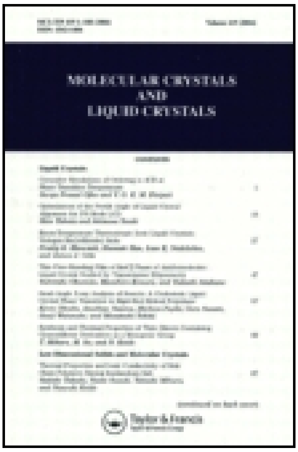

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The Crystal and Molecular Structure of 4-Pentylphenyl-4′-Pentioxythiobenzoate (5S5)

J. Chruściel [a], B. Pniewska [a] & M. D. Ossowska-Chruściel [a]
[a] Department of Chemistry, Agricultural and Pedagogical University, 3 Maja 54, 06-110, Siedlce, Poland

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The Crystal and Molecular Structure of 4-Pentylphenyl-4′-Pentioxythiobenzoate ($\bar{5}$S5)

J. CHRUŚCIEL, B. PNIEWSKA, M. D. OSSOWSKA-CHRUŚCIEL

Department of Chemistry, Agricultural and Pedagogical University, 3 Maja 54, 08-110 Siedlce, Poland

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The 4-pentylphenyl-4′-pentoxythiobenzoate ($\bar{5}$S5), $C_{23}H_{30}O_2S$, crystallizes in the monoclinic system: space group $P2_1/c$, $a = 19.817$ (2) Å, $b = 5.585$ (1) Å, $c = 20.238$ (2) Å, $\beta = 104.792$ (8)°, $z = 4$. The structure was solved by direct methods and refined to the final $R = 0.065$, for 3415 observed reflections. The pentoxythiobezoate moiety is nearly planer. Molecular rows form an interclated structure. C—H···O type short intermolecular contacts were found.

Keywords: Liquid crystal, crystal and molecular structure.

INTRODUCTION

Thiol esters belonging to the homologous series of 4-pentylphenyl-4′-*n*-alkoxythiobenzoates ($\bar{n}$S5) have been the subject of systematic studies for more than ten years. A few experimental methods have been applied: namely adiabatic and differential scanning calorimetry,[1] dielectric relaxation[2–9] and quasielastic neutron scattering.[10,11] Thioesters are rod-like polar molecules with a degree of flexibility within the molecular body and in the end chains. Complementary dielectric studies evidently show that the elongation of the alkoxy chain of six members of the $\bar{n}$S5 homologous series, in which n varies from $n = 5$ to $n = 10$ (the length of the alkyl group is constant), has a great impact on the reorientational dynamics of the molecular reorientations around their principal inertial axes.[8,10]

The structural investigation of liquid crystals plays an important role in the studies of their physical properties. The crystal structures of 4, 4′-disubstituted phenylthiobenzoates have recently been described by Haase and his group.[13–15] In addition it was found that there is a simple structural correlation between the solid crystalline and nematic phases.[15] It is interesting to compare the crystal and molecular structure and as well the molecular packing and conformation of the thiobenzoates. In this paper, we present the results of X-ray investigations of 4-pentylphenyl-4′-pentoxythiobenzoate, hereafter denoted as $\bar{5}$S5, in the crystalline state.

EXPERIMENTAL

Crystal Data

The substance under study has the following chemical formula

$$H_{11}C_5O—C_6H_4—COS—C_6H_4—C_5H_{11}$$

The $\bar{5}$S5 sample was synthesized in the Institute of Chemistry of the Agricultural and Pedagogical University at Siedlce (Poland). The thioester contains two terminal groups, pentyl ($—C_5H_{11}$) and pentoxy ($—OC_5H_{11}$), connected to the benzene rings. Two groups in this molecule are polar: $-COS-$ and pentoxy group.

The phase behaviour, obtained by DSC method using a differential scanning calorimeter DSC-2 (Perkin–Elmer) is the following: Cr – 66.1°C – N – 82.0°C – I.

Colourless elongated plate crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution. A crystal measuring 0.43 × 0.21 × 0.08 mm was used for data collection with CAD-4 diffractometer, using graphite-filtered Cu Kα radiation. Cell parameters were refined from the setting angles of 25 reflections having $20.0 \leq \theta \leq 27.1°$. Intensities were measured for 5056 reflection with 2θ up to 150°, in the ranges $0 \leq h \leq 24$, $-7 \leq k \leq 0$, $-25 \leq l \leq 25$, using $\omega/2\theta$ scans, scan width $\Delta\omega = (0.66 + 0.14 \tan\theta)°$. Three standard reflections monitored after 100 measurements showed no significant deviations (0.2%) from their mean intensities. No absorption corrections were applied. There were 4395 unique reflections ($R_{int} = 0.0126$) 3417 of which with $Fo = > 4\sigma(Fo)$ were used in the structure refinement. X-ray diffraction measurements were carried out at 22°C. The crystal and experimental data are shown in Table I.

