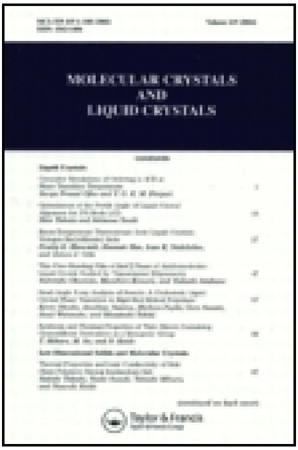

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Crystal and Molecular Structure of 4-n-Pentylphenyl-4′-n-Hexyloxythiobenzoate (6OS5)

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To cite this article: Z. Karczmarzyk, M. D Ossowska-Chruściel & J. Chruściel (2001): The Crystal and Molecular Structure of 4-n-Pentylphenyl-4′-n-Hexyloxythiobenzoate (6OS5), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 357:1, 117-125

To link to this article: http://dx.doi.org/10.1080/10587250108028248

Mol. Cryst. Liq. Cryst., Vol. 357, pp. 117-125
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The Crystal and Molecular Structure of 4-n-Pentylphenyl-4′-n-Hexyloxythiobenzoate (6OS5)

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(Received May 15, 2000; In final form September 25, 2000)

The title compound, 4-n-pentylphenyl-4′-n-hexyloxythiobenzoate (6OS5), $C_{24}H_{32}O_2S$, crystallizes in the orthorhombic system, space group Pbca, with cell constants a =5.668(2), b =52.400(10), c = 15.587(4) Å, Z = 8. The structure was solved by direct methods and refined to the final R = 0.0941 for 1717 observed reflections. The hexyloxythiobenzoate moiety is nearly planar. In the crystal, molecules form molecular layers parallel to the (001) plane and within the layer, they are linked in molecular chains parallel to [100] direction by C – H···O weak intermolecular hydrogen bond.

Keywords: Liquid crystal; thioester; crystal and molecular structure

INTRODUCTION

Studies of the properties of liquid crystals are of great interest as they are often regarded as a new state of matter incorporating properties of solid on liquids. It has been shown that is a relationship between the mesomorphic properties and molecular structure.[1] Thioesters belonging to the homologous series of 4-n-pentylphenyl-4′-n-alkoxythiobenzoate (nOS5) have been systematic study a few experimental methods (see, for example[2] and references therein). This research showed evident influence the elongation of the alkoxy chain (the length of the alkyl group is constant) on the reorientational dynamics in liquid crystalline phases of nOS5. The crystal structures of few 4,4′-disubstituted phenylthioben-

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zoates have been described by Haase and his group.[3–5] We reported, recently, the crystal and molecular structure of 4-n-pentylphenyl-4′-n-pentyloxythiobenzoate, 5OS5,[6] as part of a larger structural study on a homologous series of mesogenic 4-n-pentylphenyl-4′-n-alkyloxythiobenzoates, nOS5 (n vary from n = 5 to n = 10), in the crystalline state. In this paper we present the results of the X-ray structure determination of 4-n-pentylphenyl-4′-n-hexyloxythiobenzoate 6OS5, the next compound in the investigated series. In our researching we want to find probable correlation, which can take place between the crystalline state and liquid crystalline phase. The substances 4OS5, 5OS5 and 6OS5 of the thiobenzoates homologous exhibit nematic phase only. Higher homologous show smectic polymorphism: namely, 7OS5 exhibits a monotropic smectic C, 8OS5 possesses enantiotropic phases A and C and the monotropic smectic J, etc.. The substances belonging to the homologous series of nOS5 differ only in length of the terminal group – the alkoxy group. The principal aims of this structure determination were to establish the mutual orientation of the main structural fragments of the molecule 6OS5, the packing of the molecules in the unit cell and comparison these data with those obtained for closely related compound 5OS5.

