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X-Ray and Thermoanalytical Investigations on Two Isomeric *n*-Pentylphenyl Cyano-Thiolbenzoates

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The isomeric compounds 4-*n*-pentylphenyl 4′-cyanothiolbenzoate (NCS5) and 4-cyanophenyl 4′-*n*-pentylthiolbenzoate (5SCN) have been studied by X-ray diffraction and thermoanalytical methods. The crystal data are (NCS5): $a = 31.020$ (8), $b = 8.366(2)$, $c = 15.043(4)$ Å, $\beta = 114.15(2)°$; monoclinic, space group C2/c with eight molecules in the unit cell and (5SCN): $a = 37.128$ (10), $b = 6.055(2)$, $c = 24.325(8)$ Å, $\beta = 107.39(2)°$; monoclinic, space group $P2_1/c$ with twelve molecules in the unit cell.

The crystal structure of NCS5 has been solved by direct methods and refined to an R-value of 0.086. The molecule is in an extended form. The torsion angle between the two phenylrings is 69.0(5)°. The molecules are arranged parallel to each other, and perpendicular to [010], with $y \sim 0$ or $y \sim 1/2$ in a head-to-tail configuration.

X-ray investigations have established different semibilayer structures for the nematic phases of the two isomeric compounds. The nematic phase of NCS5 has coexisting mass-density fluctuations (heavily damped) of two distinct wavelengths.

Both compounds show solid state polymorphism. The transition temperatures and enthalpies are given. The binary phase diagram for NCS5 and 5SCN is described.

INTRODUCTION

In 1976 Krause *et al.*[1] and Reynolds *et al.*[2] reported on the nematic liquid crystalline 4,4′-disubstituted phenyl thiolbenzoates. The diamagnetic properties,[3] the densities and the optical properties[4] of the

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isomeric compounds 4-*n*-pentylphenyl 4′-cyanothiolbenzoate (hereafter NCS5) and 4-cyanophenyl 4′-*n*-pentylthiolbenzoate (5SCN), as well as 4-*n*-pentylphenyl 4′-*n*-hexyloxy-benzoate and 4-*n*-hexyloxyphenyl 4′-*n*-pentylbenzoate have been determined. The investigations[5] showed that these physical properties were not influenced by changing the positions of the substituents. An interesting point is the question concerning the molecular packing in the crystalline state for each of the isomeric compounds.

In this respect we report here, in detail, on the crystal and molecular structure of NCS5, on X-ray investigations of the nematic state of the two isomeric compounds NCS5 and 5SCN, as well as on their binary phase diagram, qualitatively determined by Lauer.[6] The data collection and the crystal and molecular structure determination for 5SCN are under way. Thus far no crystal and molecular structure determinations had been made for phenyl thiolbenzoates.

EXPERIMENTAL

Crystal data

Crystals of NCS5 suitable for X-ray investigations were obtained by slow evaporation of a methanolic solution. A crystal of needle-like habit of 0.3 × 0.4 mm cross section was chosen for the measurements. Lattice constants and intensity measurements were made on an automatic STOE-4-circle-diffractometer with monochromatic MoK_α radiation. The systematic absences hkl: $h + k \neq 2n$, $h0l$: $1 \neq 2n$ led to the space groups C2/c and Cc, respectively. The centrosymmetric space group was confirmed by the structure determination.

The crystal data for NCS5 and 5SCN are given in Table I. Comparison of these data shows that the crystal structures of NCS5 and 5SCN should differ.

Structure determination and refinement of NCS5

For the intensity data, Lorentz and polarization corrections were performed. The structure has been solved by direct methods using the SHELX program. The second best E-map depicts the whole molecule. Least-squares refinement with anisotropic thermal parameters for all but the hydrogen atoms led to $R = 0.086$ ($R_w = 0.064$) for 1723 independent reflections with $F_0 \geqslant 2\sigma(F_0)$. The coordinates for the hydrogen atoms were calculated from the molecular geometry, using a C—H bond length of 0.96 and were not refined. Their temperature

