacing ratio of the smectic layers of the components used for preparing the mixture.

In Figure 1c, relating to the pair of compounds: 4DBT (smectic A_1 with $d_1 = 1.8$ nm) and 80CB (smectic A_d with $d_2 = 3.2$ nm), we see that the smectic regions of the pure components are separated

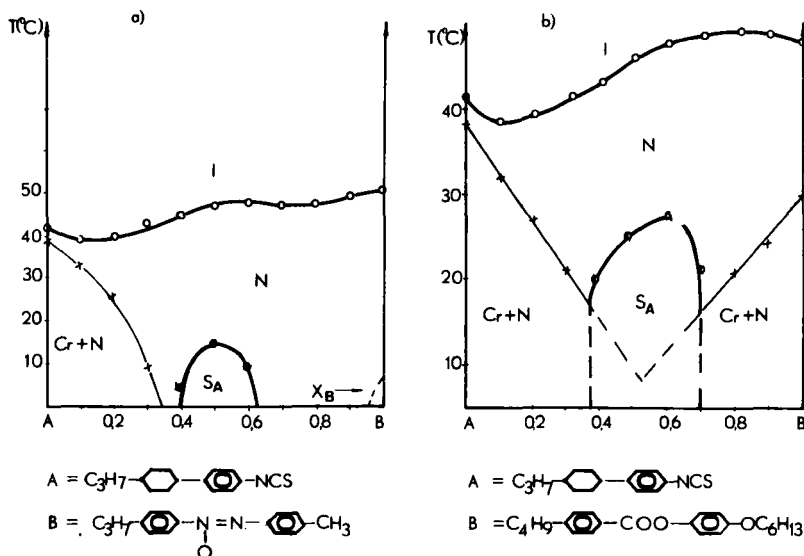


FIGURE 3 Phase diagrams of binary systems composed of 4-(*trans*-4'-*n*-propylcyclohexyl)isothiocyanatobenzene and 4-*n*-propyl-4'-methylazoxybenzene—*a* or 4-hexyloxyphenyl 4-butylbenzoate—*b*.

by a nematic region. In a mixture, the stability of the smectic phase decreases rapidly especially that of the component with the A_d smectic phase. In the case of the pair of compounds considered, the ratio $d_2/d_1 = 1.77$. However, for another pair of compounds of the same kind, 80CB—10DBT (Figure 1d), for which this ratio is much lower, $d_2/d_1 = 1.23$, we observe a continuous smectic region in the whole concentration range. This phenomenon, described earlier by us¹⁸ for other compounds, is connected with the incommensurability of the dimensions of the smectic layers. In the present work we have gathered further proof confirming that this behavior is not coincidental, but has a general character and should always be observed when the differences between the smectic layer spacings of the components of the mixture are large. The system shown in Figure 1c shows interesting properties in the concentration range at which transition of a mixture with smectic features to a mixture having both a nematic phase and a smectic phase is observed. This fragment of the plot in Figure 1c is shown in greater detail in Figure 4. In the concentration range of 95%–75% of 4DBT, we observe a large temperature interval in which

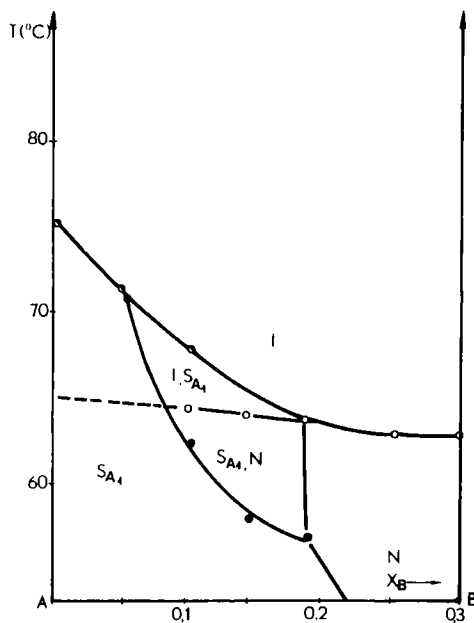


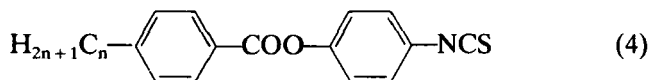
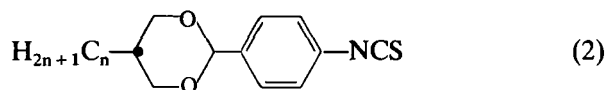
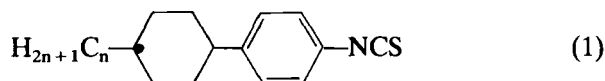
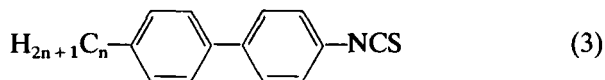
FIGURE 4 Part of the phase diagrams from Figure 1c in the vicinity of the triple I, S_{A_1}, N point. The phase transition: $S_{A_1} \rightarrow I$ — \bullet , $N \rightarrow I$ — \circ , $N \rightarrow S_{A_1}$ — \bullet .

the $S \rightarrow I$ and $S \rightarrow N$ phase equilibrium is established. On cooling, initially the isotropic and smectic phases coexist, and then the nematic and smectic phases. The estimated virtual $N \rightarrow I$ temperature for pure 4DBC is 65°C.

