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The Crystal and Molecular Structure of the Mesogenic 4-Cyanophenyl-4′-*n*-pentylthiolbenzoate (5SCN)

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The crystal and molecular structure of the mesogenic 4-cyanophenyl-4′-n-pentylthiolbenzoate (5SCN) has been determined by X-ray diffraction method. The crystal data are: monoclinic, space group $P2_1/c$, a = 37.204(10) Å, b = 5.992(2) Å, c = 24.408(8) å, β = 107.45(2)° and Z = 12 with three symmetry independent molecule positions. All the molecules occur in their extended form and the two phenyl rings are twisted against each other. Shorter intermolecular distances were observed.

Keywords: crystal structure, molecular structure, 4-cyanophenyl-4′-n-pentylthiolbenzoate

INTRODUCTION

The liquid crystalline 4,4′-disubstituted phenylthiolbenzoates were prepared by Krause *et al.*[1] and by Reynolds *et al.*[2] The diamagnetic properties,[3] the densities and the optical properties[4] of the isomeric compounds 4-*n*-pentylphenyl-4′-cyanothiolbenzoate (NCS5) and 4-cyanophenyl-4′-*n*-pentylthiolbenzoate (5SCN) were determined in order to study the influence of changing the positions of the substituents on these physical properties.

The crystal and molecular structure of the isomer of the title compound, NCS5, and the X-ray investigations on the nematic phase of the two isomeric compounds NCS5 and 5SCN, as well as the phase diagram of their binary mixture were reported elsewhere.[5] Such investigations were made to understand better the relation between the molecular packing in the crystallline state and the mesogenic behaviour.

In this work we report on the crystal and molecular structure of 5SCN.

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EXPERIMENTAL

Crystal Data

Crystals of 5SCN suitable for X-ray diffraction measurements were obtained by slow evaporation of a methanolic solution. Lattice constants and intensity measurements were performed on an automatic STOE-4-circle diffractometer with monochromatic CuK_α radiation. For the data collection the intensities of three strong standard reflections were measured after every 3600 s and seem to be constant within the error bar. The systematic absences oko: $k = 2n$ and hol: $l = 2n$ proved the space group to be $P2_1/c$. The crystal data for 5SCN are listed in Table I.

Structure Determination and Refinement

The structure was solved by direct methods using the program SHELX-76[6] after performing Lorentz and polarization corrections. Least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms led to $R = 0.0868$ ($R_w = 0.0828$) for 4474 independent reflections with $F_o > 3\sigma$ (F_o). The coordinates for the hydrogen atoms were calculated from the molecular geometry using a C—H bond length of 1,080 Å and were not refined. The fractional coordinates and thermal parameters (U_{eq}) for all 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.

RESULTS AND DISCUSSION

Molecular Structure

The molecular structure of 5SCN is depicted in Figure 1 for molecule III as a projection perpendicular to the plane of the phenyl ring A, the phenyl ring to

TABLE I

Crystal data of 5SCN

Molecular formula	$C_{19}H_{19}NOS$
Molar mass ($g \cdot mol^{-1}$)	309.41
$F(000)$	1968
Space group	$P2_1/c$
a(Å)	37.204(10)
b(Å)	5.992(2)
c(Å)	24.408(8)
β(°)	107.45(2)
V(Å^3)	5190.74
$D(g \cdot cm^{-3})$	1.18
Z	12
Reflections measured	7359
Independent reflections	6097
Reflections for calculation	4474
$\mu(CuK_\alpha)(cm^{-1})$	15.6

TABLE II

Positional and thermal parameters with e.s.d.'s for 5SCN

Each first line: molecule I, each second line: molecule II, each third line: molecule III