TABLE I

Crystal data

	NCS5	5SCN
Molecular formula	$C_{19}H_{19}NOS$	$C_{19}H_{19}NOS$
Molecular weight [$g \cdot mol^{-1}$]	309.41	309.41
F(000)	1313	1313
Space group	C2/c	$P2_1/c$
a [Å]	31.020(8)	37.128(10)
b [Å]	8.366(2)	6.055(2)
c [Å]	15.043(4)	24.325(8)
β [°]	114.15(7)	107.39(2)
V_c [$Å^3$]	3562.3	5218.6
D_c [$g \cdot cm^{-3}$]	1.15	1.18
Z	8	12
Independent reflections	2324	
Reflections for calculation	1723	
μ (MoK_α)	0.15	0.15

factor was held fixed at 1.1 times the factor of the connecting carbon atoms. The atomic parameters for the non-hydrogen atoms are given in Table II. A list of the observed and calculated structure factors and the anisotropic thermal parameters is available from the authors on request.

X-ray investigations of the liquid crystalline phase

The samples were introduced in 0.7 mm Lindemann glass capillaries. The capillaries were held in a copper block permitting a temperature constancy of ±0.2 K. The temperature of the samples was determined with a calibrated thermocouple. Ni-filtered Cu radiation was used. Flat-plate photographs were taken with exposure times of four hours. The optical density of the X-ray photographs was measured by a Joyce MKIIIC-microdensitometer.

To calibrate the distance from the sample to the film, we measured the diameter of the (111) reflection of silicon (lattice spacing 5.4306 Å), using capillaries filled with silicon powder.

Photographs were taken for the nematic phase, subsequent to cooling of the samples from the isotropic phase in an electromagnet with a field strength of 1 Tesla.

Phase diagram

The samples had been recrystallized from methanol. The transition temperatures for the two isomeric compounds NCS5 and 5SCN and

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TABLE II

Atomic parameters for the nonhydrogen atoms of NCS5

Atom	x/a	y/b	z/c	$U_{eq}{}^a$
Cyano group				
N	0.4592(1)	0.4045(7)	0.3753(3)	0.145
C(1)	0.4357(1)	0.4179(8)	0.4156(4)	0.111
Phenyl ring A				
C(2)	0.4047(2)	0.4375(6)	0.4656(3)	0.087
C(7)	0.3578(1)	0.3923(5)	0.4195(3)	0.092
C(6)	0.3284(1)	0.4169(6)	0.4654(3)	0.088
C(5)	0.3439(2)	0.4842(5)	0.5571(3)	0.071
C(4)	0.3914(2)	0.5247(6)	0.6030(3)	0.088
C(3)	0.4213(2)	0.5040(6)	0.5580(4)	0.099
Thiolbenzoate group				
C(8)	0.3128(1)	0.5167(6)	0.6081(3)	0.078
O	0.3264(1)	0.5702(5)	0.6878(2)	0.121
S	0.2534(0)	0.4694(2)	0.5402(1)	0.121
Phenyl ring B				
C(9)	0.2259(1)	0.5158(6)	0.6186(3)	0.078
C(14)	0.1921(2)	0.6310(6)	0.5904(4)	0.099
C(13)	0.1665(2)	0.6602(6)	0.6442(3)	0.102
C(12)	0.1732(1)	0.5763(6)	0.7268(3)	0.085
C(11)	0.2076(1)	0.4596(6)	0.7542(3)	0.087
C(10)	0.2334(1)	0.4301(6)	0.7010(3)	0.085
Pentyl group				
C(15)	0.1453(2)	0.6099(7)	0.7858(4)	0.130
C(16)	0.1092(2)	0.5013(8)	0.7754(5)	0.171
C(17)	0.0784(4)	0.5629(14)	0.8346(9)	0.258
C(18)	0.0706(4)	0.4639(12)	0.8784(7)	0.229
C(19)	0.0391(2)	0.5121(9)	0.9347(4)	0.233

$^aU_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)$

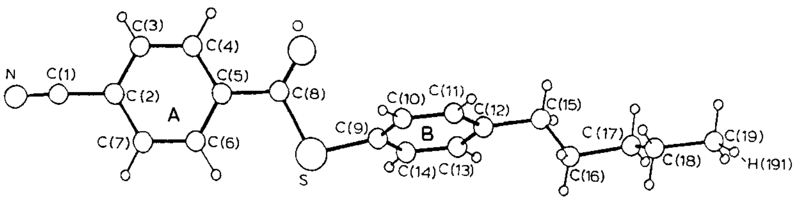

FIGURE 1 NCS5-molecule, projected perpendicular to the plane through the atoms C(2), C(4) and C(6).