The results obtained from the polymorphism of nematic liquid crystalline mixtures of compounds belonging to the thioester homologous series nOS5 show that by mixing two nematics a considerable extension of the nematic phase temperature range (up to 50 deg) in relation to pure mixture components.[7]

EXPERIMENTAL

Crystal Data

The investigated compound, having the following chemical formula

$$H_{13}C_6O - C_6H_4 - COS - C_6H_4 - C_5H_{11}$$

The 6OS5 sample was synthesised in the Institute of Chemistry of the University of Podlasie at Siedlce (Poland). The thioester contains two terminal groups, pentyl ($-C_5H_{11}$) and hexyloxy ($-OC_6H_{13}$), connected to the benzene rings. Two groups in the molecule are polar: -COS- and hexyloxy group.

The phase behaviour, obtained by DSC using a differential scanning calorimeter (Pyris 1 DSC) and polarizing microscopy (with Linkam programmable heating stage THMSE 600) methods is the following: Cr-59.9°C-N-85.9°C-I. This substance possess only enantiotropic nematic phase.

Colourless prismatic crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a cyclohexane solution. A crystal 0.65 × 0.20 ×

0.10 mm was used for diffractometer measurements. Data were collected with Enraf-Nonius CAD-4 four-circle diffractometer using CuKα radiation and a graphite monochromator. The crystal and experimental data are shown in Table I.

TABLE I Crystal data and structure refinement

Crystal data	
Empirical formula	$C_{24}H_{32}O_2S$
Formula weight	384.56
Crystal system	orthorhombic
Space group	Pbca
Unit cell parameters	a = 5.668(2) Å
	b = 52.400(10) Å
	c = 15.587(4) Å
Volume	V = 4629(2) $Å^3$
Molecular multiplicity	Z = 8
Density (calculated)	1.104 Mg/m^3
Cell parameters from	25 reflections
θ range for lattice parameters	11.70° – 27.00°
Absorption coefficient	$\mu = 1.340$ mm^{-1}
Temperature	T = 293(2) K
Data collection	
Collection method	$\omega/2\theta$ scans
Absorption correction	none
θ range for data collection	1.69° – 70.11°
Index ranges	$h = 0 \rightarrow 6$, $k = 0 \rightarrow 52$, $l = 0 \rightarrow 17$
3 standard reflections monitored every 100 reflections	
Intensity decay	0 %
No. of measured reflections	4150
No. of independent reflections	4059
No. of observed reflections	1717 with $I > 2\sigma(I)$
Refinement	
Refinement method	Full-matrix least-squares on F^2
Final R indices	R = 0.0941, wR = 0.2752
Weigth scheme	$w = 1/[\sigma^2(F_o^2) + (0.1868P)^2]$
	where $P = (F_o^2 + 2F_c^2)/3$
Goodnes-of-fit	S = 1.359
Data/parameters	1717/245
Extinction coefficient	0.0036(8), extinction correction: SHELXL
Largest diff. peak and hole	+0.381 and –0.390 $eÅ^{-3}$
$(\Delta/\sigma)_{max}$	–0.001

Structure Determination and Refinement

The crystal structure was solved by direct methods using SHELXS86[8] and refined by full-matrix least squares with SHELXL93.[9] Non-hydrogen atoms were refined anisotropically. All H atoms were placed in calculated positions and refined using a riding model with isotropic displacement parameters taken as 1.5 times those of respective parent atoms. Atomic scattering factors were as supplied by the program. Five strong reflections affected by secondary extinction were suppressed during the last few cycles of refinement. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table II. Complete listing of thermal parameters and listings of observed and calculated structure factors are available from the authors on request. The molecular plot was prepared with SHELXTL-plus XP[10] and the geometrical calculations were produced using PARST.[11]

TABLE II Fractional atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for non-H atoms with e.s.d.'s in parentheses