DISCUSSION AND CONCLUSIONS

The mesomorphic properties of two ring compounds with the isothiocyanato terminal group change very drastically with relatively small changes in the structure of the molecular rigid core.

Among the four homologous series of binuclear compounds (series 1, 2, 3, 4) tested so far with an isothiocyanato terminal group in the molecule:



- compounds (1) (CHBT) have solely a nematic phase even if the alkyl substituent has a long chain, $n = 10$.

- compounds (2) (DBT) give only the smectic A_1 phase in the whole homologous series from $n = 2$ to $n = 10$, even when the alkyl chain is branched.

- compounds (4) have also a smectic A phase when n is even, whereas, for the members in which n is odd, the nematic phase is also observed, but over a narrow temperature range.⁷

- compounds (3) give solely a highly ordered smectic E phase.

This is a behaviour opposite to that observed in analogous homologous services of compounds with the ---CN terminal group; in

these, the character of the mesophase changes but little. For all these compounds mentioned with the —CN group, we observe only the nematic phase when $n \leq 7$.

It is interesting to note that the compounds from series (2) and (3) which have solely smectic phases are characterized by much higher clearing temperatures ($S \rightarrow I$ transition temperatures) as compared with those belonging to the remaining two series (1 and 4) and with the analogous series of nematic compounds with the —CN group. The virtual $N \rightarrow I$ transition temperatures estimated from the phase diagrams of mixtures for series (2) and (3) are also higher than the $N \rightarrow I$ values for the series of compounds with the —CN group. In distinction, the clearing temperatures of series (1) and (4) compounds are equal to or only slightly lower than those observed for the analogues with the —CN group.

The significant differences in the mesophase structures between the compounds with the —NCS group (series 1–4) and the corresponding analogues with the —CN group reduce to the fact that the former do not yield dimers with an antiparallel arrangement of the molecules and exist in the mesophase as single molecules or clusters composed of single molecules in parallel ordering. Such conclusions can be drawn primarily by comparing the smectic layer spacings of compounds with the isothiocyanato group with those having the cyano group. The spacings of the smectic layers in the isothiocyanates are almost equal to the lengths of the single molecules, $d_1 \approx 1$. For instance in 4DCB $d = 1.8$ nm and $l_m = 1.90$ nm; in 4'-isothiocyanatophenyl 4-n-butylbenzoate, $d \approx 2.6$ nm, $l_m = 2.6$ nm; in 4-pentyl-4'-isothiocyanatobiphenyl, $d = 2.0$ nm, $l_m = 2.1$ nm. In distinction, most compounds with the —CN group have a dimeric structure,^{19,20} perhaps with the exception of cyanophenyl alkylbenzoates, which probably have a monomeric structure, as confirmed by the high electric permittivity and lack of a smectic phase at high values of n .

The dimerization of the compounds with the —CN terminal groups results in the formation of antiparallel pairs of molecules; this cancels the individual differences in the shapes of the rigid cores, and hence results in the small differences between the mesophase properties of the different types of compound. A further confirmation of the different structures arising with the molecules with the —NCS and —CN groups are the differences in their melting points and the temperature dependence of the electric permittivity.

In the series with the —NCS group, higher melting points are revealed by the members with odd numbers of carbon atoms in the alkyl group, whereas in compounds with the —CN group, this occurs

for the members with even numbers of carbon atoms. In compounds with the —CN group, the electric permittivity increases in the isotropic phase with temperature (due to splitting of the dimers), whereas in compounds with the —NCS group the permittivity decreases.²¹

The observed correlation between the molecular structure and the smectic and nematic properties of the compounds is due to the competition between the intermolecular repulsive and attractive forces. Increase in the attractive forces favours the smectic ordering, while a local increase of the repulsive forces destroys such an ordering. Even small changes in the shape of the rigid core lead to a different ordering of the molecules and may affect significantly the equilibrium between the attractive and repulsive forces. Such a conclusion follows from a comparison of the properties of compounds (1) and (3). In this case the change of the biphenyl core of homogeneous cylindrical form to a cyclohexylphenyl core consisting of two geometrically different elements is sufficient for the conversion of the smectic to a nematic ordering.

The conclusion as to the great significance of steric factors and spatial arrangement results also from the character of the phase diagrams presented in Figures 1c and 1d. A mixture consisting of smectic compounds differing largely in the smectic layer spacings is not capable of preserving the smectic phase structure, since the attractive forces decrease in it. The nematic state ensures a denser spatial packing for the same mixture as compared with the smectic state.

The CHBT are a new type of low-melting, polar nematic materials characterized by low viscosity and high chemical stability, and which yield with many compounds simple eutectic systems. From this point of view, they seem to be interesting components of low-melting nematic compositions for displays. They may be also considered as orienting solvents for spectroscopy by virtue of the simpler internal structure of their nematic phases as compared with those of nematogenes with the —CN group.

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