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their binary mixtures were determined using a Leitz Orthoplan-polarizing microscope, equipped with a Mettler FP52 hot stage and using a Du Pont differential scanning calorimeter. About 4 mg of the mixture were placed in an aluminium sample pan with cover. The sample chamber was continuously flushed with nitrogen.

RESULTS AND DISCUSSION

Molecular structure of NCS5

The molecular structure is presented in Figure 1 as a projection perpendicular to the plane of the phenyl ring A. This figure shows that the conformation of the molecule is an extended one.

The distance N...H(191) is 18.81 Å (the crystallographic H(191)-position is: $x/a = 0.026$, $y/b = 0.426$, $z/c = 0.957$). Considering the covalent radii N = 0.55 Å, H = 0.30 Å, the molecular length amounts to 19.66 Å. For the discussion of the X-ray data in the nematic state, the following distances are also important:
N...C(5): 5.36 Å; N...C(12): 12.13 Å; C(5)...H(191): 13.50 Å and C(12)...H(191): 6.88 Å.

Whereas all the bond distances and bond angles of the core part of the molecule (N to C(12)) are of normal magnitude (Table III), some of the bond distances and angles in the pentyl group are anomalous. This results from the relatively high thermal parameters of the C-atoms in the pentyl group (Table II).

The bond distance N—C(1) = 1.130(6) Å and the bond angle N—C(1)—C(2) = 179.7(5)° are comparable with the corresponding literature data, e.g. 4′-cyanophenyl 4-*n*-pentylbenzoate:[7] N—C = 1.140(9) and 1.138(10) Å, N—C—C = 177.9(7) and 178.7(8)°; 4-*n*-pentylcyclohexyl-4′-cyanobiphenyl:[8] N—C = 1.139(5) Å, N—C—C = 178.7(4)°; *p*-cyanobenzoic acid:[9] N—C = 1.149(8) Å, N—C—C = 176.4(5)°; trans, trans-4′-*n*-pentylbicyclohexyl-4-carbonitrile:[10] N—C = 1.127(7) Å, N—C—C = 177.8(6)°.

An interesting point of consideration is the torsion angle between the two phenyl groups A and B. As a result of the planarity of the thiolbenzoate group this angle is nearly equivalent to the torsion angle between C(8)—S and C(9)—C(10) = 69.0(5)°.

The torsion angle between the bonds C(4)—C(5) and C(8)—O is 3.0(5)°, and the torsion angle between the bonds C(5)—C(8) and S—C(9) is 178.8(5)°. Analogous torsion angles were found in the substituted phenyl benzoates (Birner *et al.*,[11] Haase *et al.*[12] and literature therein).

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TABLE III

Bond lengths [Å] and angles [°] (including standard deviations) for NCS5

N—C(1)	1.130(6)	N—C(1) —C(2)	179.7(5)
C(1)—C(2)	1.450(6)	C(5)—C(8) —O	123.6(5)
C(2)—C(3)	1.386(6)	C(5)—C(8) —S	114.2(3)
C(3)—C(4)	1.366(6)	O —C(8) —S	122.1(3)
C(4)—C(5)	1.388(7)	C(8)—S —C(9)	104.1(3)
C(5)—C(6)	1.382(6)	C(12)—C(15)—C(16)	116.2(5)
C(6)—C(7)	1.365(7)	C(15)—C(16)—C(17)	110.7(7)
C(7)—C(2)	1.385(7)	C(16)—C(17)—C(18)	113.2(8)
C(5)—C(8)	1.484(6)	C(17)—C(18)—C(19)	116.4(7)
C(8)—O	1.184(6)		
C(8)—S	1.747(4)		
S —C(9)	1.759(4)		
C(9)—C(10)	1.367(7)		
C(10)—C(11)	1.366(7)		
C(11)—C(12)	1.377(7)		
C(12)—C(13)	1.366(7)		
C(13)—C(14)	1.369(6)		
C(14)—C(9)	1.357(6)		
C(12)—C(15)	1.500(7)		
C(15)—C(16)	1.401(8)		
C(16)—C(17)	1.632(12)		
C(17)—C(18)	1.144(12)		
C(18)—C(19)	1.585(10)		