	X/a	*Y/b*	*Z/c*	U_{eq}*
S	0.6892(0)	0.0234(3)	0.2769(1)	0.098
	0.7147(0)	0.5445(3)	0.3921(1)	0.087
	0.0884(0)	0.0523(3)	0.4413(1)	0.094
O	0.6710(1)	0.3834(7)	0.2139(2)	0.102
	0.7282(1)	0.9090(7)	0.4550(2)	0.095
	0.0713(1)	−0.3066(7)	0.3760(2)	0.104
N	0.4905(2)	−0.0428(11)	0.2056(3)	0.130
	0.9136(1)	0.5191(9)	0.4634(2)	0.101
	−0.1101(1)	0.0390(9)	0.3845(2)	0.109
C(1)	0.5220(2)	−0.0325(12)	0.2172(3)	0.100
	0.8820(2)	0.5250(10)	0.4528(3)	0.085
	−0.0781(2)	0.0404(10)	0.3943(3)	0.085
C(2)	0.5622(2)	−0.0188(11)	0.2307(3)	0.087
	0.8423(2)	0.5341(10)	0.4395(2)	0.075
	−0.0382(2)	0.0395(10)	0.4070(2)	0.078
C(3)	0.5811(2)	0.1668(11)	0.2593(3)	0.094
	0.8225(2)	0.3519(10)	0.4505(2)	0.085
	−0.0206(2)	0.2261(10)	0.3922(3)	0.088
C(4)	0.6194(2)	0.1810(10)	0.2733(3)	0.090
	0.7836(2)	0.3625(10)	0.4375(2)	0.083
	0.0183(2)	0.2236(10)	0.4027(3)	0.088
C(5)	0.6395(2)	0.0158(10)	0.2583(3)	0.083
	0.7638(1)	0.5489(10)	0.4121(2)	0.072
	0.0394(2)	0.0399(11)	0.4281(2)	0.079
C(6)	0.6211(2)	−0.1701(11)	0.2302(3)	0.097
	0.7831(2)	0.7282(10)	0.4005(3)	0.089
	0.0217(2)	−0.1410(10)	0.4432(2)	0.079
C(7)	0.5827(2)	−0.1867(11)	0.2153(3)	0.099
	0.8224(2)	0.7231(10)	0.4143(3)	0.088
	−0.0168(2)	−0.1412(10)	0.4327(2)	0.079
C(8)	0.6963(2)	0.2740(10)	0.2421(2)	0.078
	0.7038(2)	0.7909(9)	0.4264(2)	0.077
	0.0959(2)	−0.1811(10)	0.4006(2)	0.076
C(9)	0.7361(2)	0.3298(10)	0.2525(2)	0.077
	0.6638(2)	0.8295(10)	0.4165(2)	0.073
	0.1363(2)	−0.2068(10)	0.4012(2)	0.075
C(10)	0.7454(2)	0.5356(12)	0.2334(4)	0.102
	0.6355(2)	0.6815(10)	0.3887(2)	0.091
	0.1363(2)	−0.2068(10)	0.4012(2)	0.087
C(11)	0.7829(2)	0.5960(12)	0.2435(3)	0.112
	0.5981(2)	0.7247(12)	0.3811(3)	0.101
	0.1995(2)	−0.0748(12)	0.4215(3)	0.096
C(12)	0.8122(2)	0.4559(18)	0.2711(3)	0.119
	0.5870(2)	0.9257(12)	0.3996(3)	0.090
	0.2094(2)	−0.2711(15)	0.4000(3)	0.116

TABLE II (*continued*)

Each first line: molecule I, each second line: molecule II, each third line: molecule III

	X/a	*Y/b*	*Z/c*	U_{eq}*
C(13)	0.8030(2)	0.2537(15)	0.2886(3)	0.117
	0.6150(2)	1.0728(11)	0.4265(3)	0.101
	0.1822(2)	−0.4357(12)	0.3820(3)	0.122
C(14)	0.7663(2)	0.1925(11)	0.2798(3)	0.099
	0.6531(2)	1.0307(11)	0.4354(3)	0.090
	0.1463(2)	−0.4020(11)	0.3807(3)	0.103
C(15)	0.8512(2)	0.5427(21)	0.2852(3)	0.189
	0.5468(2)	0.9728(12)	0.3903(3)	0.113
	0.2489(2)	−0.3119(17)	0.3932(4)	0.165
C(16)	0.8712(3)	0.5425(28)	0.2424(4)	0.261
	0.5278(2)	0.8273(13)	0.4235(3)	0.116
	0.2703(2)	−0.4261(19)	0.4329(5)	0.202
C(17)	0.9121(3)	0.5880(25)	0.2658(5)	0.236
	0.4849(2)	0.8726(14)	0.4098(4)	0.140
	0.3138(3)	−0.4716(19)	0.4356(5)	0.185
C(18)	0.9263(3)	0.7650(26)	0.2376(6)	0.294
	0.4664(2)	0.7169(20)	0.4377(5)	0.210
	0.3181(4)	−0.6792(30)	0.4133(5)	0.243
C(19)	0.9679(3)	0.7593(23)	0.2564(6)	0.213
	0.4254(3)	0.7733(25)	0.4217(6)	0.264
	0.3579(4)	−0.7433(22)	0.4224(7)	0.250