Atom	*x/a*	*y/b*	*z/c*	$U_{eq}{}^a$
S(1)	2022(3)	6950(1)	6612(1)	104(1)
O(1)	5883(7)	6937(1)	5674(2)	87(1)
O(2)	5947(8)	8126(1)	6498(2)	87(1)
C(1)	4577(10)	7074(1)	6088(3)	75(1)
C(2)	4942(9)	7350(1)	6199(3)	68(1)
C(3)	3357(9)	7505(1)	6633(3)	76(1)
C(4)	3728(9)	7761(1)	6702(3)	76(2)
C(5)	5718(10)	7873(1)	6364(3)	72(1)
C(6)	7322(9)	7720(1)	5921(3)	75(1)
C(7)	6942(9)	7462(1)	5838(3)	70(1)
C(8)	8034(11)	8250(1)	6190(4)	85(2)
C(9)	7906(12)	8524(1)	6476(4)	92(2)
C(10)	9928(12)	8682(1)	6142(4)	94(2)
C(11)	9785(15)	8958(1)	6452(4)	108(2)
C(12)	11733(15)	9126(1)	6114(6)	132(3)
C(13)	11544(22)	9397(2)	6436(7)	189(5)
C(21)	2133(11)	6626(1)	6351(4)	83(2)
C(22)	325(11)	6514(1)	5895(4)	92(2)
C(23)	284(12)	6262(1)	5750(4)	101(2)
C(24)	1984(13)	6099(1)	6041(4)	97(2)
C(25)	3816(12)	6207(1)	6498(4)	100(2)
C(26)	3898(13)	6467(1)	6650(4)	98(2)

Atom	x/a	y/b	z/c	$U_{eq}{}^{a}$
C(27)	1940(15)	5817(1)	5861(6)	137(3)
C(28)	59(18)	5679(1)	6335(7)	148(3)
C(29)	−89(22)	5396(2)	6120(8)	185(5)
C(30)	−2109(31)	5265(2)	6416(11)	274(9)
C(31)	−2256(30)	4996(2)	6261(11)	320(10)

a. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

RESULTS AND DISCUSSION

The bond distances and valence angles are given in Table III. A view of the molecule with numbering of the atoms is shown in Fig. 1.

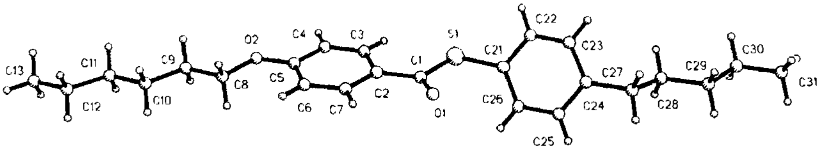

FIGURE 1 A view of the molecule with the atomic labelling

TABLE III Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

S(1)-C(21)	1.746(6)	C(21)-S(1)-C(1)	102.6(3)
S(1)-C(1)	1.785(6)	C(5)-O(2)-C(8)	118.1(4)
O(1)-C(1)	1.215(6)	O(1)-C(1)-C(2)	123.8(5)
O(2)-C(5)	1.352(6)	O(1)-C(1)-S(1)	121.5(4)
O(2)-C(8)	1.432(7)	C(2)-C(1)-S(1)	114.7(4)
C(1)-C(2)	1.470(7)	C(3)-C(2)-C(7)	118.4(5)
C(2)-C(3)	1.388(7)	C(3)-C(2)-C(1)	122.9(5)
C(2)-C(7)	1.395(7)	C(7)-C(2)-C(1)	118.7(5)
C(3)-C(4)	1.363(8)	C(4)-C(3)-C(2)	121.0(5)
C(4)-C(5)	1.375(7)	C(3)-C(4)-C(5)	121.0(5)
C(5)-C(6)	1.393(7)	O(2)-C(5)-C(4)	115.9(5)
C(6)-C(7)	1.377(7)	O(2)-C(5)-C(6)	125.3(5)
C(8)-C(9)	1.504(7)	C(4)-C(5)-C(6)	118.8(5)
C(9)-C(10)	1.509(8)	C(7)-C(6)-C(5)	120.5(5)
C(10)-C(11)	1.525(8)	C(6)-C(7)-C(2)	120.2(5)
C(11)-C(12)	1.507(10)	O(2)-C(8)-C(9)	107.0(5)