TABLE IV

Deviation [Å] of some atoms from the best planes through phenyl ring A and B, respectively, for NCS5

	phenyl ring A	phenyl ring B
N	0.114	1.928
C(1)	0.054	1.816
C(5)	0.010[a]	1.386
C(8)	0.055	1.310
O	0.025	2.174
S	0.162	−0.178
C(9)	0.165	0.001[a]

[a] Atoms were included in the best planes calculations.

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The situation in the central part of the molecule is also characterized by the positioning of some atoms in relation to the best planes, formed through the phenyl rings A and B, respectively (Table IV).

Molecular packing

The packing of NCS5 in the crystalline state is demonstrated in Figures 2 and 3. It is characterized in such a manner that the molecules are extended parallel to each other and lie perpendicular to [010] alternating in $y \sim 0$ and $y \sim 1/2$ in a head-to-tail configuration. The projection of the long molecular axis on the (010) plane makes an angle of ~ 45° with the c-axis.

Two types of layer can be discussed. The first type lies in the (100) plane. These layers (Figure 2) would have a thickness of half of the crystallographic a-axis multiplied by sin β; this is 14.15 Å. The second type of layer is perpendicular to the 2_1-axis with a thickness of $b/2$ (= 4.18 Å; Figure 3).

The alternating head-to-tail arrangement results in a stack formation along the b-axis. The plane of the phenyl ring A of one molecule forms an angle of ~ 69° with the plane of the phenyl ring B of the next molecule. These phenyl-phenyl distances are of the order

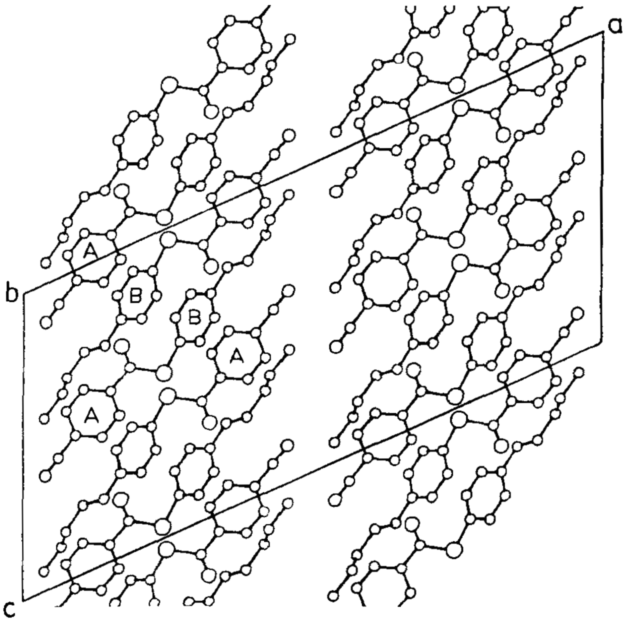

FIGURE 2 NCS5, projection along [010].

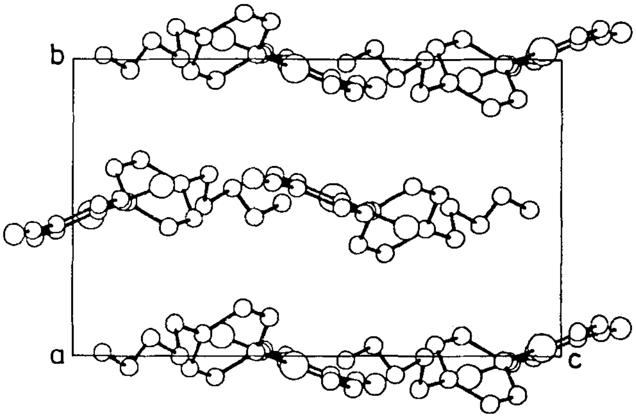

FIGURE 3 NCS5, projection along [100], $0 < x < 0.5$.

