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4-/TRANS-4'-n-ALKYLCYCLOHEXYL/ISOTHIOCYANATOBENZENES

A NEW CLASS OF LOW-MELTING STABLE NEMATICS

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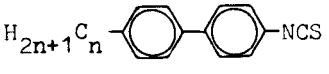
The mesogenic properties of four series of compounds with the isothiocyanate terminal group are compared, viz.: 4-n-alkyl-4'-isothiocyanatobiphenyls /1/, 4-/trans-4'-n-alkylcyclohexyl/benzeneisothiocyanates /2/, isothiocyanatophenyl 4-n-alkylbenzoates /3/ and isothiocyanatophenyl 4-/trans-4'-n-alkylcyclohexyl/benzoates /4/. It has been found that compounds 2 have only the nematic phase in the homologous series from 2 to 10 carbon atom in the alkyl chain, and compounds 4 the nematic and smectic A phases, while the so far known compounds 1 and 3 are E or A smectics.

Liquid-crystalline isothiocyanates have not attracted hitherto greater interest because of their smectogenic properties[1]. In the present work we retested the mesogenic properties of compounds with the isothiocyanate group and our results confirmed those of Van der Veen[1], i.e. that 4-n-alkyl-4'-isothiocyanatobiphenyls 1 reveal only the smectic E phase, while isothiocyanatophenyl 4-n-alkylbenzoates 3 reveal solely the smectic phase when the number of carbon atoms in the alkyl chain is even. In esters with odd numbers of atoms in the chain we observed the nematic phase also.



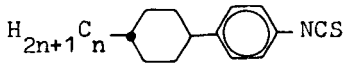
1

The phase transition temperatures, °C

n	C		S_E		I
5	•	53	•	74.5	•
	•	55[1]	•	73	•
6			•	77	•
7	•	56	•	73	•

We found, however, that smectogeneity is not a general property of compounds with the NCS group. Other compounds, which have in their molecule a cyclohexane ring, were found to be nematics. This relates to 4-/trans-4'-alkylcyclohexyl/benzeneisothiocyanates 2 and isothiocyanatophenyl 4-/trans-4'-alkylcyclohexyl/-

benzoates 4.



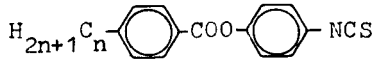
2

The phase transition temperatures, °C

n	C		N		I
2	.	23.0	(.	-4	.)[xx]
3	.	38.5	.	41.5	.
4	.	34.5	.	32.0	.
5	.	67.5	(.	49.5	.)
		36[x]	.		
6	.	12.5	.	43.0	.
7	.	37.0	.	52.0	.
8	.	28.0	.	48.0	.
10	.	42.0	.	50.0	.

x metastable form observed directly after crystallization of the supercooled nematic phase,

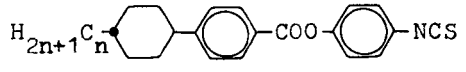
xx estimated value.



3

The phase transition temperatures, °C

n	C		S_A		N		I
2	.	68	-		-		.
3	.	73	-		-		.
4	.	60	(.	37.5	-		.)
	.	60	.	40[1]	-		.
5	.	88			(.	45	.)
6	.	52	(.	49.5	-		.)
	.	51	(.	49[1]	-		.)
7	.	62	(.	57.0	.	57.5	.)
8	.	49	.	56.5	-		.



4

The phase transition temperatures, °C

n	C		S_A		N		I
2	.	148	-		.	214	.
5	.	119	.	129	.	235	.
10	.	95	.	187	.	201	.