Structure Determination and Refinement

The crystal structure was solved by direct methods using SHELXS-86[16] and refined using SHELX76[17] programs. Non H-atoms were refined anisotropically; H atoms were placed in calculated positions (C—H = 1.08 Å) and refined with isotropic thermal parameters. Full matrix least-squares refinement, with function minimized $\sum w(|Fo| - |F_c|)^2$ where $w = [\sigma^2(Fo)]^{-1}$, gave $R = 0.065$, $wR = 0.064$ for 3415 reflections and 265 parameters: the maximal Δ/σ ratio was 0.040. The final difference Fourier map showed the residual electron density within $+0.31$ eÅ^{-3} and -0.42 eÅ^{-3}. Atomic scattering factors were as supplied by the program. Two strong reflections affected by

TABLE I

Crystal and experimental data

Molecular Formula	$C_{23}H_{30}O_2S$
Formula weight (g. mol^{-1})	370.55
Space group	$P2_1/c$
a (Å)	19.817(2)
b (Å)	5.585(1)
c (Å)	20.238(2)
β (°)	104.792(8)
V (Å^3)	2165.7(5)
z	4
Dc (g. cm^{-3})	1.137(2)
F(000)	800
μ [Cu K$_\alpha$] (cm^{-1})	13.79
No. of reflections measured	5056
No. of unique reflections	4395
No. of observed reflections with Fo < 4σ(Fo)	3417
R [wR, w = $1/\sigma^2$ (Fo)]	0.065 [0.064]

secondary extinction were suppressed during the last few cycles of refinement. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table II.

Lists of structure factors, anisotropic thermal parameters and H-atom parameters are available from the authors on request.

Geometrical calculations were performed using CSU, Vickovic[18] (1988) and for drawings SHELXTL, Sheldrick[19] (1990) programs.

RESULTS AND DISCUSSION

Molecular Structure

The bond lengths and angles are listed in Table III. The molecule with the numbering scheme is shown in Figure 1.

The bonds and angles for central part of the molecule and both benzene rings are similar in experimental error ranges with those found for $\bar{4}$S6 by Ibrahim, Paulus[15], (1991). However, there is a major structural difference between the $\bar{4}$S6[15] the $\bar{5}$S5 molecules in the relative orientations of either the alkoxy and alkyl chains with respect to the thiobenzoate group. These differences are shown by the dihedral angles in Table IV.

TABLE II

Non-hydrogen fractional atomic coordinates ($\times 10^4$)*, equivalent temperature factors ($Å^2 \times 10^3$) with e.s.d.'s in parentheses

Atom	x/a	y/b	z/c	$U_{(eq)}$
S(1)	2980(0)	1326(2)	2123(0)	104(0)
O(1)	3489(1)	−2394(4)	1617(1)	75(0)
O(2)	5520(1)	−2757(4)	4615(1)	76(0)
C(1)	3542(1)	−1171(5)	2122(1)	61(1)
C(2)	4067(1)	−1569(5)	2779(1)	55(1)
C(3)	4138(1)	−21(5)	3334(1)	67(1)
C(4)	4629(1)	−469(5)	3934(1)	68(1)
C(5)	5059(1)	−2472(5)	3994(1)	60(1)
C(6)	5000(1)	−4028(5)	3444(1)	62(1)
C(7)	4500(1)	−3547(5)	2842(1)	60(1)
C(8)	5993(1)	−4761(5)	4720(1)	68(1)
C(9)	6444(1)	−4554(5)	5441(1)	66(1)
C(10)	6981(1)	−6555(5)	5612(1)	69(1)
C(11)	7428(2)	−6391(6)	6346(1)	80(1)
C(12)	7964(2)	−8398(7)	6528(2)	107(1)
C(21)	2424(1)	1246(6)	1285(1)	74(1)
C(22)	1935(2)	−534(6)	1086(2)	86(1)
C(23)	1466(2)	−436(6)	445(2)	83(1)
C(24)	1487(1)	1418(5)	−3(1)	69(1)
C(25)	1991(1)	3164(6)	207(1)	77(1)
C(26)	2462(2)	3081(6)	844(1)	79(1)
C(27)	965(2)	1573(6)	−696(2)	86(1)
C(28)	426(2)	3473(7)	−725(2)	89(1)
C(29)	−75(2)	3833(7)	−1425(2)	100(1)
C(30)	−552(2)	5893(8)	−1472(2)	122(1)
C(31)	−1017(3)	6331(11)	−2159(2)	144(2)