of ~ 4.2 Å. Also the phenyl ring B of one molecule forms an angle of ~ 42° with the plane of the phenyl ring B of the next molecule. The crystallographic plane ($\bar{1}02$) lies perpendicular to the largest extension of the molecules and perpendicular to all the phenyl rings A and B of the molecules in an alternating sequence ABBA within the layer (Fig. 2). The thiolester groups are nearly parallel to the (010) plane with their largest dipole moment component perpendicular to the molecular long axis. The inter-cyano distances of N...N′ = 3.906(6), N...C(1)′ = 3.787(6) as well as C(1)...C(1)′ = 3.996(7) Å are related by the inversion centre of symmetry. A similar situation is found in trans, trans-4′-propylbicyclohexyl-4-carbonitrile.[10] Moreover, a distance of 3.85 Å is found for the sulphur-sulphur atoms which is slightly greater than twice the van der Waals radius of sulphur (1.85 Å). A larger sulphur-sulphur distance of ~ 5.0 Å resulted additionally along the *b*-axis.

Molecular arrangement in the nematic phase

Table V summarizes the results of the X-ray investigations on NCS5 and 5SCN in the nematic phase. Thus, in this phase, NCS5 has coexisting mass-density fluctuations (heavily damped) of two distinct wavelengths, such that the wave vector $q_2 \neq q_1$ ($q = 4\pi \sin\Theta/\lambda$).[13] The larger wavelength (q_1) corresponds to a bilayer structure, whilst the shorter wavelength (q_2) corresponds to a monolayer structure. The intensity of the fluctuation varied with the temperature. The monolayer predominates at lower temperatures, whereas the bilayer predominates at higher temperatures. The q values are independent of temperature.

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TABLE V

Fluctuation wavelengths and intermolecular distances (D) in the nematic state. The molecular length l of NCS5 in the crystalline state (including the covalent radii) is 19.66 Å

Compound	T [K]	$2\pi/q_1$ [Å]	$2\pi/q_2$ [Å]	D [Å]
NCS5	345.0 (N)	29.3 ± 0.5	18.6 ± 0.5	5.1 ± 0.1
	378.0 (I)			5.3 ± 0.1
5SCN	352.0 (N)	21.3 ± 0.5		5.1 ± 0.1
	378.0 (I)			5.2 ± 0.1

The presence of mass density fluctuations of two wavelengths has been observed for the first time by Brownsey and Leadbetter[13] on different compounds. The nematic phase of 5SCN exhibits a rather simple structure with weak correlations in local order.

Possible semibilayers of NCS5 and 5SCN are shown schematically in Figure 4, in which the molecules partially overlap. With the above cited dimensions of the parts of the molecule NCS5, a total distance of ~ 32.9 Å was calculated for the bilayer model in Fig. 4. For the bilayer of 5SCN in Fig. 4, the analogous value is estimated to be ~ 26.3 Å. Leadbetter *et al.*[14,15] have suggested an electronic overlap of the cyano groups with the phenyl rings, e.g., in case of the cyano-

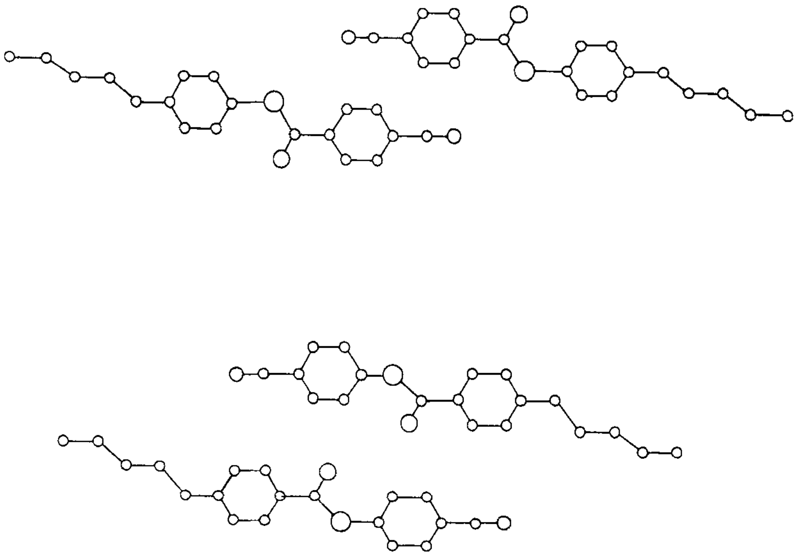

FIGURE 4 A schematic representation of the molecular arrangement of a possible semibilayer structure for the nematic phases of NCS5 (top) and 5SCN (bottom).