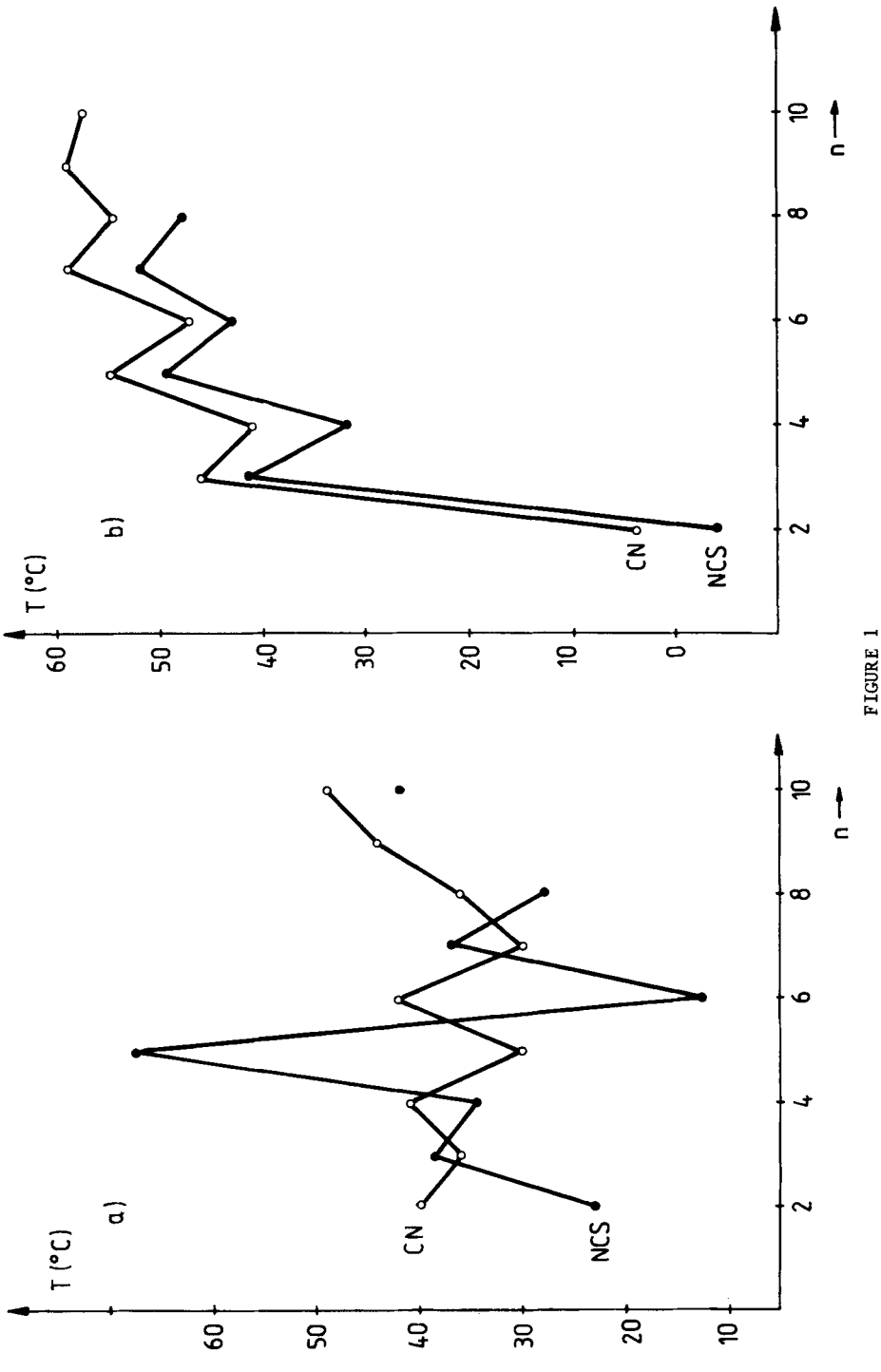


FIGURE 1

In compounds of formula 2 we observed only the nematic phase even when long alkyl chains were present. For the compound with the alkyl as large as n=10 we detected no smectic phase even after deep supercooling, while in the analogous series of compounds, 4-/trans-4′-alkylcyclohexyl/cyanobenzenes /PCH/, a monotropic smectic phase is observed for that member[2].

Compounds 4 reveal only the nematic phase if $n<5$ and the nematic and smectic A phases simultaneously if $n\geqslant 5$.

Characteristic differences are observed at melting temperatures when isothiocyanates 2 are compared with compounds of analogous structure but with the terminal group CN /PCH/, see Fig.1a. The isothiocyanates 2 reveal higher melting points when the number of carbon atoms in the alkyl chain is odd while the compounds with the CN terminal group have higher melting points for compounds with even numbers of carbon atoms in the chain. Attention should be drawn to the particularly pronouced irregularities in the melting points of series 2 compounds. This refers especially to two successive members with n=5 and n=6. The former compound melts at 67.5°C / ΔH = 30.7 kJ/mole/, while the latter melts at 12.5°C / ΔH = 26.8 kJ/mole/. 4-/Trans-4′-pentylcyclohexyl/benzeneisothiocyanate also reveals a lower melting metastable solid: m.p. = 36°C, ΔH = 13.6 kJ/mole, which is formed directly from the nematic phase on cooling at ca.30°C. At a lower temperature it transforms subsequently into a stable form of higher melting temperature with an exothermal effect of 17.1 kJ/mole. The clearing temperatures /Fig.1b/ vary in the homologous series 2 like in the corresponding series with the group CN. The clearing points being in the series with the NCS group only slightly lower /by 3-8°C/ as compared with those with the CN group. For the series of esters 3 and 4 we find that the compounds with the NCS group have lower, equal or higher clearing points.