* $U_{(eq)}$ defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE III

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

S(1)—C(1)	1.785(3)	C(1)—S(1)—C(21)	102.4(1)
S(1)—C(21)	1.772(2)	C(5)—O(2)—C(8)	119.0(2)
O(1)—C(1)	1.211(3)	S(1)—C(1)—O(1)	121.5(2)
O(2)—C(5)	1.361(3)	S(1)—C(1)—C(2)	114.3(2)
O(2)—C(8)	1.440(3)	O(1)—C(1)—C(2)	124.2(2)
C(1)—C(2)	1.481(3)	C(1)—C(2)—C(3)	122.2(2)
C(2)—C(3)	1.396(3)	C(1)—C(2)—C(7)	118.6(2)
C(2)—C(7)	1.385(4)	C(3)—C(2)—C(7)	119.2(2)
C(3)—C(4)	1.371(3)	C(2)—C(3)—C(4)	120.2(2)
C(4)—C(5)	1.393(4)	C(3)—C(4)—C(5)	120.3(2)
C(5)—C(6)	1.393(3)	O(2)—C(5)—C(4)	115.2(2)
C(6)—C(7)	1.386(3)	O(2)—C(5)—C(6)	124.4(2)
C(8)—C(9)	1.509(3)	C(4)—C(5)—C(6)	120.4(2)
C(9)—C(10)	1.521(3)	C(5)—C(6)—C(7)	118.5(2)
C(10)—C(11)	1.526(3)	C(2)—C(7)—C(6)	121.5(2)
C(11)—C(12)	1.523(5)	O(2)—C(8)—C(9)	106.6(2)
C(21)—C(22)	1.375(4)	C(8)—C(9)—C(10)	111.8(2)
C(21)—C(26)	1.374(4)	C(9)—C(10)—C(11)	112.1(2)
C(22)—C(23)	1.391(5)	C(10)—C(11)—C(12)	112.8(3)
C(23)—C(24)	1.384(5)	S(1)—C(21)—C(22)	121.2(2)
C(24)—C(25)	1.383(4)	S(1)—C(21)—C(26)	118.6(2)
C(24)—C(27)	1.518(4)	C(22)—C(21)—C(26)	120.0(3)
C(25)—C(26)	1.386(3)	C(21)—C(22)—C(23)	119.9(3)
C(27)—C(28)	1.496(5)	C(22)—C(23)—C(24)	121.1(3)
C(28)—C(29)	1.522(5)	C(23)—C(24)—C(25)	117.8(3)
C(29)—C(30)	1.477(6)	C(23)—C(24)—C(27)	121.4(3)
C(30)—C(31)	1.479(5)	C(25)—C(24)—C(27)	120.8(2)
		C(24)—C(25)—C(26)	121.6(2)
		C(21)—C(26)—C(25)	119.6(3)
		C(24)—C(27)—C(28)	112.8(3)
		C(27)—C(28)—C(29)	114.8(3)
		C(28)—C(29)—C(30)	114.7(3)
		C(29)—C(30)—C(31)	115.1(4)

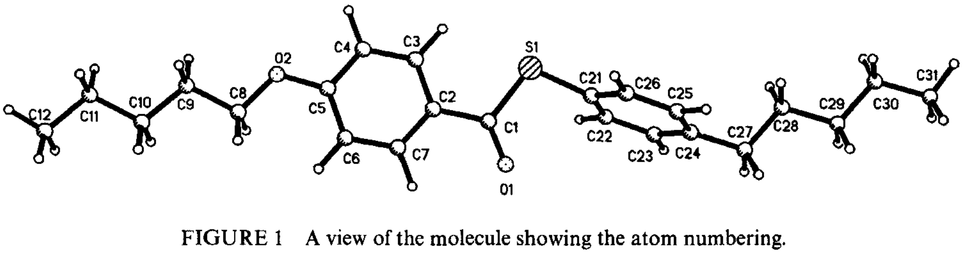

FIGURE 1 A view of the molecule showing the atom numbering.

The C(2)—C(7) phenyl ring is quite planar [to within 0.004(2) Å].C (1) and O(2) atoms deviate out of the best ring plane by −0.012(2) and −0.022(2) Å, respectively. The almost planar pentoxy chain [to within 0.014 (2) Å] is bent slightly out of the adjacent benzene ring plane by 1.2(1)° and has all-trans planar extended conformation. The planar [to within 0.010(3) Å] C(21)—C(26) benzene ring is twisted about S(1)—C(21) bond out of the central S(1), C(1), O(1) plane by 68.71 (9)°. The S(1) atom deviates