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biphenyls. In our case, the molecules have a bridging group (COS) between the phenyl rings. The two isomeric compounds NCS5 and 5SCN differ also in the orientation of the dipole moment component of the COS groups as related to the orientation of the cyano dipole. This leads to a different polarity with respect to the two phenyl rings of each isomer. In comparison, Brownsey and Leadbetter[13] found for 4-cyanophenyl 4′-*n*-octylbenzoate a fluctuation wavelength of 31.7 Å. The calculated molecular length is 24 Å. This compound can be compared with 5SCN. We propose an overlapping scheme analogous to 5SCN, in agreement with the experimental data.

Solid state polymorphism and phase diagram

As the temperature increases, the DSC-thermograms of NCS5 and 5SCN, recrystallized from methanol, exhibit two endothermal signals, one of which is for the crystalline solid-nematic (K–N) and the other for the nematic-isotropic liquid (N–I) phase transition (Table VI).

After cooling from the nematic phase to 298 K and heating again both compounds show more than one crystalline phase.

From NCS5 we obtain a second crystalline phase with a melting point at 339 K. 5SCN shows two additional endothermal transitions. The first one (at 349 K) is the melting point of a second crystalline phase, the other one (at 348 K) may be interpreted as a solid–solid transition. The intensity of the DSC signal at 349 K is at least ten times greater than that at 348 K. The signal intensities depend also on the thermal history. Figure 5 shows the properties in question. The existence of more than one melting point confirms the results obtained with a polarizing microscope.

Attempts to obtain only the pure lower melting crystalline forms of NCS5 and 5SCN did not succeed. Therefore, evaluations of the enthalpies of these crystalline forms were unachievable. It should be noted here that the melting enthalpies of K_I differ between both of the isomeric compounds (Table VI).

TABLE VI

Transition enthalpies for NCS5 and 5SCN

Compound	Transition	Temperature [K]	Enthalpy [kJ · mol^{-1}]
NCS5	K_I–N	339.8 ± 0.2	16.6 ± 0.8
	N–I	375.4 ± 0.1	0.6 ± 0.2
5SCN	K_I–N	350.0 ± 0.2	22.4 ± 0.9
	N–I	372.9 ± 0.1	0.6 ± 0.2

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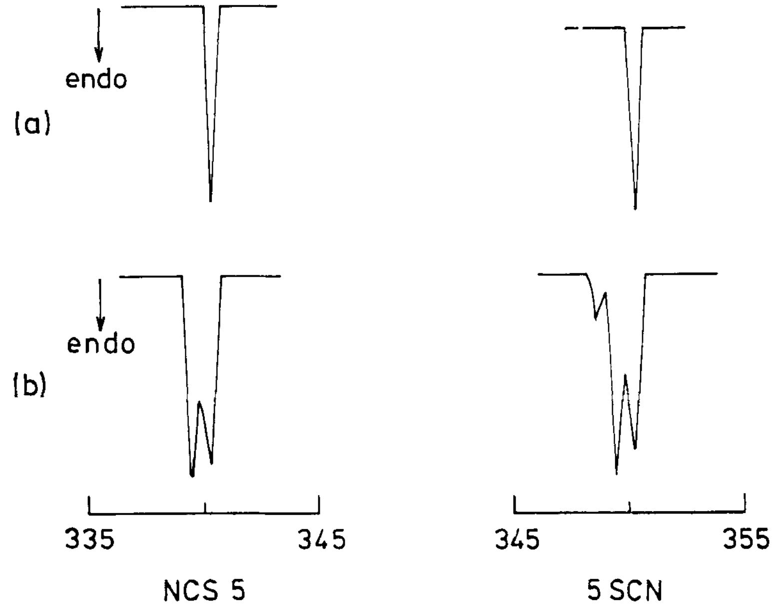

FIGURE 5 DSC thermograms of NCS5 and 5SCN; (a) melting of a single crystal; (b) after cooling (5K/min) from the nematic phase to 298 K and heating again.