C(12)-C(13)	1.509(10)	C(10)-C(9)-C(8)	112.8(5)
C(21)-C(22)	1.377(8)	C(9)-C(10)-C(11)	111.9(6)
C(21)-C(26)	1.383(9)	C(12)-C(11)-C(10)	113.8(6)
C(22)-C(23)	1.341(7)	C(13)-C(12)-C(11)	112.4(8)
C(23)-C(24)	1.366(8)	C(22)-C(21)-C(26)	117.2(6)
C(24)-C(25)	1.381(9)	C(22)-C(21)-S(1)	120.4(5)
C(24)-C(27)	1.507(9)	C(26)-C(21)-S(1)	122.2(5)
C(25)-C(26)	1.382(9)	C(23)-C(22)-C(21)	121.2(6)
C(27)-C(28)	1.484(11)	C(22)-C(23)-C(24)	123.3(7)
C(28)-C(29)	1.524(10)	C(23)-C(24)-C(25)	116.3(6)
C(29)-C(30)	1.41(2)	C(23)-C(24)-C(27)	122.8(7)
C(30)-C(31)	1.428(13)	C(25)-C(24)-C(27)	120.9(7)
		C(26)-C(25)-C(24)	121.3(6)
		C(25)-C(26)-C(21)	120.7(7)
		C(28)-C(27)-C(24)	113.3(7)
		C(27)-C(28)-C(29)	113.8(9)
		C(30)-C(29)-C(28)	116.5(11)
		C(29)-C(30)-C(31)	118.1(14)

The molecule of 4-n-pentylphenyl-4′-n-hexyloxythiobenzoate, 6OS5, consists of five roughly planar parts: two benzene rings C2 – C7 (I) and C21 – C26 (II), hexyloxy chain O2 – C13 (III), central part S1, O1, C1 (IV) and pentyl chain C27 – C31 (V). The C2 – C7 phenyl ring is planar to within 0.012(5) Å and C1 and O2 atoms are displaced from the best phenyl plane by 0.017(4) and –0.040(4) Å respectively. Similarly, the C21 – C26 phenyl ring is quite planar to within 0.003(6) Å; S1 atom is deviated out of the best ring plane by -0.154(2), while C27 atom by 0.026(9) Å. The least-squares planes of both phenyl rings are inclined by 60.6(2)° with respect to each other and by 3.4(2)° for (I) and 63.7(1)° for (II) with respect to the plane of central part (IV) of the molecule. The hexyloxy chain is slightly distorted from planarity with maximum deviations of 0.058(9) Å caused by C12 atom but this chain is almost coplanar with adjacent benzene ring; the angle between the planes of (I) and (III) is 4.0(2)°. The pentyl substituent is bent by 69.1(5)° out of the mean C21 – C26 benzene ring plane. The both pentyl and hexyloxy substituents adopts the *all trans* conformations with the torsion angles deviate from 180° by less than 12°. The mutual orientations of the considerated parts of molecule 6OS5 and comparison these data with those observed in 5OS5 are presented in Table IV. It is noteworthy, that there are not any major differences between the 5OS5 and 6OS5 molecules in the relative orientations of theirs main structural parts. Moreover, bond lengths and angles for central part of molecule 6OS5 and both benzene rings do not differ significantly from those reported for 5OS5. Some differences are observed in the side-chains geometry, what may arise from the somewhat larger temperature factors for peripheral atoms in both molecules.

TABLE IV Dihedral angles between the planes

	I/II	*I/III*	*I/IV*	*I/V*	*II/III*	*II/IV*	*II/V*	*III/IV*	*III/V*	*IV/V*
5OS5	64.8	1.2	3.9	9.5	65.9	68.7	73.2	2.9	8.7	6.0
6OS5	60.6	4.0	3.4	9.8	61.1	63.7	69.1	3.7	8.0	6.5

The length of 6OS5 molecule, i.e. the distance between H131 [x/a = 1.2819(22), y/b = 0.9496(2), z/c = 0.6207(7)] and H311 [x/a = –0.3696(30), y/b = 0.4931(2), z/c = 0.6501(11)] edge atoms (25.69 Å) including the covalent radii of the H-atoms (0.56 Å), is 26.25 Å and it is 1.03 Å larger than length of 5OS5.