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

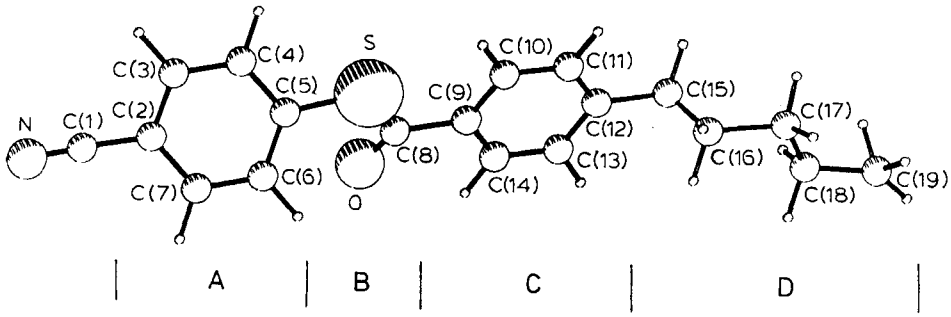

FIGURE 1 Molecule III as projection perpendicular to the phenyl ring *A*. The atomic and molecular fragment numbering schemes used are given, for calculating the dihedral angles.

which the cyano group is attached; phenyl ring C belongs to the benzoate fragment. Figure 1 shows disorder in the alkyl chain of molecule III. Also the alkyl chain of molecule I is disordered. The alkyl chain of molecule II shows trans conformation, but with some alterations in the bond distances and angles too (Tables II and III). The thermal parameters of all alkyl carbon atoms are relatively high (Table II). This seems to be the reason for the high *R*-value in the end of the refinement stage. The length of the molecule I amounts to ~19.44 Å, molecule II to 19.78 Å and

TABLE III

Selected bond distances (Å) and angles (°)

	Molecule I	Molecule II	Molecule III
N—C(1)	1.121(10)	1.127(9)	1.144(9)
C(5)—S	1.767(6)	1.745(5)	1.756(6)
S—C(8)	1.784(6)	1.802(6)	1.786(6)
C(8)—O	1.183(7)	1.197(7)	1.198(7)
(C—C)phen.A	1.372(11)	1.385(10)	1.384(9)
(C—C)phen.C	1.381(15)	1.384(9)	1.371(18)
C(12)—C(15)	1.484(12)	1.474(10)	1.545(13)
C(15)—C(16)	1.449(14)	1.502(11)	1.258(13)
C(16)—C(17)	1.484(14)	1.554(10)	1.621(15)
C(17)—C(18)	1.448(21)	1.444(15)	1.387(21)
C(18)—C(19)	1.477(14)	1.497(14)	1.482(20)
N—C(1)—C(2)	178.8(0.8)	179.6(0.5)	179.2(0.7)
C(5)—S—C(8)	101.1(0.3)	102.7(0.3)	101.0(0.3)
S—C(8)—C(9)	113.4(0.4)	114.5(0.4)	113.4(0.4)
S—C(8)—O	122.5(0.5)	121.2(0.5)	123.2(0.5)
O—C(8)—C(9)	124.1(0.6)	124.3(0.6)	123.5(0.6)

TABLE IV

Dihedral angles (°) between best planes defined in Figure 1

	(A)/(B)	*(A)/(C)*	*(B)/(C)*	*(C)/(D)*
Molecule I	58.9	50.8	8.1	46.4
Molecule II	54.6	46.8	7.9	66.5
Molecule III	61.8	47.0	14.8	41.1

Plane A: C(2) to C(7), plane B: S, O, C(8), plane C: C(9) to C(14), plane D: C(15) to (C19).

molecule III to 19.64 Å, including the covalent radii of *N* (0.55 Å) and *H* (0.30 Å), compared with that of NCS5 (19.66 Å).[5]

Selected bond distances and bond angles are given in Table III. All these values for the core part of the molecule (N to C(12)) are of normal magnitude. An interesting comparison can be done with the corresponding values for NCS5,[5] shown below*: N—C(1) = 1.130(6) Å; S—C(9) = 1.759(4) Å; C(8)—S = 1.747(4) Å; C(8)—O = 1.184(6) Å; (C—C)phen.A = 1.376(7) Å; (C—C)phen.C = 1.372(7) Å; N—C(1)—C(2) = 179.7(5)°; C(8)—S—C(9) = 104.1(3)°; C(5)—C(8)—S = 114.2(3)°; O—C(8)—S = 122.1(3)°; C(5)—C(8)—O = 123.6(5)°.

The dihedral angle between the two phenyl groups *A* and *C* as well as other interesting dihedral angles are given in Table IV. Analogous dihedral angles were found in NCS5[5] and substituted phenyl benzoates (and literature therein).[7]

Molecular Packing

The packing of 5SCN in the crystalline state is demonstrated in Figure 2. It is characterized in such a manner that the molecules are extended parallel to (001)

* C(5) and C(9) in NCS5 are in reversed function.