In comparison with NCS5 and 5SCN, 4-*n*-pentylphenyl 4'-*n*-heptyloxythiolbenzoate[16] and 4-*n*-pentylphenyl 4'-*n*-octyloxythiolbenzoate[17] also show more than one solid modification. The solid state polymorphism of mesogenic compounds has been described for a number of substances.[18]

In order to understand more of the behaviour of the two isomeric compounds with different solid phases, we investigated the binary phase diagram of NCS5 and 5SCN (Figure 6). This phase diagram is of the eutectic type. The phase regions on both sides of the eutectic are rather complicated and at this time not completely clear:

For NCS5 no solid–solid transitions have been observed.

For 5SCN we interpret the transitions (1) at 348 K, as described above, and the transition (2) at 341 K as a solid–solid transition. The transition (4) at 318 K should be of the solid–solid type or relates to a metastable eutectic point. The transition (3) is assumed to be a solid–solid transition, but there are too few experimental data for an exact description. If we postulate the existence of 3 solid phases, then one possible interpretation is the following: the transitions (1), (2) and (3) are of the solid–solid type, interpreted as transitions II → I,

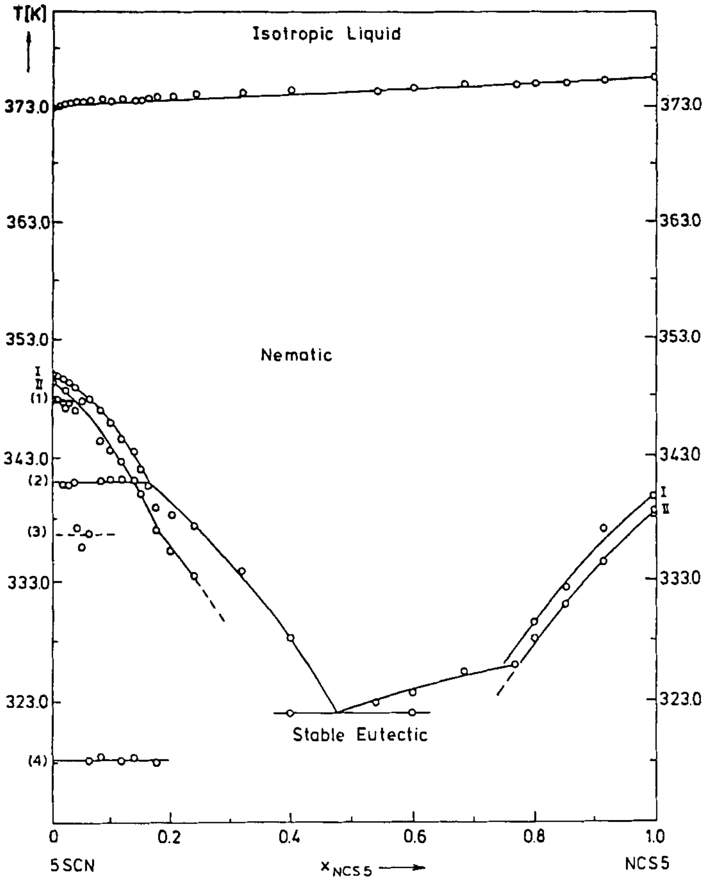

FIGURE 6 Phase diagram of the binary mixture of NCS5 and 5SCN. I and II are the melting points of the two crystalline phases. Points (1) to (4) see text.

III → I and III → II, respectively. The transition (4) then relates to a metastable eutectic transition. The melting point of the solid phase could not be found. Some points on the melting curve of phase II, seem to contradict our interpretation. They may be caused *either* by the fact that not only phase III was formed during the crystallization of the mixture *or* by the existence of a fourth solid phase.

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