Molecular Packing

The packing of the molecules in the unit cell is shown in Fig. 2. The molecules form molecular layers parallel to the (001) plane. The layers are arranged in the sequence ABCDA.... The symmetry codes of molecules laying in the considered layers are as follows: layer A -x, y-1/2, z+1/2; layer B x, y, z; layer C -x, -y+1, -z+1; layer D x, -y+3/2, z-1/2. The layers A and B (also C and D) are related by glide plane (001) type a, while the layers B and C by 2_1 screw-axis parallel to [001] direction. Within the layer (Fig. 3) molecules are joined in chains parallel to [100] by $C22^{i} - H221 \cdots O1^{ii}$ weak intermolecular hydrogen bond: C22···O1 of 3.371(7) Å, H221···O1 of 2.486(7) Å, C22 – H221···O1 of 159.1(6)° and (i) = x, y, z; (ii) = x-1, y, z. The direction of chain formed by hydrogen-bonded molecules makes angle of 111.4° with the long axis of the molecule.

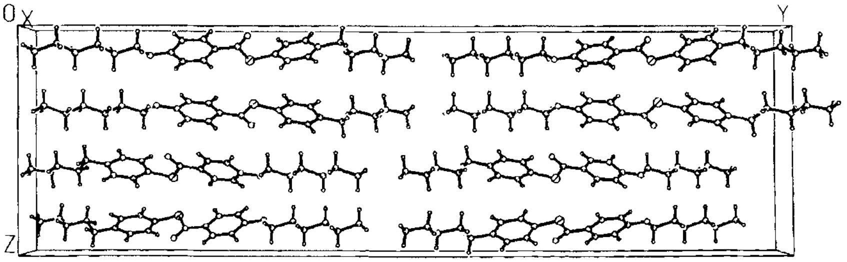

FIGURE 2 Unit-cell packing seen along the [100] direction

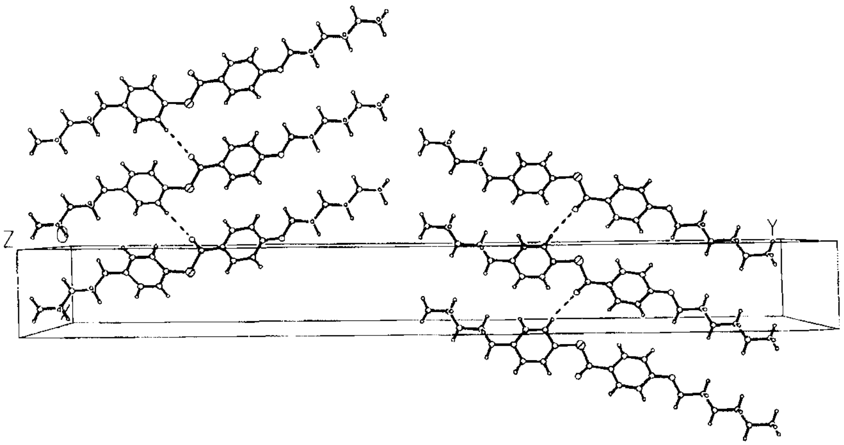

FIGURE 3 A view of the molecular layer B. The hydrogen bonds are indicated by broken lines

The packing of the 6OS5 molecules is quite different from those found for 5OS5 in spite of very similar geometry and conformation in molecules of both compared compounds. In the crystal of 5OS5, molecules in a head-tail configuration form molecular rows, which related by the symmetry elements of $P2_1/c$ space group produce a highly intercalated structure. In both 60S5 and 5OS5 structures the dipol-dipol contacts are not justified in the crystalline state, because the intermolecular minimum distances between the sulfur – sulfur and oxygen - oxygen atoms are much than twice the van der Waals radius ($2r_w$of 3.70 Å and 2.80 Å for S and O respectively). In the 6OS5 these distances are: S1 ... S1 = 3.962(4) Å, O1 ... O1 = 6.360(5) Å and 02 ... O2 = 4.217(5) Å and they somewhat differ from those calculated for 5OS5 (5.58 Å, 5.58 Å and 3.82 Å respectively).

Acknowledgements

The authors wish to express thanks to Professor J. Karolak-Wojciechowska from the Institute of General and Ecological Chemistry, Technical University of Łódź, for her kind consent to use XP program for drafts.

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