TABLE IV

Dihedral angles between the planes

Planes	I/II	I/III	I/IV	I/V	II/III	II/IV	II/V	III/IV	III/V	IV/V
Angle * (°)	64.8	1.2	3.9	9.5	65.9	68.7	73.2	2.9	8.7	6.0
Angle# (°)	−74.2	30.0	3.5	22.4	76.6	−71.8	84.8	31.9	8.2	23.9
Plane	Plane	atoms			Plane		Plane		atoms	
I	C(2)	-C(7))			IV		S(1),	0(1),	C(1)	
II	C(21)	-C(26)			V		C(27)	—	C(31)	
III	O(2)	-C(12)								

* for the present $\bar{5}$S5molecules,
\# for the $\bar{4}$S6[15] molecule.

by −0.1467 (6) Å and C(27) by −0.0464 (4) Å out of the least-squares benzene ring plane. The p-pentyl substituent is also bent by 73.2(1)° out of the mean C(21)—C(26) benzene ring plane. All atoms of the pentyl chain have the trans conformation with the torsion angles deviating from 180° by less than 6.5°.

The C(29)—C(30) and C(30)—C(31) bonds are significantly shorter than expected for Csp^3-Csp^3 connections [Allen *et al.*,[20] (1987)] and than those in the alkoxy chain. This may arise from the somewhat larger temperature factors for C(30) and C(31) atoms. However, the C—C—C angles at C(28), C(29), C(30) atoms are found to be nearly 115°, significantly greater than tetrahedral and than those in the pentoxy chain.

The largest distance between the positions of terminal H(121) and H(311) atoms amounts to 24.66(1) Å. Hydrogen positional parameters area: x/a 0.8263(2), $y/b = -0.8191(7)$, $z/c = 0.7051(2)$ for H(121) and $x/a = -0.1342(3)$, $y/b = 0.7869(11)$, $z/c = -0.2141(2)$ for H(311). The length of the $\bar{5}$S5 molecule of 25.22 Å (including the covalent radii of the H-atoms) is larger than that of the $\bar{4}$S6[15] molecule at 24.04 Å.

Molecular Packing

The packing of the molecules viewed down the *b* axis is shown in Figure 2. Molecular rows are approximately parallel to the $(10\bar{1})$ plane and the line joining the terminal C(12) and C(31) atoms makes 69.1° angle with the normal to the (010) plane. Along the rows the molecules lie in a head-to-tail configuration. In adjacent rows the molecules are related by screw axis on the one side and by the center of symmetry on the other side. As a result, molecules are crossed relative to each other when viewed along the *c* axis, producing a highly intercalated structure with A, B, C, D layers. The shortest intermolecular contacts are formed between molecules related by *b*-axis translation with distances: C(26)—H(26)...O(1) 2.336 (4) Å, C(26)...O(1) of 3.369 (4) Å and angle C(26)—H(26)...O(1) of 159.5(3)°. Symmetry code: x, y, z for C(26)—H(26) and x, 1 + y, z for O(1).

The packing of the $\bar{5}$S5 molecules is quite different from those found for $\bar{4}$S6[15] where the molecules formed separate parallel layers.

The calculated intermolecular minimum distances between the sulfur–sulfur and the oxygen–oxygen atoms are much greater than twice the van der Waals radius ($2r_W$). The distances S(1)—S(1), O(1)—O(1), O(2)—O(2) are: 5.58 Å, 5.58 Å and 3.82 Å, as

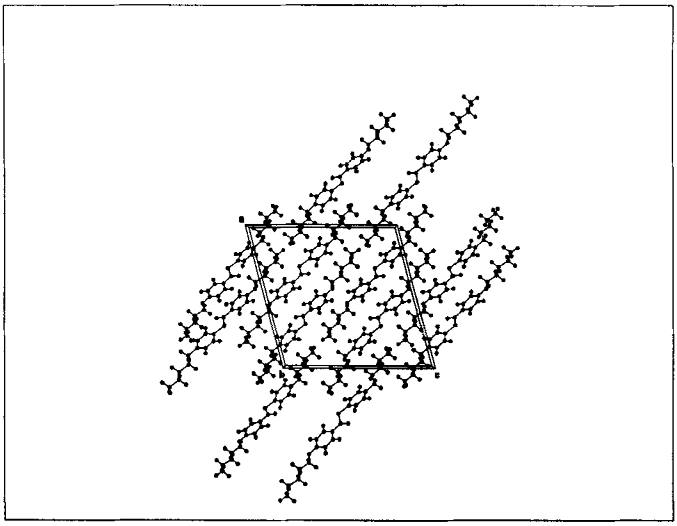

FIGURE 2 The molecular packing seen along the *b* axis.

compared with $2r_W$: 3.70 Å and 2.80 Å, respectively. This leads us to presume that the dipole–dipole contacts are not important in the crystalline state of $\bar{5}$S5.

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