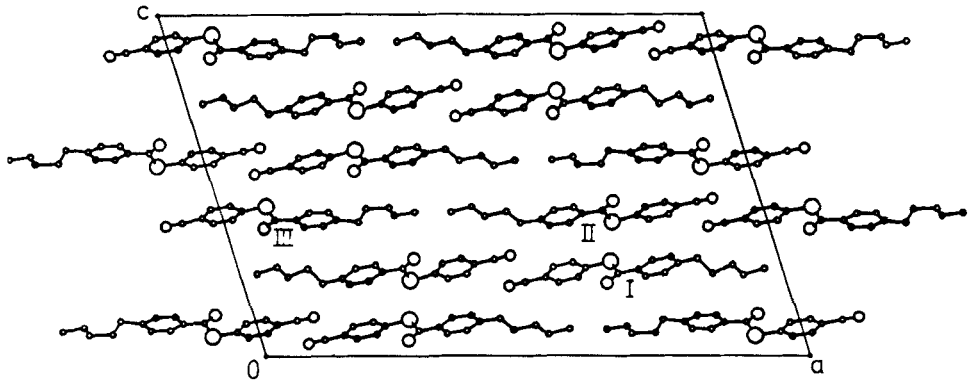

FIGURE 2 Crystal structure as projection along [010].

TABLE V

Shorter intermolecular distances in the solid 5SCN

NI–NI[a]	3.640		
NI–NI[b]	3.641	NI–CI1[a]	3.591
CI1–CI1[a]	3.972		
CI1–CI1[b]	3.974	NI–CI1[b]	3.592
SI–SII	4.118	SI–OII[c]	4.206
SI–SII[c]	3.929	OI–SII	4.272
NII–NIII[d]	3.427	NII–CIII1[d]	3.389
NII–NIII[e]	3.629	CIII1–NI[d]	3.412
CII1–CII1[d]	3.738	NII–CIII1[e]	3.607
CII1–CII1[e]	3.880	CIII1–NI[e]	3.556
NII–SIII[f]	3.481	CII1–SIII[f]	3.550
NII–SIII[g]	4.152	CII1–SIII[g]	4.261
NII–OII1[f]	3.994	CII1–OIII[g]	4.223
NII–OIII[g]	3.998		
NIII–SIII[h]	4.119	CIII–SIII[h]	4.180

[a] $1-x, \frac{1}{2}+y, \frac{1}{2}-z$.
[b] $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$.
[c] $x, -1+y, z$.
[d] $1+x, y, z$.
[e] $1+x, 1+y, z$.
[f] $1-x, 1-y, 1-z$.
[g] $1-x, -y, 1-z$.
[h] $-x, -y, 1-z$.

plane. The longest extension along the molecule inclined to the *a*-axis with an angle Φ: $\Phi(I) = 15.1°$, $\Phi(II) = -4.7°$; $\Phi(III) = 15.1°$.

On the other hand, the phenyl rings *A* and *C* make the following angles with the (001) plane:

$\varkappa(AI) = -63.1°$; $\varkappa(AII) = 68.1°$; $\varkappa(AIII) = 66.4°$; $\varkappa(CI) = 66.3°$; $\varkappa(CII) = -65.1°$; $\varkappa(CIII) = -67.1°$.

Some intermolecular distances are listed in Table V. An interesting feature are

the comparatively short sulphur-sulphur distances in the two isomeric compounds 5SCN and NCS[5] (3.93 Å and 3.85 Å, respectively).

In comparison with the cyano-cyano contacts caused by an inversion center, N—N′ = 3.906 Å, N—C(1)′ = 3.787 Å and C(1)—C(1)′ = 3.996 Å in NCS5,[5] the corresponding distances observed in 5SCN are rather short (Table V). Analogous distances were found in the 4′-alkylcyclohexyl-4-cyano-biphenyl's (BCH's)[8] and in the trans-4′-alkyl-trans-4-(1,1′-bicyclohexyl)-carbonitril's (CCH's).[9,10]

Some of the distances in Table V may be interpreted as weak intermolecular interaction.

A comparison of the calculated molecular length in the crystalline state (~19.6 Å) with that obtained from X-ray measurements[5] (21.3 ± 0.5 Å) in the nematic phase of 5SCN shows that these values are about 10% smaller.

An overlapping model discussed recently for 5SCN[5] is suggested. By NCS5 dimeric (29.3 ± 0.5 Å), and monomeric (18.6 ± 0.5 Å), units could be separated in the nematic phase[5] through different incommensurate wave length.

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