Among the four series of homologous compounds with the NCS group tested in the present work the compounds of series 2 deserve particular attention. 4-/Trans-4′-n-alkylcyclohexyl/isothiocyanatobenzenes reveal properties that are very interesting from the practical point of view: some compounds in this series have low melting points, low viscosities and satisfactory resistance to U.V. light; on exposure for 100 hours to irradia-

tion with an U.V. Q 400 lamp their colour, conductivity and phase transition temperatures did not change. The principal parameters of the compound 2 /n=6/ at the temperature 20° are given below:

Dielectric contants: $\varepsilon_{\parallel} = 12.0$, $\varepsilon_{\perp} = 5.0$
Refractive indeces: $n_e = 1.68$, $n_o = 1.52$
Viscosity: $\eta = 21$ mP.s
Density: $\varrho_o = 1.01$ g/cm^3

The dielectric anisotropy, $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ of compounds 2 is ca. 7 and is lower than for similar compounds with the CN group. This is due to the lower value of the dipole moment of group NCS as compared with group CN, which are 2.9 D and 4.0 D, respectively. Compounds 2 reveal advantageous properties as regards production of liquid-crystalline compositions, since owing to their low melting points it is possible to obtain from them low melting eutectic mixtures, e.g. a ternary one[x]:

4-/trans-4'-n-propylcyclohexyl/isothiocyanatobenzene %wt. 37.29
4-/trans-4'-n-hexylcyclohexyl/isothiocyanatobenzene 44.15
4-/trans-4'-n-octylcyclohexyl/isothiocyanatobenzene 18.56

which melts at - 8° and has a clearing point at 42.5°.

Liquid-crystalline compounds with the NCS terminal group do not yield molecular associates in the form of pairs with antiparallel arrangement of the molecules as is the case with compounds with the CN terminal group. The compounds with the NCS group have also layer smectic spacings equal to the length of a single molecules[3].

A precious property of the compounds with the NCS terminal group is, furthermore, that their presence in mixtures causes the decomposition of dimers of compounds with the CN group thanks to which the mixture achieves a dielectric anisotropy higher than it could be expected from the contributions from the pure compounds.

EXPERIMENTAL

Esters 3 and 4 have been obtained in the reaction of equimolar amounts of 4-isothiocyanatophenol and the respective acid

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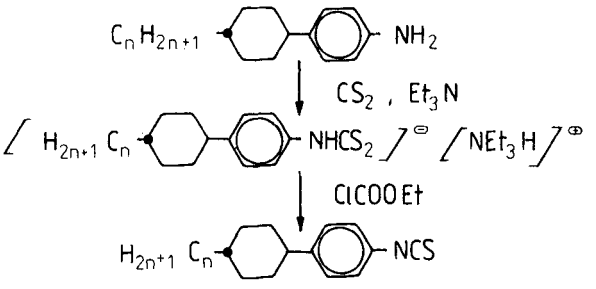
x This composition is available under the trade mark W-25 from POCH, Lublin, Poland.

chlorides in benzene-pyridine solution.

The cyclohexyl compounds 2 have been obtained by treating 4-/trans-4′-alkylcyclohexyl/anilines with carbon disulfide in Et_3N and subsequently with ethyl chloroformate in Et_3N:



The preparative procedure was similar to that described by us for 4-pentyl-1-isothiocyanatobiphenyl in an earlier paper[4].

CONCLUSIONS

The mesogenic properties of the compounds with the NCS terminal group are much more sensitive to the structure of the rigid core than are those with the CN terminal group. Small changes in the structure of the molecular core /substitution of the phenylhexane group for the biphenyl one/ change drastically the properties of the compounds: from the highly ordered smectic E to the nematic phase. 4-/Trans-4′-n-alkylcyclohexyl/benzeneisothiocyanates have only the nematic phase even in the case of a ten carbon chain. These compounds reveal low viscosity, are resistant to U.V. light and seem to be suitable as components of mixtures for displays.

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